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Mass transfer and selectivity analysis of a dense membrane contactor for upgrading biogas[☆]

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ABSTRACT

The mass transfer of a dense membrane contactor for the removal of CO_2 from a biomethane-CO_2 mixture was investigated in detail. Pure gas CO_2 experiments as well as mixed gas experiments were conducted in order to determine the transmembrane flux and the selectivity of the contactor as a function of the pressure level and the transmembrane pressure difference. Two membranes, a PDMS coated and a Teflon-AF coated composite flat-sheet gas permeation membrane (PolyActive™) were tested in the self-constructed membrane module. The mass transfer was analyzed using a rigorous mass transfer model. With this model, it was possible to determine the mass transfer resistance of the membrane and the liquid boundary layer. It was found that both resistances do significantly contribute to the overall mass transfer resistance that is governing the membrane flux and the selectivity of the dense membrane contactor. Nevertheless, an increased driving force due to an increased pressure difference across the membrane could easily compensate for the additional mass transfer resistance of the membrane. A transmembrane pressure difference of up to two bars and absorbent liquid phase pressures at the permeate side of up to five bars were applied. It could be shown that a higher permeate pressure and a large transmembrane pressure difference is favorable for both, the permeance and the selectivity of the dense membrane contactor.

1. Introduction

In the last decades, process intensification has been one of the most investigated topics in chemical engineering [1]. One of the major aims of process intensification is reducing the size of the used equipment. A common approach to size reduction is the combination of different separation principles in one apparatus. Membrane contactors provide a very promising way of process intensification for gas separation by integrating a membrane in an absorption module. Size reductions factors of 5–20 can possibly be [1–5]. Membrane contactors can be used for the removal of CO_2 from natural gas, biogas and exhaust gas but also for degassing of liquids [6] or carbonation of beverages [7]. In general, the membrane provides the high mass transfer area in the contactor while the absorbent accounts for its high selectivity. Often, these effects cannot be clearly distinguished since the membrane can also contribute to the overall selectivity of the process. Even the potentially higher mass transfer resistance of such membrane contactors can be overcompensated by the much larger specific mass transfer area so that the volumetric mass transfer is up to 3–9 times higher than in comparable absorption equipment [8–11].

According to Chabanon et al. [12], where a sound overview on the historical development of membrane contactors is given, the basic idea of this principle came up in the 1960s. As stated there, the use of membrane contactors for gas absorption can be attributed to Qi and Cussler [5]. Since that time, a lot of research has been published on membrane contactors, particularly on the removal of CO_2 [9,12–22]. A comprehensive review paper on membrane-based CO_2 capture has been published by Luis et al. [23].

The membrane used in membrane contactors can be either porous or dense. Accordingly, the term dense membrane contactor represents contactors with a dense membrane whereas the term porous membrane contactor embodies the use of a porous membrane in the membrane contactor. Most of the research focuses on porous membranes for the anticipated use in membrane contactors. Nevertheless, there are several crucial disadvantages inherent to the use of porous membranes:

- Depending on the surface tension of the solvent and the pore radius of the porous membrane, porous membranes tend to

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exhibit pore wetting.

- In order to prevent pore wetting, the transmembrane pressure difference has to be larger than the breakthrough pressure.
- If the pressure on the feed side is too high, bubbling can occur, i.e. the gas pearls uncontrolled into the solvent.

Both effects (pore wetting and bubbling) diminish the separation performance of the contactor considerably and thus have to be avoided. The pressure difference in porous membrane contactors has thus to be controlled in a very narrow operation field to avoid bubbling or pore wetting, which is particularly difficult if the flow regime of the fluids exhibits a substantial pressure drop in the membrane contactor module.

Luis et al. [24] pictured out four key aspects to make membrane contactors competitive to direct-type absorption technology. Besides the elimination of membrane wetting, the authors call for the development of membranes with long-term stability, the use of environmentally friendly absorption liquids to reduce the impact on the nature as well as the study of the impact of other compounds on the efficiency of the process. In this publication, a dense membrane contactor is used that clearly attributes the wetting issue in order to advance this technology towards industrial applicability. Moreover, dense membrane contactors

- can be operated with a large transmembrane pressure difference, i.e. the feed pressure can be many times higher than the solvent pressure on the permeate side.
- have a very high specific mass transfer area provided by the membrane.
- obtain their overall mass transfer selectivity due to both, the selectivity of the solvent and the membrane, depending on the respective mass transfer coefficient.
- are flexible and robust in operation.

By increasing the transmembrane pressure difference, the driving force of the process can be increased and thus, the necessary amount of solvent can be decreased. Therefore, the membrane material should be highly permeable for the gas components that have to be separated. The dense layer of the membrane must be impermeable for the liquid solvent but thin in order to minimize the transport resistance of the membrane. Generally, three types of membranes used in dense membrane contactors can be distinguished:

- Homogenous type membranes, where the whole membrane is made from one polymer layer that is solvent impermeable and highly permeable for gases. The membrane is self-standing, i.e. no support layer bears for the mechanical strength of the membrane. Thus, the membrane must be rather thick and has a low permeance despite the high permeability of the membrane material. Typically, these membranes are made from silicone rubber.
- Dense skin asymmetric membranes consisting of a porous support layer and a thin separation layer made from the same material (Loeb-Sourirajan type). This is advantageous since the porous support provides the mechanical strength of the membrane but does not contribute to the mass transfer resistance while the dense separation layer can be very thin.
- Composite membranes that consist of a porous support with a thin separation layer. Support and separation layer are made of different materials. Often, porous membranes are used as support and are coated with a thin separation layer. Many different polymers can thus be used as separation layer.

Apart from homogenous PDMS membranes, there is only a limited number of polymers used for the separation layer in dense membrane contactors for CO_2 separation. Only few membranes are commercially available while most self-produced membranes are only produced in small lot sizes and thus not commercially available. The group around Teplyakov [13,25–29] uses asymmetric flat-sheet PVTMS membranes provided by the A.V. Topchiev Institute of Petrochemical Synthesis (TIPS), Russia. Kosaraju et al. (DIC Inc., Tokyo, Japan) [30] and Trusov et al. (self-produced) [21] investigate asymmetric PMP hollow-fiber membranes for CO_2 separation while Chabanon et al. [12] and Simons et al. [31] use asymmetric PPO-Membranes from Parker Filtration & Separation B.V. A large group of researchers has been investigating flat-sheet and hollow-fiber PTMSP membranes [9,20,21,28,29,32,33]. Li and his coworkers [16,17] worked with self-made asymmetric PES membranes. All materials have to have a high CO_2 permeance while being impermeable for water.

From the published results, it can be deducted that using composite membranes is advantageous to porous membranes in membrane contactors since the wetting problem can be eliminated. Homogenous membranes however are not suitable for the use in dense membrane contactors since their permeance is too low compared to composite membranes, which results in poor transmembrane fluxes.

The performance-enhancing increase of the transmembrane pressure difference on the membrane flux and its effect on the selectivity has not been thoroughly considered in literature. Since the mechanical strength of homogeneous type membranes is limited, the use of asymmetric membranes is favorable for enlarged pressure differences. Composite gas permeation membranes supplied with a porous support and a solvent-impermeable top layer are thus predestined for the use in membrane contactors. To the best knowledge of the authors, commercially available PolyActive™ membranes manufactured by Helmholtz Zentrum Geesthacht, Germany (HZG) [34,35] which are used in the presented work have never been used in a dense membrane contactor for CO_2 removal. This asymmetric membrane is highly permeable for CO_2 and selective for its separation from CH_4 and N_2. The selective layer is made of a PEO-PBT block co-polymer and coated with either a PDMS or a Teflon-AF protection layer. The mass transfer resistance $k_{i,c}^{M}$ of the PolyActive™ membrane was measured and found to be larger than 10^{-4} m/s for both, CO_2 and CH_4 (see Table 3). The use of a field-tested membrane attributes the second key aspect for emerging membrane contactor technology recommended by Luis et al. [24].

In the presented work, water as a physical solvent is used for upgrading biogas. Water was chosen being a cheap and non-toxic physical solvent. An application in a dense membrane contactor using physical solvents under elevated transmembrane pressures is thus consequential. In this study

- The performance of a composite membrane with two different membrane top layer materials for the use in a dense membrane contactor is shown.
- The influence of the pressure level, the transmembrane pressure and the solvent velocity on the transmembrane CO_2 flux of a dense membrane contactor using water as physical solvent is experimentally determined for both, pure CO_2 and various CO_2/CH_4 gas mixtures.
- Two rigorous mass transfer models based on fugacities are formulated and solved simultaneously to determine the wet permeance and the liquid-side mass transfer coefficient of a dense membrane contactor.
- The influence of the membrane permeance and the liquid-side mass transfer coefficient on the overall selectivity of the process is analyzed and compared to experimentally determined selectivities.