CHEMICAL ENGINEERING RESEARCH AND DESIGN XXX (2014) XXX–XXX

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Hybrid separations combining distillation and organic solvent nanofiltration for separation of wide boiling mixtures

Jovana Micovic, Kathrin Werth, Philip Lutze[*]

Laboratory of Fluid Separations, Department of Biochemical and Chemical Engineering, TU Dortmund University,
Emil-Figge-Strasse 70, 44227 Dortmund, Germany

ABSTRACT

Membrane assisted hybrid separations offer tremendous potential for process intensification which aims at increasing resource efficiency as well as decreasing operating and capital costs. Design of such processes is challenging due to large number of degrees of freedom but also due to large experimental effort necessary for membrane screening and for characterising membranes in whole operating range. To address these issues, this paper elaborates a four-step design method for combination of organic solvent nanofiltration (OSN) and distillation in a hybrid separation of wide boiling mixtures. The design method is applied in a case study which is the separation of small amounts of heavy boiler from a mixture containing a mid- and a light-boiler. In the first step, different process options are generated based on heuristics and engineering judgement and screened for feasibility. In the second step, the options are evaluated based on quantitative metrics using rigorous models. In this step the unknown key parameters are identified, and their influences on the process performance are quantified in a detailed a priori process analysis. If hybrid separations with OSN show to be promising when compared to stand-alone distillation, experiments are conducted to (i) identify the best membrane for the operating window in which the hybrid process operates and (ii) to perform model validation and parameterisation in the third step. In the last (fourth) step, an optimisation is performed to identify the best (cost optimal) process using the experimental data gained in step three.

Keywords: Organic solvent nanofiltration; Separation of wide boiling mixtures; OSN assisted hybrid separations; Experimental investigations; Process optimisation; Optimisation under uncertainty

1. Introduction

In hybrid separations at least two unit operations are combined to solve a defined separation task; by using each unit operation in its optimal range, synergy effects arise and offer more sustainable and intensified processes (Franke et al., 2008). In particular, the combination of organic solvent nanofiltration (OSN) and distillation offers large but yet nearly unexploited potential for process intensifications in terms of improved resource efficiency (Lutze and Górak, 2013). In OSN, larger molecules (solutes) (200–2000 Da) can be separated from organic solvent streams, by applying pressures of up to 60 bars on the feed side of the membrane (Nasso and Livingston, 2008). This way, energy-efficient separation can be achieved as no energy is required for the phase transition. A first successful OSN process was developed by ExxonMobil Corporation and W.R. Grace, as a hybrid separation for recovering solvents used in the refining of lubricants (Gould et al., 2001). Besides the application as a part of hybrid separation for new processes, OSN can be integrated in existing processes (retrofit), in order to decrease operating costs by lowering the energy

---

[*] *Corresponding author*. Tel.: +49 231 755 5335; fax: +49 231 755 3035.
E-mail addresses: jovana.micovic@tu-dortmund.de (J. Micovic), kathrin.werth@bci.tu-dortmund.de (K. Werth), philip.lutze@bci.tu-dortmund.de (P. Lutze).

Received 21 October 2013; Received in revised form 31 January 2014; Accepted 8 February 2014
http://dx.doi.org/10.1016/j.cherd.2014.02.012

Please cite this article in press as: Micovic, J., et al., Hybrid separations combining distillation and organic solvent nanofiltration for separation of wide boiling mixtures. Chem. Eng. Res. Des. (2014), http://dx.doi.org/10.1016/j.cherd.2014.02.012

Nomenclature

$A_{memb,p.vessel}$	total membrane area in one pressure vessel [m^2]
$A_{memb.element}$	total membrane area of one module element [m^2]
A_{free}	effective cross-flow area [m^2]
ΔA	area of one discrete membrane element [m^2]
$cost_{memb,ann}$	cost coefficient of membrane material [€/m^2/a]
d_h	hydraulic diameter [m]
$d_{memb.leaf}$	width of the membrane leaf in spiral wound module [m]
ΔDF	driving force
$h_{feed\_channel}$	height of the feed channel [m]
J	flux [mol/h/m^2]
k	mass transfer coefficient [m/s]
$l_{memb.leaf}$	membrane leaf length in spiral wound module [m]
$\dot{m}$	mass flow [kg/h]
$N_{discrete,x}$	number of discrete elements in feed flow direction [–]
$N_{discrete,y}$	number of discrete elements in permeate flow direction [–]
$N_{envelope}$	number of membrane leaves in spiral wound module [–]
$N_{memb.elements}$	number of membrane elements in a pressure vessel [–]
$N_{p.vessel}$	number of parallel pressure vessels in a stage in OSN [–]
$\dot{n}$	molar flow
P	permeability
R	rejection [%]
R	universal gas constant [J/mol/K]
Re	Reynolds number [–]
S_{VP}	specific spacer area [m^2/m^3]
Sc	Schmidt number [–]
Sh	Sherwood number [–]
T	temperature [K]
w	weight fraction [kg/kg]
x	molar fraction in the liquid phase [mol/mol]
v_i	molar volume of component i [m^3/mol]
$\dot{V}$	volume flow [m^3/h]
p	pressure [Pa]

Greek symbols

$\alpha_{solvent/solute}$	permselectivity [–]
ε_{spacer}	porosity of the spacer [–]
ρ	density [kg/m^3]
ρ_{mol}	molar density [mol/m^3]
ϑ	temperature [°C]
ψ	friction coefficient

Sub- and super-scripts

i	running variable for all components
solute	components without one preferentially permeating component (solvent)
solvent	preferentially permeating component
feed	feed stream/side
permeate	permeate stream/side
rententate	retentate stream/side
k	running variable for discrete elements in x direction (feed flow direction)
j	running variable for discrete elements in y direction (permeate flow direction)

consumption or to increase the capacity (Vandezande et al., 2007).

However, the lack of design methods for OSN and OSN-assisted hybrid processes is one of the main obstacles for their wide scale industrial application. Following challenges in design can be identified:

- **Choosing a suitable membrane** for a given separation problem is challenging because of the complex interactions between membrane, solvent and solutes (Gevers et al., 2006). Due to these interactions, the possibilities to predict membrane performance are limited. Currently, several authors published works which aim to improve the understanding of the transport phenomena and to predict membrane performance. Hesse et al. (2013) developed a method for predicting solvent flux, which is based on diffusion and solubility measurements, and which showed satisfactory results for pure solvents in Matrimid membranes. Marchetti et al. (2012) presents a model for flux prediction in ceramic membranes. Zeidler et al. (2013) suggest heuristic to predict rejection for set of components and Schmidt and Lutze (2013) developed tools for predicting and improving rejection in ternary mixtures. Although promising to improve understanding of OSN, these predictions are (still) limited to investigated membranes and components, and may be strongly influenced by side components. Hence, for majority of technical applications, experiments are still inevitable. In addition, choosing a suitable membrane can be also difficult if several membranes perform well in the chemical system, but differ in flux, rejection or their sensitivity to presence of side components, because it is unknown what will mostly influence the particular process.
- **Describing the influence of operating conditions** has not been investigated systematically, as most experiments are usually performed in diluted systems at room temperature. Silva et al. (2010) investigated the permeation at high concentrations, and concluded that the solution-diffusion model including a term for concentration polarisation can describe flux and rejection in a large operating range for one temperature. It is not clear if this is also applicable to other chemical systems, and in complex mixtures, detailed experiments are necessary to determine the influence of the temperature, concentration and side components on flux and rejection.
- **Finding an optimal process** is challenging, since the combination of two units for one separation results in a large number of degrees of freedom. These include i.e. both structural (position of unit operations, recycle streams) as well as operation degrees of freedom (Franke et al., 2004; Marquardt et al., 2008). Furthermore, for OSN, optimal number of modules, their arrangement and internal retentate and permeate recycles need to be identified. This is not trivial, since it cannot be solved independently from points 1 and 2. For example, if permeate recycling is allowed, permeate quality may be improved which means that membranes

Please cite this article in press as: Micovic, J., et al., Hybrid separations combining distillation and organic solvent nanofiltration for separation of wide boiling mixtures. Chem. Eng. Res. Des. (2014), http://dx.doi.org/10.1016/j.cherd.2014.02.012