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Mass transfer studies on the dehydration of supercritical carbon dioxide using dense polymeric membranes

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ABSTRACT

Continuous drying processes using supercritical CO_2 ($scCO_2$) as a water extraction agent require 24/7 operational dehydration units for $scCO_2$ regeneration. Dehydration units using dense polymeric membranes are considered a cost effective, sustainable alternative to the current zeolite-based units. The focus of previous studies on the membrane-based dehydration of $scCO_2$ was always on the membrane itself whereas boundary layer effects, e.g., concentration polarization, were not taken into account. To quantify the boundary layer effects, simulations were performed using three different membrane materials: SPEEK, Nafion® 117, and PEBAX® 1074. Process conditions during the simulations ranged from 8.0 to 18.0 MPa and 40 to 100 °C. Even though the three types of membranes examined differ in their H_2O permeability and H_2O over CO_2 selectivity, in all cases 80% of the total mass-transfer resistance can be assigned to concentration polarization effects, making it the dominant parameter for water transport. Despite high but differing intrinsic water permeabilities of all three membranes materials, the H_2O transport, thus H_2O flux through the membrane is significantly reduced by concentration polarization down to similar levels. This makes it necessary to use larger membrane areas, that result in higher CO_2 fluxes. As a consequence, material selection is predominantly based on the ability to reject CO_2. Optimization of process conditions other than membrane material is briefly discussed.

1. Introduction

Supercritical CO_2 ($scCO_2$) is frequently used in industrial processes for e.g. the drying of fruits and vegetables to extent shelf life [1]. Due to its supercritical state, it has high densities values typical for liquids and simultaneously low viscosities characteristic for gases [2]. Moreover as drying is performed at relatively low temperatures and under oxygen free conditions, vitamins, pigments and proteins are preserved ensuring the nutritional value and the dried products keep their color, shape, structure and texture [3]. Although performed under pressure, $scCO_2$ drying is a very mild process.

Fig. 1 displays the typical outline of such an industrial drying process using $scCO_2$. Dry $scCO_2$ enters the extraction unit, extracts the water from the product and leaves the unit as a humidified stream. This stream is then regenerated in a dehydration unit before it is re-injected into the extraction unit for the next water extraction cycle. Typical fluid temperatures and pressures are in the range of 45 °C and 13.0 MPa [3], which is beyond carbon dioxides critical values of T = 31.04 °C and p = 7.38 MPa [2].

Currently, columns packed with adsorbents such as zeolites are applied to dehydrate the $scCO_2$. The enclosed adsorbents extract water from the $scCO_2$ until they are fully saturated. Temperatures up to 260 °C are needed to reactivate the zeolite by water desorption [4]. While this energy demanding reactivation step is carried out, a second zeolite packed column is switched in to continue the $scCO_2$ dehydration. The required reactivation energy and the additional zeolite column make the $scCO_2$ drying process economically less attractive. Lohaus et al. [4] showed with their model, based on Scholz et al. [5], that a shift towards a membrane-based dehydration process, where a second dehydration unit and reactivation steps are obsolete, could reduce the dehydration costs up to 20%. Even though Lohaus et al. simulated and discussed water vapor concentration profiles and the driving force profiles along the membrane unit, the combined mass transfer of the skin layer material, its porous support and the feed- and permeate boundary layers were not taken into account in their analysis. Each of these stacked layers is very different constituted, especially under highly pressurized $scCO_2$ conditions, where the fluids density and viscosity are very different to those in conventional gas separation applications. It stands to

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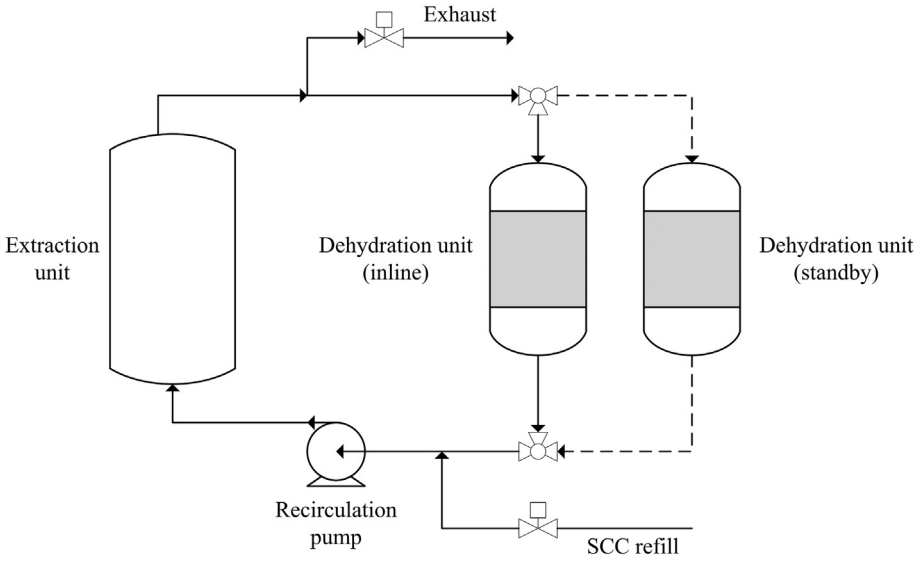

Fig. 1. Schematic view of a typical currently existing dehydration process using $scCO_2$ as the water-extraction agent (left unit) and zeolite to dehydrate (regenerate) $scCO_2$ (right units). To enable continuous regeneration a second dehydration unit is in standby mode.

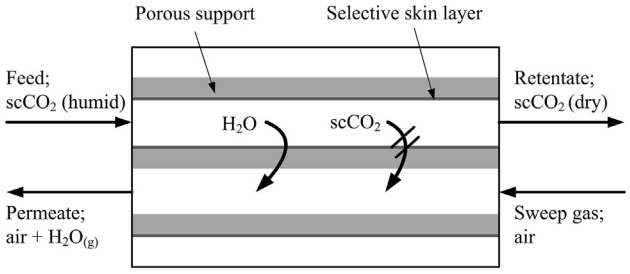

Fig. 2. Scheme of the flat sheet membrane stack considered for the mass transfer examination. Water, enters the unit via the humid feed stream and permeates through the skin layer while $scCO_2$ is rejected. This leads to a gradual decay of the water content within the feed stream. The permeated water is entrained by the dry air entering the unit as a sweep gas. The dried $scCO_2$ is ready for its reuse as an extraction agent whereas the humidified air is emitted into the environment.

reason that in the special case of exposure to $scCO_2$ the contribution of each single layer contributes differently to the total water transport resistance and thus to the water permeance.

Composite membranes, consisting of a thick porous support and a thin selective, water permeable, skin layer, can withstand transmembrane pressures of more than 10.0 MPa. Due to polarization effects in the boundary layers, evoked by severe $scCO_2$ conditions, the overall selectivity and permeability can be very different from those of the membrane (or skin layer) itself. Therefore, polarization effects need to be included in any analysis of mass transfer resistances during membrane transport.

Metz et al. [6] concluded that concentration polarization effects, enhanced by the relatively low H_2O diffusion across the feed gas boundary layer, compromise the water vapor permeability and H_2O/CO_2 selectivity already at low feed pressures. At constant temperature and increasing pressure, molecules start gathering more densely, leading to a reduced mean free path of motion, an increased molecular collision resulting in a lower diffusion coefficient. The relationship between the declining diffusion coefficient and increasing fluid density was also pointed out by Magalhães et al. [7]. Considering the high fluid density under $scCO_2$ conditions, up to 200 times higher compared to the low pressure experiments of Metz [6], it is expected that concentration polarization effects become even more dominant. Scholz et al. [5] analyzed non-ideal effects during gas permeation, including concentration polarization, the pressure drop along the flow channels and the Joule-Thomson effect. Even though we focused exclusively on the effect of concentration polarization, allowed maximum pressure drops along the flow channels are implicitly accounted for. Because of applying a sweep gas (in contrast to Schulz et al. [5]), the Joule-Thompson effect has been ignored during our simulations.

During the dehydration process of $scCO_2$ and when moving from the feed bulk to the permeate bulk solution, the water vapor (and CO_2) passes four layers in series: the feed boundary layer, the active skin layer, the porous membrane support and the permeate boundary layer, as depicted in Section 2.1 Transport model. The three highly water vapor permeable and H_2O/CO_2 selective membrane materials: SPEEK, Nafion® 117 and PEBAX® 1074, were included in this study. The aim of this simulation study is to delineate the contribution of each of these layers to the overall mass transport resistance. Recommendations for membrane material selection as well as process conditions to optimize the membrane-based dehydration will be discussed.

2. Theory

The membrane design considered in this study contains multiple flat sheet membranes arranged in parallel and separated by feed and permeate channels (Fig. 2). Ideally, the membrane is highly permeable for H_2O but not for $scCO_2$. As a result, humid $scCO_2$ that enters the feed channel, gets dehydrated and exits the feed channel as a dry $scCO_2$ stream ready for being reused as drying agent. A sweep gas, being pre-dried air, is used to maintain a high driving force for water vapor transport. A with water saturated $scCO_2$ feed stream, having pressures and temperatures of 13.0 MPa and 45 °C, is considered in this study.

2.1. Transport model

The system analyzed in this study is schematically depicted in Fig. 3. The product drying, hydrated $scCO_2$ is the bulk feed solution from which the water is transported via the feed boundary layer, (selective) skin layer of the membrane, porous support of the membrane, permeate boundary layer into the bulk permeate solution.

Assuming well-stirred conditions in the bulk solutions, the overall mass transfer resistance R_{ov} as well as the overall mass transfer coefficient k_{ov} can be represented by four mass flow resistances in series: