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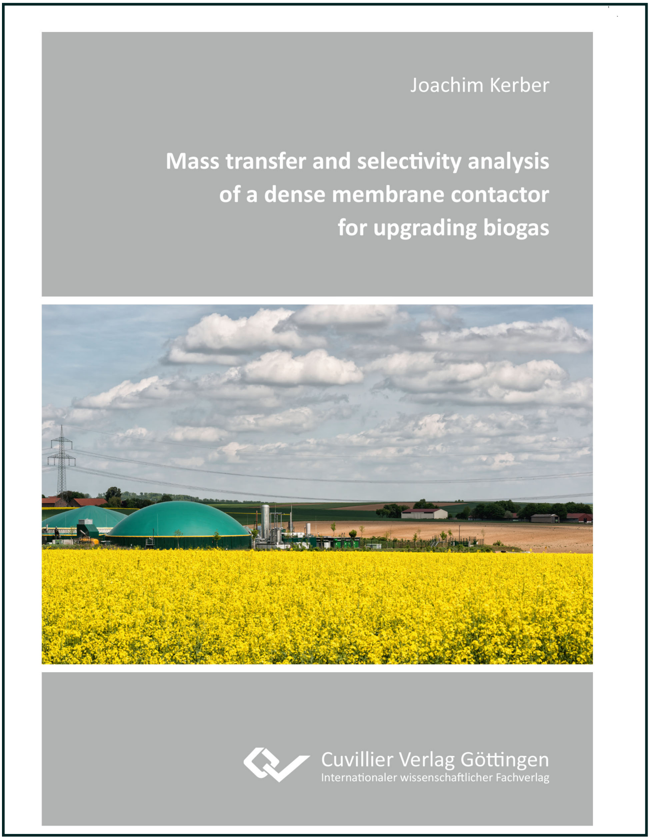

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CHAPTER 1

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 for 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 achieved [1, 2, 3, 4]. Membrane contactors can be used for the removal of CO_2 from natural gas, biogas and exhaust gas but also for degassing of liquids [5] or carbonation of beverages [6]. 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. Using such membrane contactors instead of state-of-the-art absorption columns can reduce the equipment size as well as the necessary amount of solvent for the gas separation task since the specific mass transfer area of membrane contactors is in general much higher than in absorption columns [7]. 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 rate is up to 3-9 times higher than in comparable absorption equipment [8, 9, 10, 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 [7]. Since that time, a lot of research has been published on membrane contactors, particularly on the removal of CO_2 [9, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. A comprehensive review paper on membrane-based CO_2 capture has been published by Luis et al. [13]. Criscuoli and Drioli [25] recently published a review article on membrane contactors for CO_2 absorption. In Pabby et al. [26], a detailed overview on the industrial use of membrane contactors is given. The membrane used in membrane contactors can either be 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. In dense membranes, the mass transfer in the membrane occurs only by diffusion whereas in the pores of a porous membrane, convective transport is taking place. Other than dense membranes, porous membranes in membrane contactors do not account for the selectivity of the process since the membrane pores are much larger than the gas molecules. The selectivity of porous membrane contactors is thus solely provided by the solvent whereas the porous membrane must have the ability to keep the gas and the liquid phase separated. Most of the research focuses on porous membranes for the anticipated use in membrane contactors due to their supposedly lower mass transfer resistance compared to dense membranes. 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 exhibit pore wetting.
- In order to prevent pore wetting, the solvent pressure may not be higher than the breakthrough pressure (i.e. the maximum tolerable solvent pressure before the solvent starts wetting the membrane pores).
- If the solvent pressure is too low, 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. To subsume, the pressure difference in porous membrane contactors has 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. Dense membrane contactors however can be robustly operated, even with substantial transmembrane pressure differences.

Upgrading biogas to bio natural gas (BNG) is a promising approach to substitute regenerative biogas for finite fossil gas. Moreover, the upgraded gas can be fed in the existing natural gas grid and thus be used more efficiently than CO_2-rich biogas. For producing bio natural gas, the main part of the carbon dioxide needs to be removed from the biogas, which is crucial for the economic feasibility of the upgrading process [27]. This is necessary since the physical properties of bio natural gas have to comply with the requirements and regulations of natural gas, e.g. the heating value, before blending it into the existing natural gas grid. There are different commercially applied processes for the upgrading step, e.g. amine scrubbing, pressure swing adsorption, high-pressure water scrubbing (HPWS) and, recently increasing, gas permeation membrane processes [28]. The conventional separation processes are technically mature but do not make use of synergies between the respective processes, which could offer additional benefits. Gas permeation membrane processes, in contrast, have a high potential to lower the separation costs due to their simple operation but lack high separation efficiencies within the demanded limits. Hence, for process intensification, the integration of a dense gas separation membrane in other unit operations is advantageous [29]. A comprehensive overview of commercial manufacturers of gas permeation membranes for upgrading biogas, including the respective active polymer membrane material is given in Scholz et al. [30]. More than that, the membrane used in this work (PolyActive^{TM}) and its application in a gas permeation process for biogas separation is depicted in Brinkmann et al. [31].

1.1. Objective of this study

Luis et al. [32] pictured out four key aspects to make membrane contactors more competitive to conventional 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, and the study of the impact of other compounds on the efficiency of the process. This work clearly attributes the first three issues in order to advance this technology towards industrial applicability.

In order to eliminate the membrane wetting issue, composite gas permeation membranes supplied with a porous support and a solvent-impermeable top layer have been used in this work since the mechanical strength of homogeneous type membranes is limited. To the best knowledge of the author, the applied commercially available PolyActive^{TM} membranes manufactured by Helmholtz Zentrum Geesthacht, Germany (HZG) [33, 31] have never been used in a dense membrane contactor for CO_2 removal. These membranes are highly permeable for CO_2 and selective for its separation from CH_4 and N_2. The selective layer is a PEO-PBT block co-polymer and available with a strongly hydrophobic PDMS and a Teflon-AF protection top layer. The use of a field-tested membrane attributes the second key aspect for emerging membrane contactor technology recommended by Luis et al. [32].

The overall mass transfer in the dense membrane contactor incorporating the respective membrane-based and solvent-based mass transfer resistances as a function of the transmembrane pressure difference, the pressure level, and the solvent flow rate has not been extensively considered in literature. This work clearly attributes this topic. Thus, the mass transfer in the dense membrane contactor is thoroughly analyzed in order to better understand the mass transfer principles and the influence of decisive process parameters such as pressure level and transmembrane pressure difference on the membrane permeance and the overall mass transfer resistance. More than that, the solvent-deduced effects on the membrane permeance are thoroughly investigated. This work thus contributes substantially to the better understanding of dense membrane contactors since it is of great importance for a precise and efficient process design.

A flat-sheet membrane contactor has been constructed in order to investigate the mass transfer in the membrane contactor. Single gas CO_2 and mixed gas CO_2/CH_4 experiments have been carried out in a self-constructed flat-sheet membrane contactor using pure water, a 1M K_2CO_3 solution and glycamal as solvents in order to assess the performance of the contactor for different physical and chemical solvents. The influence of the top layer material of two different composite membranes on the performance of the membrane contactor is shown. In order to deduce the respective mass transfer resistances from the experimental measurements, two rigorous simulation models have been developed.

The main focus of this work is on the description of the mass transfer principals in the dense membrane contactor rather than the detailed process design. An economic evaluation as well as an exhaustive comparison of this technology with other existing biogas upgrading processes is thus not possible. Even so, in order to duly consider the overall biogas upgrading framework of this work, this topic is given an own chapter where a rather short summary of all aspects of biogas upgrading is given.

1.2. Thesis overview

After being briefly introduced in this chapter, a detailed overview of dense membrane contactors is given in Chapter 2 where their advantages are explained, the polymer membranes used in membrane contactors are introduced, and the state of the art of dense membrane contactors is elaborated. Chapter 3 describes the required biogas purification steps for the production of biomethane from raw biogas. Here, the emphasis is on absorption processes that membrane contactors for biogas upgrading mostly compete with. The intention of this chapter is to give a compact overview on biogas upgrading. It has thus more of an informative nature in order to frame this work into the overall context. At the end of the chapter, however, the volumetric transmembrane flux is introduced, which allows an efficient comparison of membrane contactors with conventional absorption equipment which will be used all over the results section of this work (Chapter 9 and Chapter 10). In Chapter 4, the fundamental principles of the mass transfer in a dense membrane contactor are defined. More than that, the thermodynamic and reaction engineering fundamentals are described in detail. In order to gain a deeper understanding of the abstract matter, a first evaluation of the fundamental correlations has been carried out in this chapter, based on the physical and mathematical context of the phenomena introduced. Hence, several graphs were being integrated that illustrate the theoretical correlations introduced in this chapter. Based on the mathematical equations deduced from thermodynamic and fluid dynamic principles introduced in Chapter 4, two rigorous simulation models of the membrane contactor were developed. The *resistance-in-series model* that is used for calculation the overall mass transfer coefficient of the membrane contactor and the *boundary layer model* that allows the detailed investigation of the respective mass transfer coefficients of the applied membrane and the liquid. The full set of equations for these models is depicted in Chapter 5. In Chapter 6, the applied materials but also the design of the test cell for the experimental data and the routine for the conduction of the experiments are illustrated. More than that, the evaluation of the experimental data using the simulation models in order to determine the mass transfer resistances depicted in Chapter 9 and Chapter 10 is explained. The results of the solvent characterization for physical solvents are depicted in Chapter 7, the gas permeation experiment results of the applied membranes are shortly discussed in Chapter 8. In Chapter 9, the results of the water experiments are presented whereas in Chapter 10, the results for all investigated solvents (water, a 1M K_2CO_3 solution and the physical solvent glycamal) are summarized. The thesis results in Chapter 11 with a short summary and the conclusion of the work.

CHAPTER 2

Dense Membrane contactors

The principal sketch of a dense membrane contactor for CO_2 removal from biogas is shown in Figure 2.1. The CO_2 containing biogas stream is channeled along the dense polymer membrane, the solvent flows in countercurrent direction on the permeate side of the membrane. CO_2 is selectively absorbed through the membrane into the solvent. Hence, the retentate stream is enriched with CH_4. A transmembrane pressure difference can be applied in order to increase the driving force of the process.

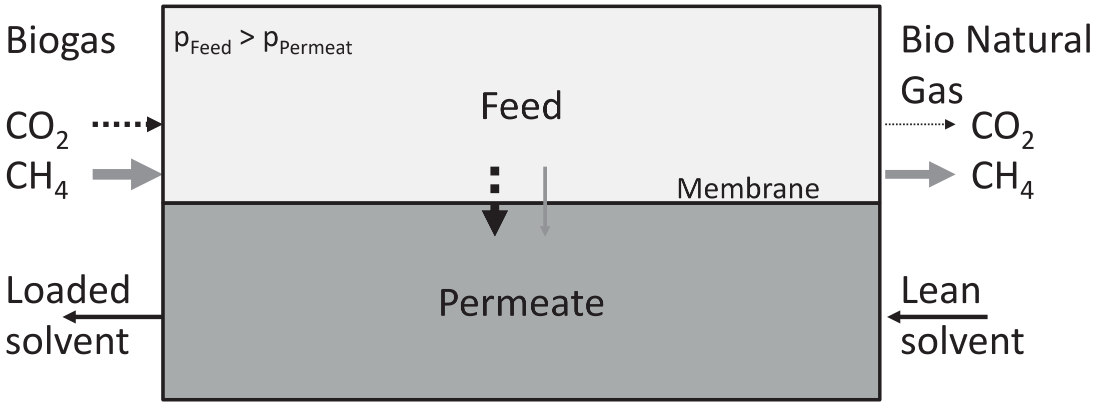

Figure 2.1: Principal sketch of a membrane contactor

2.1. Advantages of dense Membrane contactors

Dense membrane contactors show certain advantages compared to absorption columns and porous membrane contactors since the transmembrane pressure difference can be set independently for the respective phase. Dense membrane contactors

- 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.
- 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.
- are flexible and robust in operation - solvent and feed gas flow rate can be adjusted independently and thus optimized for a good absorption performance.

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. Other than in absorption