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 K_2CO_3) concerning the separation efficiency of CO_2. 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 CO_2. Certain applications of the hydrogen demand pure quality. A couple of well established processes, applied in the chemical industry, are available to separate the CO_2. 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 dose 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.

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 Polyvenyltrimethylsilan (PVTMS) has been chosen as the one with the highest permeability and commercial availability.
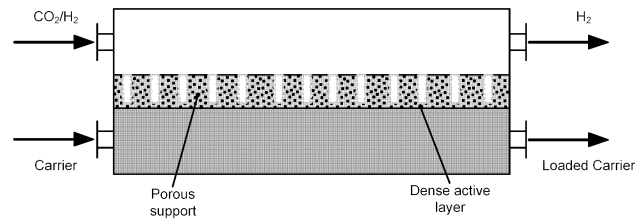

Figure 1: Membrane contactor

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.
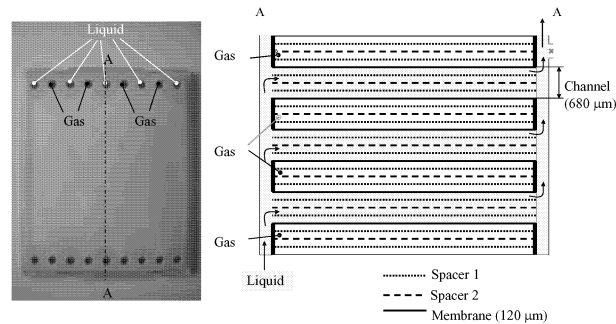

Figure 2 Membrane contactor module

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 cm². 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 cm² 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_2CO_3 can be applied in this case

2.2 Absorbent Liquids

Potassium carbonate (K_2CO_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_2CO_3). For reference deionised H_2O 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.

$$CO_2 + 2\,RNH_2 => RNCOO^- + RNH_3^+ \qquad\qquad \text{Eq. 1}$$

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_2CO_3 had been chosen for its low desorption energy demand (15.5 kJ/mol_{CO2}) (Cullinane et al, 2004).

$$CO_2 + K_2CO_3 + H_2O => 2\,KHCO_3 \qquad\qquad \text{Eq. 2}$$

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.
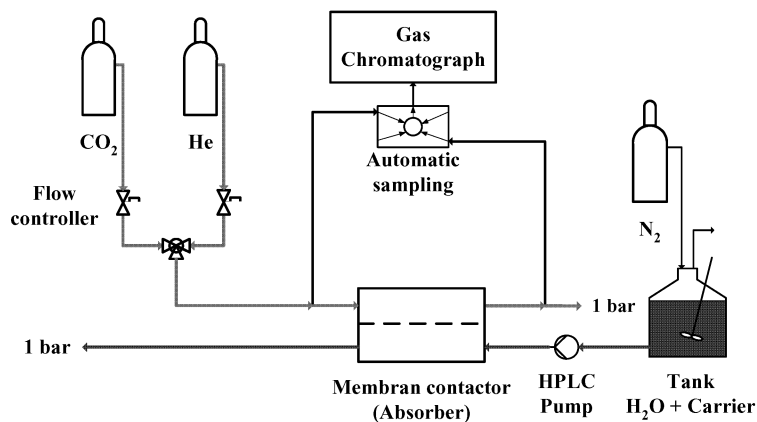
Figure 3: Flow sheet of the test facility for membrane contactor tests

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 CO_2 and helium instead of CO_2 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 asses 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

Experiment	Absorbent solution	Liquid flow rate [ml/min]	Gas flow rate [ml/min]	Gas composition [Vol-% CO_2]
1	0.25 M K_2CO_3	1 - 10	200	13.0
2	deionised water	1 - 10	200	12.5
3	1 M MEA	1 - 10	200	13.5

3 Results

3.1 Experiments with K_2CO_3

Experiments with K_2CO_3 were carried out in counter current mode and a constant CO_2 concentration. In Fig. 4 the results for the relative CO_2 concentration as a function of carrier solution flow rate with 0.25 M K_2CO_3 is given. As reference experiments with deionised water were performed. It can be seen that only the chemical absorption can separate the CO_2 effectively. Physical absorption is not applicable with the given

boundary conditions. With K_2CO_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 $mol_{CO2}/l_{solution}$ which is lower than the maximal loading of 0.25 $mol_{CO2}/l_{solution}$. 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_2CO_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_2CO_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.
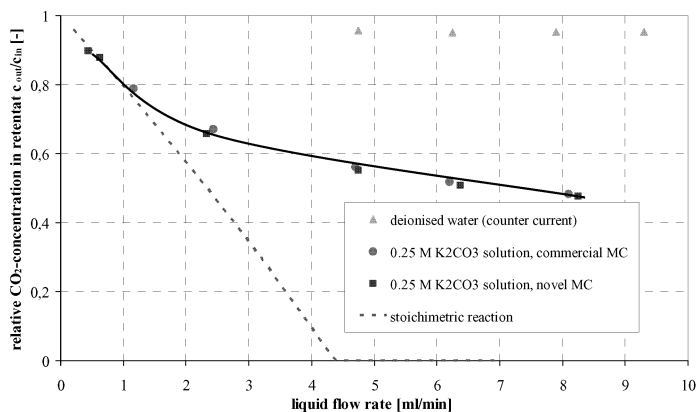

Figure 4: Relative retentate concentration of the novel and commercial membrane contactor as a function of carrier solution flow rate for counter current flow (Carrier 0.25 M K_2CO_3, gas flow rate 200 ml/min, feed concentration 13.0 mol-% CO_2 diluted in helium, ambient temperature and pressure). Reference 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_2CO_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.
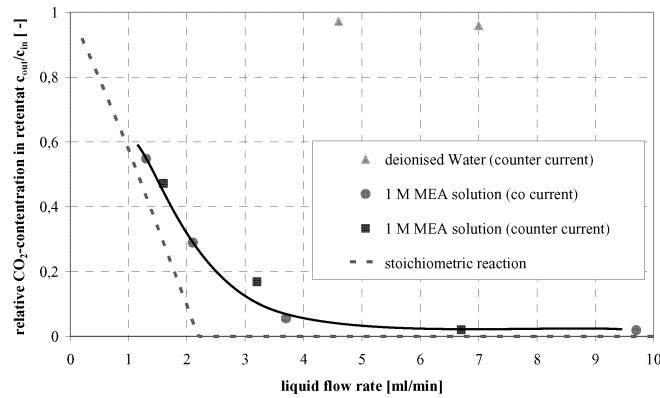
Figure 5: Retentate concentration c_{out} of the novel membrane contactor as a function of carrier solution flow rate for co and counter current flow (Carrier 1 M MEA, gas flow rate 200 ml/min, feed concentration 13.5 mol-% CO_2 diluted in helium, ambient temperature and pressure). Reference is deionised water.

4   Summary

Experiments with MCs equipped with dense and porous membranes were performed to asses the CO_2 separation efficiency. with MEA and K_2CO_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_2CO_3 shows a poor performance with a loading of about 0.077 $mol_{CO2}/l_{solution}$ 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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