Novel membrane contactor for gas upgrading in biohydrogen production

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A novel membrane contactor (MC) system with dense membranes has been tested with different absorption media (MEA and K₂CO₃) concerning the separation efficiency of CO₂. To classify the prototype in terms of mass transfer resistance and separation capacity compared to MCs with porous membranes, a commercial available MC was tested under same conditions.

1 Introduction

The production of hydrogen from biological matter is always accompanied by the production of CO₂. Certain applications of the hydrogen demand pure quality. A couple of well established processes, applied in the chemical industry, are available to separate the CO₂. Widely used are absorption processes, such as chemo-absorption in the Amin-processes or physical absorption processes in the Rectisol-process. All these show high selectivity and reliability, but for their application in the bio process they have some serious disadvantages. The pressure drop in the gas phase is high which does not fit with the operational conditions of the bioreactors which produce the gases under ambient pressure. Secondly both phases, gas and absorbents, are in direct, intensive contact which results in evaporation of the chemicals which gives environmental problems.

A novel type of gas-liquid contactor, the membrane contactor (MC), gives the possibility to realize a high mass-transfer area with low pressure drop (Gabelman et al, 1999). The flow of the gas- and liquid phase is well separated by membranes. The area of the membrane corresponds with the mass-transfer area. By choosing proper geometries of the membranes a high volume related area and additionally low pressure drops in both phases can be achieved. Commercially available MC’s make use of porous membranes which give direct contact of both phases in the pores. This results in high transfer coefficients (Wang et al, 2005) and demands careful operation of the pressure to avoid leakage of the phases. Additionally, the direct contact will result in the above mentioned evaporation of absorbent.

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In the paper at hand first results of experiments with a membrane contactor equipped with dense membranes, designed as asymmetric membranes, are reported. This MC combines large transfer area with high fluxes and additionally a certain degree of freedom for the choice of absorbents, because both phases are hermetically separated.

2 Experimental

2.1 Membrane contactors

In the following the experimentally applied MCs are described. The main differences are the employed membrane materials and characteristics. In the novel apparatus, selectivity of the membrane proves to be irrelevant since the separation of the gaseous species mainly takes place due to selective chemical absorption of one component in the liquid phase. For membrane material Polyvinyltrimethylsilan (PVTMS) has been chosen as the one with the highest permeability and commercial availability.

![Figure 1: Membrane contactor](image)

The membrane itself shows an asymmetric structure with a dense active layer of about 5 μm with a supporting porous layer of 120 μm of the same material (cf. Fig. 1). Thus evaporation of carrier solution into the gaseous feed phase is avoided. This results in a clean product and no loss of carrier solution which is problematic when conventional contactors with porous membrane are used.

![Figure 2 Membrane contactor module](image)

With these specifications, a contactor module was constructed, consisting of stacked layers of PVTMS membranes (cf. Fig. 2). The layers between are alternating fed and
passed by gas or liquid. To obtain constant volumes spacers are applied on liquid and gas side. In total 6 membrane sheets are included in one module. All membranes have a width of 14 cm and a length of 17 cm resulting in an active membrane area of 1430 cm$^2$. The gas volume is about 65 ml and the liquid phase takes about 49 ml. The contactor can be operated under co and counter current flow conditions.

The commercial MC was supplied by MEMBRANA GmbH and is commercially applied as degasifier. The active surface area of 1800 cm$^2$ is in the same range as the introduced one. In contrast the membrane is porous with high porosity. Since the material of the commercial MC is not resistant against MEA only K$_2$CO$_3$ can be applied in this case.

2.2 Absorbent Liquids

Potassium carbonate (K$_2$CO$_3$) and monoethanolamine (MEA) solutions were tested as absorption media, both acting according to a chemisorptive reaction mechanism (Eq. 1 for MEA and Eq. 2 for K$_2$CO$_3$). For reference deionised H$_2$O was applied. The maximum loading of 1M MEA solution is given by 0.5 mol$_{CO2}$/l$_{solution}$. MEA had been chosen for testing purposes due to a fast reaction mechanism and its commercial application.

$$\text{CO}_2 + 2 \text{RNH}_2 \rightarrow \text{RNCOO}^- + \text{RNH}_3^+ \quad \text{Eq. 1}$$

Equation 2 shows the reaction of potassium carbonate with CO$_2$. In the experiments 0.25 M solution was applied resulting in a maximal loading of 0.25 mol$_{CO2}$/l$_{solution}$. K$_2$CO$_3$ had been chosen for its low desorption energy demand (15.5 kJ/mol$_{CO2}$) (Cullinane et al, 2004).

$$\text{CO}_2 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2 \text{KHCO}_3 \quad \text{Eq. 2}$$

2.3 Setup

A flow sheet of the experimental setup is given in Fig. 3. Gas cylinders supply the gases with technical purity of 5.0 and a simple 3-end cross blends the single gas streams after regulation by mass flow meters. Field-point-adapters control the flow meters and are connected to a computer and operated by the software DASYlab 8.0. After gas mixing the gas flow enters the module. The carrier solution is mixed in a tank with deionised water. During mixing and the experiment the tank is continuously purged by nitrogen to avoid CO$_2$-absorption from air. The solution is drained off at the bottom by a pump. The pump secures a constant liquid volume flow through the contactor with a flow rate in the range of 0.5 -10 ml/min.
Figure 3: Flow sheet of the test facility for membrane contactor tests

Before the start of an experiment, the contactor is flooded with carrier solution until no gas bubbles leave the outlet. This is necessary to ensure the coating of the whole membrane surface and its participation in the mass transfer.

By applying automated sampling via GC short before and behind the gas inlet and outlet, the gas composition can be evaluated and the separation efficiency can be calculated.

2.4 Experiments
All experiments were performed with CO₂ and helium instead of CO₂ and hydrogen for security reasons. This is tolerable because helium behaves like hydrogen as an inert component and is not absorbed by the carrier solution. Chosen test conditions were ambient temperature and ambient pressure.

To assess the performance of the membrane contactors they were tested with different liquid volume flow rates of 1 to 10 ml/min and a constant gas flow of 200 ml/min (cf. Table 1).

Table 1: Absorption experiments

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<td>2</td>
<td>deionised water</td>
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<tr>
<td>3</td>
<td>1 M MEA</td>
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3 Results

3.1 Experiments with K₂CO₃
Experiments with K₂CO₃ were carried out in counter current mode and a constant CO₂ concentration. In Fig. 4 the results for the relative CO₂ concentration as a function of carrier solution flow rate with 0.25 M K₂CO₃ is given. As reference experiments with deionised water were performed. It can be seen that only the chemical absorption can separate the CO₂ effectively. Physical absorption is not applicable with the given
boundary conditions. With K$_2$CO$_3$ the relative retentate concentration of CO$_2$ does not fall below 0.4 with applied flow rates. This is equivalent to a carrier loading of 0.077 mol$_{CO_2}$/l solution which is lower than the maximal loading of 0.25 mol$_{CO_2}$/l solution. As reference, the stoichiometric reaction was calculated representing the maximum performance of the contactor under ideal conditions. The difference between the ideal and the experimental case can be explained by the slow reaction kinetics of K$_2$CO$_3$ resulting in dissolved CO$_2$ as carbonate on the liquid side. This leads to a reduction of driving force resulting in a low mass transfer. Additionally, Fig. 4 shows the results of the measurements with the commercial available MC and 0.25 M K$_2$CO$_3$ solution. The values of the two contactors are in good accordance. It can be assumed that to mass transfer resistance of the dense membrane is of minor importance and comparable to that of porous membranes. During the experiments carrier solution evaporated through the pores in the gas stream.

![Graph](image)

**Figure 4:** Relative retentate concentration of the novel and commercial membrane contactor as a function of carrier solution flow rate for counter current flow (Carrier 0.25 M K$_2$CO$_3$, gas flow rate 200 ml/min, feed concentration 13.0 mol-% CO$_2$ diluted in helium, ambient temperature and pressure). Reference is deionised water

### 3.2 Experiments with MEA

Fig. 5 shows the results of absorption tests in co and counter current flow conditions for a 1 M MEA solution with the novel MC. The results are showing no influence of the flow conditions on the CO$_2$ separation efficiency. This can be explained by the fast reaction of CO$_2$ with MEA. The mass transfer is reaction controlled. The difference between stoichiometric and experimental in regions of lower flow rates can be explained by the mass transfer limitation by non-reacted carbonate. Contrary to the experiments with K$_2$CO$_3$ an almost complete separation of CO$_2$ from the gas stream is possible when a carrier solution flow rate of 6 ml/min is applied. This corresponds, compared to the stoichiometric calculation and accordingly ideal case, to an additional input of absorption solution by the factor of 3. A relative CO$_2$ end-concentration of 0.03 in the retentate can be identified. This remaining CO$_2$ fraction documents the membrane resistance.
Figure 5: Retentate concentration $c_{\text{ret}}$ of the novel membrane contactor as a function of carrier solution flow rate for co and counter current flow (Carrier 1 M MEA, gas flow rate 200 ml/min, feed concentration 13.5 mol-% CO$_2$ diluted in helium, ambient temperature and pressure). Reference is deionised water.

4 Summary

Experiments with MCs equipped with dense and porous membranes were performed to assess the CO$_2$ separation efficiency with MEA and K$_2$CO$_3$. The novel MC with a dense membrane shows a separation efficiency of 99.7% if 3 times more MEA solution is applied than in the ideal case. K$_2$CO$_3$ shows a poor performance with a loading of about 0.077 mol CO$_2$/mol solution for a 0.25 M solution and reaches a separation efficiency of 50%. The performance of the novel MC matches with commercial available contactors. It is demonstrated that the dense membrane has no disadvantages compared to a porous membrane concerning its mass-transfer resistance. The dense membrane has the advantage that the gas phase is not in contact with the absorbents.

5 References


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