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## CO<sub>2</sub> absorption with membrane contactors vs. packed absorbers- Challenges and opportunities in post combustion capture and natural gas sweetening

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### Abstract

The present work presents a case study where membrane contactors are compared with absorption towers for post combustion CO<sub>2</sub> capture and for natural gas sweetening. Simulations are performed using a absorber model which has been validated with experiments in a membrane contactor setup. The design of the membrane contactors is made with emphasis on the constraints in gas and liquid side pressure drop and size limitations of membrane modules, in addition to the common design criteria for industrial absorbers. Results show that absorber size may potentially be reduced by 75%, given that liquid is flowing on the shell side of the membrane units. Natural gas sweetening is a more viable option than post combustion capture due to the potentially large gas side pressure drop and the need for many membrane units in parallel in the latter case.

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### 1. Introduction

Membrane contactors represent a novel absorber design that can offer several improvements over conventional packed columns. These are mainly related to the operability and to the size and volume of the equipment. The overall process topology is the same as in a conventional absorption desorption cycle and the energy requirement for CO<sub>2</sub> capture is still a result of solvent performance and process optimization (Figure 1).

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Even if membrane contactors have received significant interest in the literature, see review by Favre and Svendsen (2012), thorough evaluations of the technology in a realistic process environment are still lacking. This requires a fundamental understanding of membrane contactor performance combined with knowledge of optimal process design for absorption/desorption cycles. The latter has received significant attention during the previous 5-10 years, especially within the field of post combustion CO<sub>2</sub> capture.

The current work presents results from a case study of membrane absorbers compared with conventional absorbers. The current work is based upon three different gas treatment options, all of significant industrial importance:

1. Post combustion CO<sub>2</sub> capture from offshore gas turbines
2. Sweetening of natural gas with 10% CO<sub>2</sub> to pipeline specification of 2.5%
3. Same as 2 with LNG specification of 50 ppm

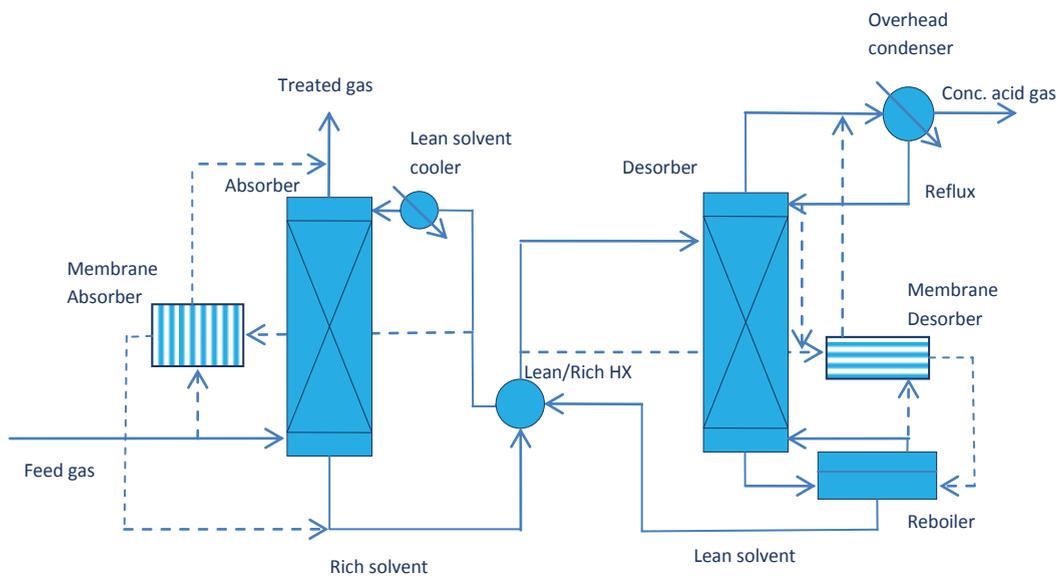


Figure 1 Simplified absorption-desorption cycle showing how membrane contactors may replace the packed columns

## 2. Membrane contactors and packed absorbers

### 2.1. Principle

The principle of membrane gas absorption is illustrated in Figure 2. A microporous membrane works as a non-selective barrier between the gas and the solvent. As long as the mass transfer resistance is located on the liquid side and the membrane material is not wetted by the solvent, the mass transfer resistance of the membrane will be limited. This requires the pore size to be larger than the mean free path of diffusing gas. With a typical aqueous chemical solvent it is important that the membrane material is hydrophobic. Materials used in this application are polymers like PTFE or polypropylene and the membranes are typically made as hollow fiber bundles or sheets with fibers of 0.5-3mm ID.

The main positive features of membrane contactors are:

**No flooding, entrainment, channeling and foaming:** The presence of a membrane between gas and liquid prevents these phenomena from occurring, as opposed to packed columns where they may drastically reduce separation performance.

**No sensitivity to motion:** Even minor tilting of an absorption tower will reduce performance. This is an important issue when operating on an offshore unit. In post combustion operation on e.g. gas turbine exhaust, the low specific liquid load may not utilize the packing surface area completely. Membrane contactors can therefore represent a significant improvement in this case.

**Higher specific area/reduced size of equipment:** Packed columns typically offer an active interfacial area of 100-250m<sup>2</sup>/m<sup>3</sup>. Hollow fiber membranes units can be stacked in principle with very high specific surface area. It is often claimed >1000 m<sup>2</sup>/m<sup>3</sup>. However, the packing density of fibers in a membrane contactor is limited by pressure drop constraints both for the gas and the liquid flow. Secondly, in a system with mass transfer followed by chemical reaction within a thin concentration boundary layer near the membrane surface, the membrane porosity reduces the true mass transfer area to some extent.

**Liquid side mass transfer:** When liquid is flowing inside the hollow fibers in undisturbed, laminar flow, the mass transfer coefficient is low. Mass transfer can be significantly enhanced by introducing liquid mixing points, thus reducing the residence time of liquid elements on the interface. (Hoff et al. 2006). The simplest way of introducing liquid mixing is to pass the liquid on the shell side and gas on the tube side.

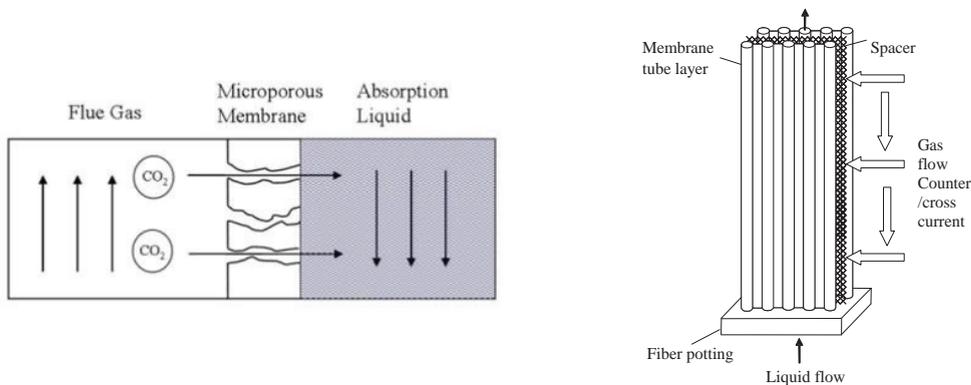


Figure 2 Principle of membrane contactors

## 2.2. Design considerations

Design of absorption columns and membrane contactors are subject to some of the same constraints as well as some differences. The fundamental relationship between capture rate, gas flow and liquid circulation is valid for both:

$$Q_L = \frac{y_{CO_2}^{in} \varepsilon Q_G P / (RT_G)}{m(\alpha_{rich} - \alpha_{lean})} \quad (1)$$

where  $m$  is the solvent concentration,  $\alpha$  is the CO<sub>2</sub> loading,  $y_{CO_2}^{in}$  is the mole fraction of CO<sub>2</sub> in the feed gas,  $\varepsilon$  is the CO<sub>2</sub> recovery.  $Q_G$  is the volumetric flow of gas and  $Q_L$  is the volumetric liquid circulation rate. The rich and lean loadings are critical parameters for optimal operation of an absorption process.  $\alpha_{rich}$  is given by the need to achieve a high approach to equilibrium in the absorber bottom. For MEA absorbers in post combustion operation >90% approach to equilibrium is common, corresponding to values of >0.45 mol CO<sub>2</sub>/mol MEA. Lean loading is typically 0.25 in a MEA design optimized for low reboiler duty.

For natural gas sweetening with MDEA based solvents, the approach to equilibrium is usually lower and also less critical to the energy requirement. 60-80% of equilibrium is more common. MDEA based solvents can normally be regenerated to almost zero loading by a combination of flash stages and stripping. The main point is that rich and lean loadings are more or less fixed for a given separation problem and that the liquid flow,  $Q_L$ , as well as the liquid to gas ratio  $Q_L/Q_G$  will be the same in a membrane contactor system as in a packed absorber.

When designing a conventional absorption tower the following additional constraints are important:

- For post combustion capture, the total pressure drop on the gas side should not be higher than 0.1 bar, in order to utilize a conventional blower for the flue gas. Higher pressure drop will also lead to higher duties on the blower, which is the largest consumer of electric power in the plant.
- The superficial gas velocity should be as high as possible to minimize tower diameters, but is limited by flooding in the column and the desire for low pressure drop. Gas velocities of 2-3 m/s are typical in post combustion capture.
- The packing should be wetted by liquid distributed over the whole tower cross section. For a typical natural gas exhaust case, the liquid load will be around 10 m<sup>3</sup>/m<sup>2</sup>h. This is in the low range of liquid loads where incomplete wetting sometimes may arise. The packing bed must be split in several sections for liquid redistribution.

For membrane contactors, the constraints are the following:

- The constraint in terms of gas side pressure drop is the same as for towers. Gas side pressure drop will increase as the packing density/the specific surface area increases. Also, if gas is flowing on the tube side, long membrane passes will increase the total pressure drop.
- The liquid entry pressure represents an upper limit at which penetration into the membrane pores should not occur. The liquid side pressure drop will therefore be constrained by the maximum fiber length allowed. This can partially be compensated by utilization of head pressure in vertically oriented units.

There are limitations related to the physical dimensions of the membrane modules. Depending on the membrane manufacture/spinning process, the length of the hollow fiber cannot be more than a few meters. Commercial hollow fiber membrane modules manufactured today typically still have diameters less than 1m (Marquez and Brantana, 2006).

### 3. Model development and validation

Earlier, a rigorous modeling and design tool for membrane absorbers was developed (Hoff et al. 2004). The model was developed over several years and validated vs. more than 500 experiments in membrane absorbers both in bench and pilot scale.

The model is based upon the solution of the 2-dimensional equations for conservation of mass and energy in a membrane hollow fiber. Details are given in Hoff et al. (2004) but the model has gone through some significant further development recently. These improvements are important in terms of designing large scale units.

- Improved thermodynamic models for the MEA and MDEA/Piperazine based systems
- Development of a design model based upon mass transfer coefficients for the liquid side
- Implementation of liquid mixing geometry
- Simulation of liquid flow on the shell side
- Improved models for gas and liquid side pressure drop
- Better mass transfer models, incorporating effects of partial liquid penetration, as well as Knudsen diffusion in the membrane pores.

The following description highlights some important aspects of the model relevant for the current work:

### 3.1. Mass transfer flux

The transfer flux across the membrane is modelled using the simple resistance in series approach, including the gas film and the membrane mass transfer coefficients.

$$N_i = \frac{1}{ZRT_g \left( \frac{1}{k_{i,g}} + \frac{1}{k_m} \right)} \cdot (f_i - f_i^{eq}) + x_i \sum_i N_i \quad (2)$$

where  $f_i$  and  $f_i^{eq}$  are the fugacities of the transferable components, actually in the gas phase and at equilibrium with the liquid. The last term in Eq. 2 is the convective flux. The gas film coefficient,  $k_{i,g}$  is given by a correlation based upon lab-scale measurements in a gas controlled regime, using SO<sub>2</sub> absorption in NaOH as model system. The membrane mass transfer coefficient,  $k_m$ , is given by

$$k_m = \frac{\varepsilon D_p}{\tau R_i \ln R_o / R_i} \quad (3)$$

where  $\varepsilon$  is the membrane porosity,  $\tau$  is the membrane tortuosity while  $R_i$  and  $R_o$  are the inner and outer radii, respectively.  $D_p$  is a combined term accounting for molecular diffusion and possible contributions from (a) Knudsen diffusion (facilitated by small pore diameters/low pressures) and (b) partial liquid penetration in the membrane pores:

$$D_p = \frac{1}{(1-x_l) \left( \frac{1}{D_m} + \frac{1}{D_{Kn}} \right) + x_l \frac{1}{D_{m,liq}}} \quad (4)$$

To reduce the computational times, a simplified model has been formulated. This is also required in order to simulate liquid on shell side. In this model, equation (2) is reformulated, including a mass transfer coefficient for the tube side, in the following case with liquid inside the fibers:

$$N_i = \frac{1}{ZRT_g \left( \frac{1}{k_{i,g}} + \frac{1}{k_{i,m}} + \frac{H}{Ek_{i,l}} \right)} \cdot (f_i - f_i^*) + x_i \sum_i N_i \quad (5)$$

The tube side coefficient can be given by the Graetz-Nusselt solution for the local mass transfer coefficient (Cussler, 2009). When the hydrodynamics of the liquid phase are described by a physical mass transfer coefficient, an enhancement factor is required to account for the effects of chemical reaction. Here is used the approach by De Coursey et al. (1982), combined with the enhancement factor for an instantaneous reversible reaction,  $E_i$ , based upon Olander (1960).

### 3.2. VLE model

An equilibrium model for the CO<sub>2</sub>/amines/water system is included, describing the complex chemistry of the CO<sub>2</sub>/amine/water system. This is based upon the Desmukh-Mather approach, while non-idealities for the gas phase are calculated by the Peng-Robinson Equation of state. This is particularly important for the current work since both the compressibility factor and the fugacity coefficients deviate significantly from 1. Compared to the original Desmukh Mather model (Weiland et al. 1993), a modified Debye-Hückel model was adopted, similar to the paper by Kuranov et al. (1997). This gave a slightly better fit to the data. The model is developed for the solvents MEA/water and MDEA/Piperazine/water.

### 3.3. Model validation

Figure 3 shows model predictions of the absorption flux in a lab-scale membrane absorber unit operating on 30wt% MEA. The experimental conditions span a wide range in terms of liquid velocity, temperature, gas phase CO<sub>2</sub> concentration and liquid loading.

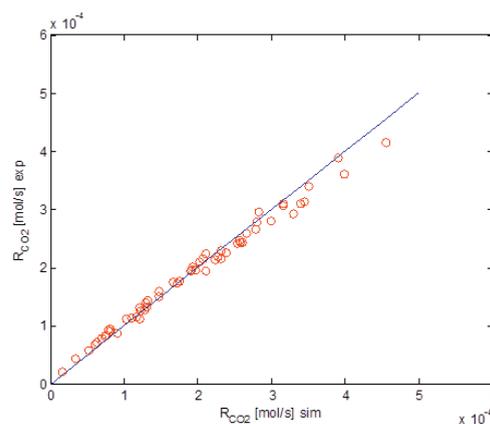


Figure 3 Model prediction vs. experimental absorption rates, 30wt% MEA.

## 4. Present study

### 4.1. Reference simulation with packed tower

A complete process simulation was built for the post combustion and natural gas sweetening cases. For the post combustion case, the SINTEF/NTNU software CO2SIM (Tobiesen and Schumann-Olsen, 2011) was used, while the natural gas cases were simulated in Protreat (Optimized Gas Treating Inc.). Results and absorber dimensions are given in Table 1. The gas and liquid flows were used as input to the membrane contactor model to design an absorber system for the same purification targets. Membranes simulated in this work are microporous PTFE hollow fibers of similar type as in Hoff et al. (2004).

For post combustion the membrane modules are arranged in a cross flow pattern. The rectangular modules have a fiber length of 3m, 3m width and 1m depth. The high pressure modules used for natural gas treatment are designed as cylindrical canisters like a shell and tube heat exchanger, with maximum diameter 2-2.5m and maximum length 5m. These dimensions are not related to any specific membrane manufacture process and are only used as a basis. Further work is required in order to investigate the limitations in module size.

Results from the design of the membrane absorber units are shown in Table 2. It is seen that the total absorber volume is reduced by typically 75% compared to towers. This requires liquid flow on the shell side, as tube side flow provides too low liquid side mass transfer coefficients.

However, for the post combustion case, this comes at a price of too high pressure drop on the gas side. An additional challenge with post combustion is the large volumetric gas flows, requiring a high number of membrane modules in parallel. For natural gas treatment, gas flow is lower and liquid flow is higher, and the separation can be achieved with only 3 membrane modules in parallel.

Table 1 References cases with packed absorbers, based upon simulations in CO2SIM and Protreat

Treated gas	Post combustion (PC)	Natural gas (NG)	Natural gas (NG)
Specification	90% capture	2.5% CO <sub>2</sub>	50 ppm
Solvent	30% MEA	49% MDEA	45% MDEA + 5% Pz
Tot pressure, feed gas (kPa)	100	7 000	7 000
CO <sub>2</sub> content, feed gas (vol%)	3	10	10
CO <sub>2</sub> recovery (%)	90.00	77.25	99.96
Lean loading	0.21	0.0029	0.011
Rich loading	0.45	0.361	0.314
Liquid flow (m <sup>3</sup> /h)	1 183	1 429	1 944
Gas flow (actual, m <sup>3</sup> /h)	1 311 619	8 381	8 381
Column Diameter (m)	13.6	4.4	4.6
Packing height (m)	18.6	14.0	15.0
Packing volume (m <sup>3</sup> )	2 702	208	246
Packing material	Mellapak 250.Y	2.5" Nutter Ring	2.5" Nutter Ring
Superficial gas velocity (m/s)	2.5	0.16	0.14
Gas side pressure drop (kPa)	3.7	2.4	2.2

Table 2 Results from simulations of membrane contactor system

Case	Post combustion	Post Combustion	NG, pipeline	NG, pipeline.	NG, LNG
Solvent	30% MEA	30% MEA	30% MDEA	30% MDEA	30% MDEA 5% Pz
Liquid flow mode	Shell side	Tube side	Shell side	Tube side	Shell side
Module width (m)	3.0x1.0*	3.0x1.0*	2.10	2.40	2.40
Fiber length (m)	3.0	3.0	5.0	4.5	5.0
# modules in parallel	25	40	1	2	1
# modules in series	3	5	3	7	5
Pressure drop, gas (kPa)	49.20	5.7	2.32	10.54	1.03
Pressure drop, liq. (kPa)	N/A	37.1	N/A	111.6	N/A
Superficial gas vel. (m/s)	1.43	0.93	0.22	0.07	0.10
Total packed volume (m <sup>3</sup> )	675	1800	52	285	113
Volume ratio vs. tower	0.25	0.67	0.25	1.37	0.46

(\*Cross flow modules, W=3m, H=3m, D=1m)

## 5. Conclusions

The results from the present study show that significant savings are possible in terms of absorber size when replacing a conventional column with a membrane contactor. This requires liquid to flow on the shell side to enable splitting and mixing of liquid elements, similar to the liquid mixing provided by structured or random tower packings.

Membrane contactors may provide significant improvements in offshore CO<sub>2</sub> capture, both from gas turbine flue gas and in sweetening of natural gas. Pressure drops, both on the liquid and gas side, represent constraints that must be included in the design of a membrane contactor system. Modularity and size limitations of membrane systems also represent a challenge. This is especially the case for post combustion, where there will be a need for a large number of units in parallel and in series, as opposed to conventional absorption towers. It is thus uncertain whether membrane contactors can offer an advantage in this case.

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