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Drying of supercritical carbon dioxide with membrane processes

Theresa Lohaus[a], Marco Scholz[a], Beata T. Koziara[b], Nieck E. Benes[c], Matthias Wessling[a,d,*]

[a] Chemical Process Engineering AVT.CVT, RWTH Aachen University, Turmstraße 46, 52064 Aachen, Germany
[b] Membrane Science and Technology, University of Twente, Department of Science and Technology & MESA+Institute for Nanotechnology, P.O. Box 217, 7500 AE Enschede, The Netherlands
[c] Inorganic Membranes, University of Twente, Department of Science and Technology & MESA+Institute for Nanotechnology, P.O. Box 217, 7500 AE Enschede, The Netherlands
[d] DWI – Leibniz-Institute for Interactive Materials, RWTH Aachen University, Forckenbeckstraße 50, 52074 Aachen, Germany

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ABSTRACT

In supercritical extraction processes regenerating the supercritical fluid represents the main cost constraint. Membrane technology has potential for cost efficient regeneration of water-loaded supercritical carbon dioxide. In this study we have designed membrane-based processes to dehydrate water-loaded supercritical carbon dioxide and have evaluated the processes economics as compared to those of a benchmark zeolite process. Seven flowsheet configurations have been simulated in Aspen Plus®. In all processes a low-pressure carbon dioxide sweep stream removes water at the permeate side of the membrane, to maintain a sufficiently large driving force for water transport through the membrane. The performance of the single module has been analyzed to determine suitable process variables, such as the magnitude of sweep gas flow. We identify three flowsheet configurations each having individual benefits: Configuration 1 is most simple but highly sensitive towards changing process parameters, configuration 2 is CO_2-emission-free, and configuration 3 is most insensitive towards membrane selectivity. With configuration 3 a cost reduction of 20% compared to the benchmark zeolite adsorption is identified: also the process is continuous and free of cycling of gas streams.

1. Introduction

The use of supercritical carbon dioxide in extraction processes emerges due to their beneficial solvent properties, non-toxicity, and environmental friendly handling properties. As an extraction medium, supercritical carbon dioxide is long known for the decaffeination of coffee [1]. Recently, supercritical carbon dioxide is tested as a drying agent for food to replace high energy demanding freeze drying processes [2].

Fig. 1 displays a schematic supercritical fluid extraction process comprising an extraction and a regeneration step. Regenerating the supercritical fluid represents a main cost driver of the operational costs of the extraction process [3]. Conventionally, regeneration is performed with adsorptive technologies, such as zeolites, with the disadvantage of high operating costs for desorbing the loaded adsorbent. Membrane technology is a potential alternative to adsorptive processes. In membrane processes compression costs usually determine the process costs [4,5]. For supercritical fluids the feed stream is already highly compressed. Membrane technology applied to supercritical fluid processes should profit from potentially lower operational costs.

Birtigh and Brunner [6] studied different regeneration methods for loaded supercritical fluids. Several publications and patents are available on the regeneration of supercritical fluids with porous and microporous membranes such as for the separation of caffeine from supercritical carbon dioxide [7–9]. Yet limited publications have been reported on the subject of removing water from supercritical carbon dioxide with dense polymeric membranes [10]. Such dense membranes are known to accomplish the separation of sub-critical carbon dioxide and water [11,12]. For low or ambient pressure systems numerous papers and patents are available on the drying and dehumidification of air and other gases with membranes especially on the field of air conditioning systems using sweep streams. Among them are several patents with drying methods that propose flowsheet designs similar to the investigated flowsheet configurations in this study [12–15]. Little is known on process configuration for drying processes at supercritical gas conditions.

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* Corresponding author at: Chemical Process Engineering AVT.CVT, RWTH Aachen University, Turmstraße 46, 52064 Aachen, Germany. Tel.: +49 241 8095488; fax: +49 241 8092252.
E-mail address: Manuscripts.cvt@avt.rwth-aachen.de (M. Wessling).

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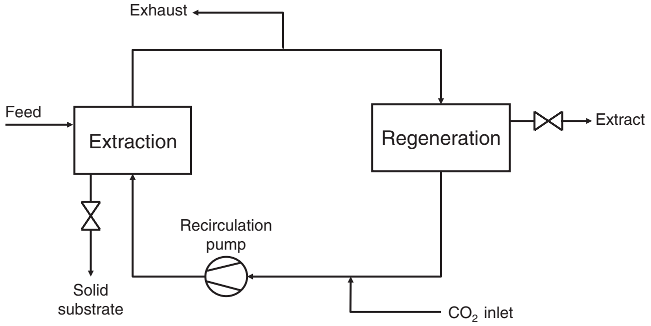

Fig. 1. Schematic supercritical fluid extraction process.

This study investigates possible process configurations in which highly selective membranes regenerate loaded supercritical carbon dioxide. We examine whether membrane technology is a suitable alternative to adsorption on zeolites. Process economics as well as particular process characteristics are critically evaluated.

2. Process description and modeling

We extended a model for a hollow fiber membrane module developed by Scholz et al. [16]. In this model the permeation through the membrane is described by the solution–diffusion model [17]. The 3-End model developed by Scholz et al. [16] was expanded to a 4-End module to allow for the use of a sweep stream. Changing the boundary conditions links the sweep's temperature T, pressure p, enthalpy h, molar composition x and molar volume v to the model variables.

The model accounts for the following non-ideal effects: (i) real fluid behavior and (ii) the temperature change according to Joule–Thomson effect at depressurization of the gas crossing the membrane. Since the behavior of a supercritical fluid close to saturation with water is highly non-ideal, properly describing real gas fluid behavior is crucial.

2.1. Process parameters

The process aims to dehydrate a water-loaded supercritical CO_2 stream. The dehydration degree D is defined as the normalized amount of water removed from the feed:

$$D = 1 - \frac{\dot{m}_{H_2O,\mathrm{Ret}}}{\dot{m}_{H_2O,\mathrm{Feed}}} \qquad (1)$$

where $\dot{m}_{H_2O,\mathrm{Ret}}$ and $\dot{m}_{H_2O,\mathrm{Feed}}$ are the water mass flow rates in retentate and feed, respectively.

Fig. 2 illustrates the relation between D and the required membrane surface area. The non-linear increase in the required membrane surface area is in particular steep for D exceeding 95% at the implemented conditions. This graph depends on the applied process variables but the main characteristic pertains. In the following, we set the required value for D to 95% for two reasons. Firstly, for higher D the sharp increase in required membrane surface area might not be justified by the moderate benefit in the process performance. Secondly, high values of D also require highly dried sweep streams.

The feed is set to a flow rate of 200 kg/h, corresponding to a pilot plant size of a food drying application in industry. We chose a respective pilot plant size to enable simple comparison of the results to perspective pilot plants. Both, feed temperature and pressure exceed the critical values of CO_2 ($p_c = 73.83$ bar, $T_c = 31.06\,°C$) with 100 bar and 50 °C. The feed stream is saturated with water.

CO_2 loss due to permeation is inevitable. Make-up CO_2 needs to compensate for the loss within the extraction cycle. For an economically competitive design a high CO_2 yield is required to limit the costs for fresh make-up CO_2 and its compression.

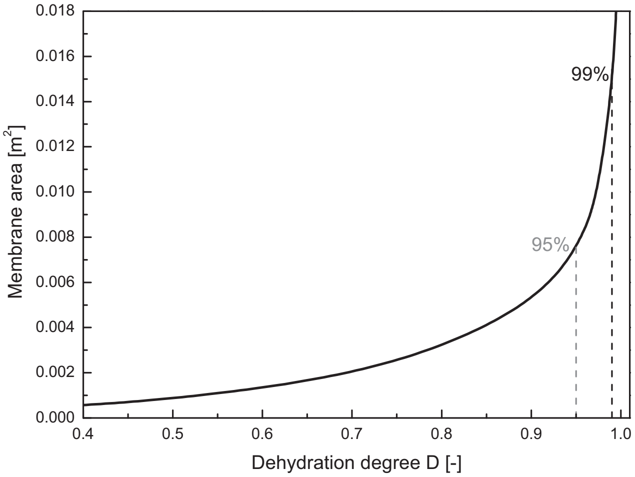

Fig. 2. Applied membrane area as a function of the depletion degree of H_2O in the product stream. Depletion degree according to Eq. (1). The simulation was performed with a single stage membrane process, a sweep to feed ratio of 0.2, a permeate pressure of 3 bar, pure CO_2 as sweep gas, and saturated feed composition according to Table 1.

Permeability values were estimated to be 20 Barrer for CO_2 and 10^5 Barrer for H_2O based on low-pressure experiments conducted by Potreck [18] at the University of Twente using sulfonated polyetheretherketone (SPEEK) membrane material. Experiments at supercritical conditions are to follow. The assumed selectivity of 5000 seems reasonable as Spiegelmann et al. [19] published values of 3300. Because the membrane model uses permeance instead of permeability the proposed permeability values are converted to GPU assuming a membrane thickness of 40 nm [20].

Several gases can be used as sweep gas. The chosen sweep gas will inevitably be present in the retentate stream because, if not present in the feed, it will permeate through the membrane against the pressure gradient until partial pressure equilibrium. Since small amounts of sweep substance enter the food drying chamber, the sweep substance should comply with the following characteristics: (i) non-toxic, (ii) odorless, (iii) inflammable, and (iv) inert. We chose CO_2 because it is cheap and already present in the process. As a feed substance CO_2 allows to recycle a sweep stream and mix it with feed or retentate stream. Air might also be interesting if the amount of reactive oxygen can be tolerated.

Reliable model simulations require adequately estimated physical properties. Few of the available equation of states in Aspen Plus® are able to determine physical properties close to the critical point realistically. However, appropriate choice of the method is crucial for simulation results. Fig. 3 shows isothermal saturation curves simulated with two different models next to measured data from different literature sources. Below, the processes have been simulated with Predictive Soave Redlich Kwong (PSRK). For comparison all processes were also simulated with the second-best method Schwarzentuber–Renon (SR-Polar). This comparison quantifies the sensitivity of the simulation to different property models. Table 1 summarizes the fixed process parameters.

2.2. Economics

To evaluate the proposed flowsheet designs their economics, i.e., operational and investment costs, are compared with a benchmark zeolite process. Table 3 lists all relevant economic parameters.

The annual operating costs of each process include energy consumption of the process equipment for heating, cooling, and