



HAL
open science

Evaluation of a dense skin hollow fiber gas-liquid membrane contactor for high pressure removal of CO₂ from syngas using Selexol as the absorbent

Bouchra Belaissaoui, Eric Favre

► **To cite this version:**

Bouchra Belaissaoui, Eric Favre. Evaluation of a dense skin hollow fiber gas-liquid membrane contactor for high pressure removal of CO₂ from syngas using Selexol as the absorbent. *Chemical Engineering Science*, 2018, 184, pp.186-199. 10.1016/j.ces.2018.02.028 . hal-02939693

HAL Id: hal-02939693

<https://hal.science/hal-02939693>

Submitted on 29 Apr 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Evaluation of dense skin hollow fiber membrane contactor based process for CO₂ removal from high pressure syngas using Selexol as physical absorbent

Bouchra Belaisaoui ^{*a}, Eric Favre^a

^a *LRGP-CNRS Université de Lorraine, 1 rue Grandville 54001 Nancy, France*

Manuscript submitted to Chemical Engineering Science

*Corresponding author: Tel: +33 372 74 37 98; fax : +33 383 32 29 75
E-mail address: bouchra.belaisaoui@univ-lorraine.fr (B.Belaisaoui)

Abstract

CO₂ removal from syngas is required for combined hydrogen production and CO₂ capture at integrated gasification combined cycle (IGCC) power plants. Conventional absorption in packed column using pressurized physical solvents such as Dimethyl Ether of Polyethylene Glycol (DEPG) (Selexol™) is largely used for this application. In this work, a dense skin hollow fiber membrane contactor (HFMC) based process for CO₂ absorption and desorption using Selexol as physical absorbent is investigated by simulation and compared to the conventional process. Thanks to the ability of dense membrane to withstand high transmembrane difference, absorbent circulates in close loop at a pressure which can be set independently of syngas pressure. Thus, contrary to the conventional process, neither absorbent depressurization before the desorber nor absorbent recompression before the absorber is needed. Under the investigated operating conditions, the process was able to recover up to 94.6 % of CO₂ with CO₂ and H₂ purity of 92.4 % and 96.6% respectively. The corresponding energy requirement for absorption and desorption loop is of 0.19 MJ_{el}/kg CO₂ which is approximately two times lower than that reported in literature under comparable gas inlet conditions and separation specifications using packed column. Without flash recovery, the corresponding H₂ loss was of 4.8%. The overall mass transfer coefficient was of 1.2.10⁻⁵ m/s and 6.8.10⁻⁶ m/s in the absorber and desorber respectively. Membrane mass transfer lower or comparable to that of absorbent combined with higher CO₂/H₂ membrane selectivity is required for H₂ loss decrease. Lower H₂ loss is achieved at the expense of increased contactor size and liquid energy pumping energy. Finally, perspectives for process optimization are exposed.

Keywords

Syngas purification, pre-combustion, physical absorbent, dense hollow fiber membrane contactor, Selexol, gas-liquid absorption

Highlights

1. Thanks to dense membrane fiber, absorbent recompression is not required for its recycling
2. Compared to packed column, the energy requirement for absorption and desorption loop can be halved
3. Without flash recovery, H₂ loss is of 4.8%
4. Process selectivity is mainly controlled by the absorbent
5. Membrane mass transfer lower or comparable to that of absorbent combined with higher CO₂/H₂ membrane selectivity is required for H₂ loss decrease.
6. Lower H₂ loss is achieved at the expense of increased contactor size and liquid energy pumping energy.

1. Introduction

Pre-combustion CO₂ capture in an integrated gasification combined cycle (IGCC) associates both CO₂ capture and H₂ production for power generation and greenhouse emission mitigation. Carbonaceous fuels are first gasified to produce the syngas which after water gas shift reaction (WGS) is composed mainly of H₂ and CO₂ (30-40% CO₂) under high pressure (20–70 bar) and temperature (190–210°C) with trace components such as H₂S, NH₃, HCN as well as heavy metals and particulates (Scholes *et al.*, 2010). Acid gas (CO₂ and H₂S) removal and trace elimination are needed to fulfil the requirement for hydrogen use and CO₂ capture standards for transport and storage. In IGCC pre-combustion carbon capture (Figure 1), syngas is treated to remove CO₂ prior to combustion to avoid emission of this greenhouse gas. In the purified gas, H₂ purity above 96% is generally aimed. For CO₂ capture and sequestration, CO₂ concentration should be above 90% together with low ppm level of other components (Davidson and Metz, 2005, Padurean *et al.*, 2012).

The biggest efficiency loss associated with precombustion in IGCC is incurred in the WGS section. The latter is responsible for 44% (3.5%-points) of the total efficiency, mainly due to the use of steam for the WGS reaction. CO₂ removal section causes about 1.7%-points and the CO₂ compression and drying section are responsible for 3.0%-points efficiency loss (Jansen *et al.*, 2015). So far CO₂ capture in IGCC power plant has only been tested and demonstrated at pilot scale (Casero *et al.*, 2014).

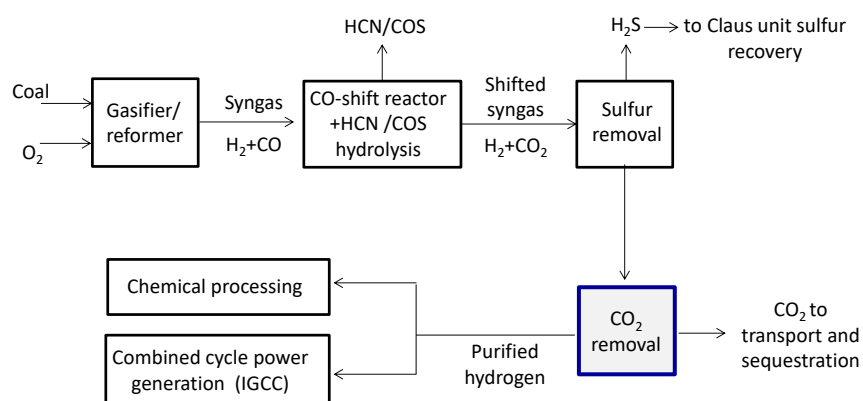


Figure 1: Typical IGCC and pre-combustion carbon capture process flow sheet.

The available driving force for CO₂ capture is higher in the pre-combustion IGCC approach than in post-combustion where flue gas is typically at atmospheric pressure and contains only 4–13% CO₂. These conditions favor the use of gas-liquid absorption processes using physical solvent. Most of physical solvents are more selective for acid gas than for the main constituent of the gas (e.g. hydrogen, carbon monoxide, methane, etc.). Absorption in packed column using pressurized physical solvents such as Dimethyl Ether of Polyethylene Glycol (DEPG) (Selexol™) is largely used for acid-gas removal from high-pressure gases such as natural gas streams and syngas in a pre-combustion IGCC power plant (Padurean *et al.*, 2012, Kapetaki *et al.*, 2015, Park *et al.*, 2015). Other techniques include chemical absorption, membranes and cryogenic fractionation (Jansen *et al.*, 2015). At the difference of chemical absorbents, physical absorbents can usually be stripped of impurities by reducing the pressure without extra heating supply. The major limitations of this process are:

- In physical absorption, liquid mass transfer resistance is predominant with liquid mass transfer coefficient about two order of magnitude lower compared to chemical absorption. Moreover, non-aqueous physical solvents usually have larger viscosity compared to aqueous solvents. All this contributes to lower the mass-transfer coefficient of physical solvent which is in the range of 10⁻⁶.

10^{-4} m/s while this range is of 10^{-4} - 10^{-2} m/s for chemical solvents (Chabanon *et al.*, 2014), leading to relatively large columns size and high absorbent circulation rates.

- The need to recompress the liquid after the regeneration step: this induces a high-quality energy input (electricity), associated with a potential temperature increase of the liquid circulated in the loop. The solvent recompression step is effectively considered to require 20–30% overall energy requirement (Gottlicher and Pruschek, 1997).

Thus, the possibility to either decrease the size of the installation through process intensification strategies or enable improved energy efficiency through new solvent, novel technologies, or process strategies is of great interest.

Membrane contactor is considered as one of the best promising technology to achieve intensified gas-liquid mass transfer (Gabelman, and Hwang, 1999, Drioli *et al.*, 2005) thanks to their very high interfacial area, up to 30 times that encountered in packed column (Figure 2). Given that non-aqueous physical solvents have lower surface tension compared to water and aqueous chemical solvents, they are more subject to wetting by absorbent breakthrough when porous membrane are used [Dindore *et al.*, 2004a]. Thus, the use of porous membrane with physical solvents is unrealistic and the use of dense skin based HFMC is thus required. Dense membranes have indeed shown to offer a remarkable wetting protection effect because no pores are present. Moreover, in physical absorption, liquid mass transfer resistance is predominant, thus either composite or self-standing dense materials can be used. In addition, they can possibly withstand a high transmembrane pressure offering unique possibilities for increased energy efficiency as the liquid solvent can be maintained under pressure during the regeneration step.

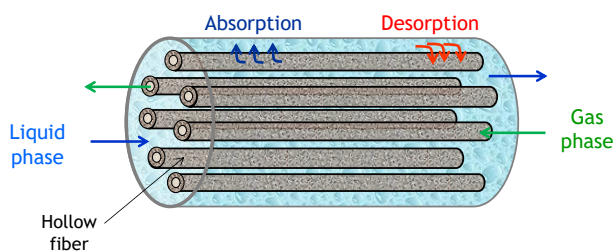


Figure 2: Illustration of hollow fiber membrane contactor for gas-liquid absorption and desorption

Despite these potentialities, a limited number of studied investigated however the technology with non-aqueous physical solvents for this application (Chabanon *et al.*, 2014). The potentiality of either composite or self-standing dense materials remains largely unexplored for CO₂ removal from high pressure syngas streams using physical absorbents. Additionally, to our knowledge, the evaluation of process intensification and energy requirement of HFMC for this application, using the potentialities exposed above and offered by dense membrane contactor has not been addressed.

This paper focus on the evaluation of intensification and energy penalty reduction of CO₂ removal section using membrane contactor technology compared to absorption in packed column technology using (DEPG) (Selexol™) as physical solvents. The evaluation of dense skin HFMC based process for CO₂ absorption and desorption for the treatment of high pressure acid gas streams using physical absorbents is proposed. The concept is illustrated in the case of shifted syngas treatment using Selexol as absorbent and the performance is compared to the reference packed column technology.

First, a brief presentation of conventional packed column for acid gas removal by physical solvent is given. Second, the novel process based on dense skin HFMC is shown and its potentialities highlighted. Then, a state of the art of dense skin membrane HFMC for CO₂ removal using physical solvents is

presented. Next, modeling and simulation framework is presented. Finally, the simulation results are shown and the performance of HFMC based process is compared to state of the art packed column for CO₂ removal from shifted syngas.

2. Conventional packed column for acid gas removal by physical solvent

Depending on the degree of contaminant removal and their concentration in the feed gas, a wide variety of regeneration schemes are available (Kohl and Nielsen, 1997).

The simplest version of a physical solvent process involves absorption followed by regeneration of the solvent by flashing to atmospheric pressure or vacuum, or by inert gas stripping (Figure 3)(Kwak et al., 2014). In order to limit valuable product loss, the solvent leaving the absorption column is transferred to a flash tank where dissolved non-acidic gases are released and returned back to the absorber. If important H₂S amount is present, then H₂S removal, typically achieved by using Selexol as absorbent, prior to CO₂ removal is required. One of the most important process factor impacting energy and capital cost is the solvent circulation rate. The latter can be reduced by decreasing temperature, thus increasing the acid gas absorption solvent capacity. Another benefit from cooling the solvent is the reduction of the absorbed amount of H₂ present in the shifted syngas application as the latter solubility shows generally little change with temperature (Kapetaki et al., 2015). However, decreasing solvent temperature increases its viscosity thus resulting in reduced solvent mass transfer performances and increased solvent pressure drop.

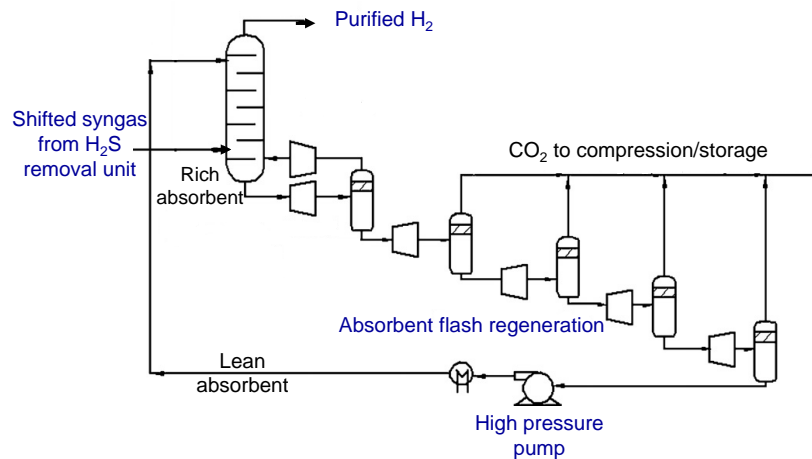


Figure 3: Process flow diagram of a typical physical solvent process for absorption of acid gases from feed gas streams.

A number of physical solvents are available for use in acid gas treating processes (Kohl and Nielsen, 1997). Typical operating conditions of commercial physical solvent processes and main characteristics are given in Table 1. Data of gas solubility and industrial physical absorbents selectivities as well as their main physico-chemical properties is given in Appendix A, in Table A1 and Table A2 respectively.

Table 1: Operating conditions of commercial physical solvent processes and main characteristics.

Process	solvent	Absorption conditions	Main characteristics
Selexol	Dimethyl Ether of Polyethylene Glycol (DEPG)	-10°C to 40°C, 20 to 50 bar ^{a,b,d,e}	Efficient for both CO ₂ and H ₂ S removal High selectivity for H ₂ S over CO ₂ Higher viscosity Good H ₂ S and CO ₂ removal efficiency
Rectisol	Methanol	-40 to -60°C ^{abc} , 20 to 36 bar ^{d,a}	High purity cleaned gas Requires more electrical energy for refrigeration
Purisol	NMP (N-Methyl-2-Pyrrolidone)	-20 to 40 ^d , 40 to 70 bar ^{d,a}	High selectivity for H ₂ S over CO ₂ More volatile solvent Need water washing
Morphysorb	Morpholine	49°C, 69 bar ^a	Selective removal of H ₂ S and CO ₂ High solvent capacity load Low process maturity level
Fluor	Propylene carbonate	-17 to 25 °C ^a , 30-70 bar ^{d,a}	High solubility of CO ₂ Uneconomical to achieve high product purity

^a Theo *et al.*, 2016 , ^b Padurean *et al.*, 2012, ^c Jansen *et al.*, 2015 , ^d Kohl and Nielsen,1997, ^e Park *et al.*, 2015.

3. Novel process based on dense HFMC for CO₂ absorption and desorption using physical absorbents

The principle of the use of dense skin based membrane for the absorption and desorption under high pressure is shown in **Figure 4**. **Figure 5** shows the novel dense skin HFMC based absorption/desorption loop for CO₂ removal from shifted syngas. First, the shifted syngas enters the absorber under high pressure (20 to 70 bar). The gas leaving the absorber has an increased concentration of H₂. CO₂ removal above 90% is typically aimed. The CO₂ enriched absorbent with some dissolved H₂ leaving the absorber is sent to the desorber, without its depressurization. Indeed, as explained above, dense membrane is able to withstand high transmembrane pressure difference. CO₂ is stripped from the rich solvent using vacuum pumping or sweep gas. The regenerated absorbent leaving the desorber is recycled back to the absorber in a closed loop.

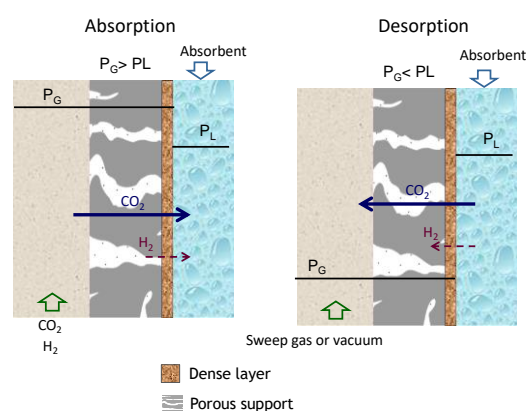


Figure 4: Illustration of absorption and desorption using dense skin based membrane contactors. CO₂ removal from shifted syngas.

The main advantages of this novel approach are the following:

- (i) Thanks to the ability of dense membrane to withstand high transmembrane difference, absorbent circulates in close loop at a pressure which can be set independently of syngas pressure. Thus, neither absorbent depressurization before the desorber nor absorbent recompression before the absorber is needed.
- (ii) Liquid recompression is not required before it is recycled to the absorption step. Thus, compared to the conventional process, the high pressure pump, the flash vessel and the heat exchanger are substituted by a simple pump leading to a significant decrease of the energy requirement of the process (i.e. OPEX). A single cheap equipment (circulating pump) is needed, which generates lower capital expenses (i.e. CAPEX).
- (iii) CO₂/H₂ selectivity of dense skin is typically up to 5 for polymeric membranes, up to 12 for advanced cross-linked membrane and up to 100 for advanced facilitated transport membranes (**Scholes et al., 2012**). This offers possible H₂ loss limitations.

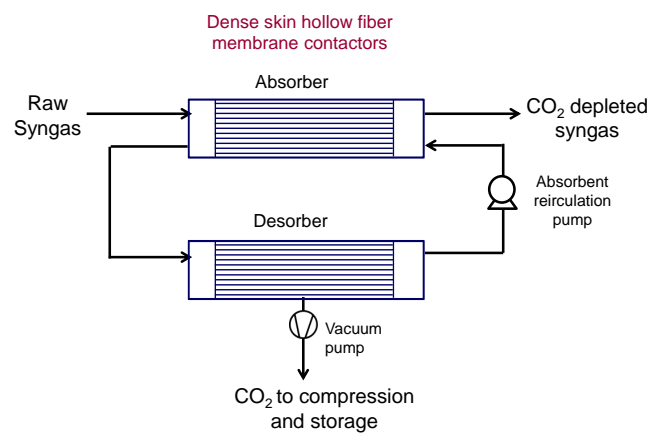


Figure 5: Scheme of the proposed process based on dense HFMC for CO₂ absorption and desorption using physical absorbents

4. Dense membrane based HFMC for CO₂ absorption/desorption using physical solvent : a state of the art

Experimental studies investigating physical absorbent for CO₂ absorption or stripping using dense skin based membrane contactor are summarized in **Table 2**. **Trusov et al., 2011** studied high permeability glassy polymers such as PTMSP, PTMGP and PMP for acid gas removal processes at conditions which are typical for the regeneration of physical solvents (water, propylene carbonate, N-Methyl-2-pyrrolidone-NMP) and chemical solvents (MEA, MDEA, PZ). They presented a detailed chemical, physical stability of glassy membranes in contact of aforementioned solvents at 100°C during 300 h (membrane samples was soaked in the absorbent). No detectable chemical changes in the polymer structure or macroscopic properties were evidenced. They showed experimentally that water and alkanolamines can be regenerated by pressure and temperature swing ($\Delta p_m = 40$ bar, $T = 100$ °C) in the investigated gas-liquid contactors. In **Dai et al., 2016b**, membrane contactors using nonporous polymeric hollow fiber membranes with ionic liquids as absorbent were tested experimentally for pre-combustion CO₂ capture at elevated temperature and pressures (80°C, 1 to 20 bar). A CO₂ flux of about 2×10^{-4} mol.m⁻².s⁻¹ was obtained using nonporous Teflon-PP membrane contactor at 10 bar with a gas flow rate of 100 ml.min⁻¹ and liquid flow rate of 20 ml.min⁻¹. The Teflon-PP composite membrane exhibited good stability in a 14 days test.

To our knowledge, no studies reported on long term stability during absorption or desorption experiments of non-aqueous physical absorbent under high temperature and transmembrane pressure. In all the reported studies using physical solvent and membrane contactor presented briefly above, no values have been given of energy requirement and overall CO₂ flux under relevant industrial conditions and product specification of gas absorption and desorption, and compared to the reference packed column technology.

Regarding the mechanical resistance of dense membranes, **Trusov et al., 2011** showed experimentally that symmetric glassy membrane (thickness of 20µm to 40µm) can operate successfully under transmembrane pressure difference of 40 bar when tested for CO₂ desorption from pressurized water. Based on theoretical calculation, it has been shown that a thickness as low as 5µm can support up to 10 bar transmembrane difference (**Chabanon et al., 2014**).

Dense skin thickness varies typically between 2 to 10 µm for PDMS (polydimethyl siloxane) and 0.1 to 1 µm for PMP (polymethylpentene) (**Nguyen et al., 2011, Falk-Pedersen and Dannstroem**). Dense skin membranes based on polydimethyl siloxane (PDMS), poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and Teflon AF2400 on microporous PP supports are among the more CO₂ permeable membranes. Commercial selfstanding dense membranes based on PDMS or Teflon AF 2400 shows k_{m,CO_2} around 10⁻⁵ m/s with membrane thickness of 30 to 200 µm (**Ozturk and Hughes, 2012, Heile et al., 2014**). CO₂ membrane mass transfer coefficient of composite or self-standing dense materials can range between 10⁻³ to 10⁻⁵ m/s depending on the membrane material and dense skin thickness.

Among commercially available polymeric membranes, rubbery polymers such PDMS and Pebax 3533 are considered as good candidates for CO₂/H₂ separation thank to their high permeances, albeit their low selectivity. Their performance is limited by the Robeson upper bound for CO₂/H₂ separation as shown in **Figure B1 in Appendix B**.

Table 2: Non-porous membranes for CO₂ absorption and stripping using non-aqueous physical absorbent

References	Feed gas	T	Pressure conditions	Absorbent	membrane	comments
Dai et al., 2016 <i>CO₂ Absorption</i>	CO ₂ 45%/He 55%	80°C	P _G =1- 20bar P _G /P _L ≈1	Ionic liquid : [Bmim][TCM] ¹	Composite Teflon- Polypropylene (PP), porous PTFE	Better stability compared to porous PTFE ² membranes in 14 days test, at 20 bar and 100°C.
Trusov et al., 2011 <i>Chemical and physical Stability tests</i>	Pure CO ₂	100°C	-	Water, propylene carbonate, NPM ³	Symmetric glassy membranes : PTMS ⁴ , PMP ⁵ , PTMGP ⁶	No changes in the chemical structure and macroscopic properties of those polymers, on long term tests under at 100°C during 300 h
Chabanon et al., 2014 <i>CO₂ desorption</i>	N ₂ as a sweeping gas	Amb.	P _G = 1 atm P _L =2 bar	Selexol	Dense self- standing PDMS ⁷	Unsteady state selexol-CO ₂ saturated regeneration was operated successfully. No long term tests.

¹[Bmim][TCM]: 1-Butyl-3-methylimidazolium tricyanomethanide PTMSP: poly[1-(trimethylsilyl)-1-propyne], ²PTFE : Polytetrafluoroethylene, ³NMP: N-Methyl-2-pyrrolidone, ⁴PTMSP : poly[1-(trimethylsilyl)-1-propyne], ⁵PMP: poly[4-methyl-2-pentyne] ,⁶ PTMGP : poly[1-(trimethylgermyl)-1-propyne], ⁷PDMS: polydimethyl siloxane.

High performing membranes include mixed matrix membrane (MMMs), facilitated transport fixed site

carrier membranes (FSCM), thermally rearranged polymers, and polymers with intrinsic micro-porosity (PIMS). Examples of polymeric membrane for CO₂/H₂ separation are shown in **Table B2**.

5. Simulation framework

5.1. 1D model – resistances in series model description

The membrane module has been modelled according to a 1D resistances in series approach, similarly to previous studies dedicated to gas-liquid absorption processes using HFMC (**Cui and Demontigny, 2013, Albarracin Zaidiza et al., 2014, 2016, 2016, Kerber et al., 2016**). The simulation methodology of the HFMC based absorption/desorption process is shown in **Figure 6**. A 1D modeling strategy systematically separately considers the three different mass transfer domains shown in **Figure 7** in order to determine the effective local mass transfer coefficient of each species..

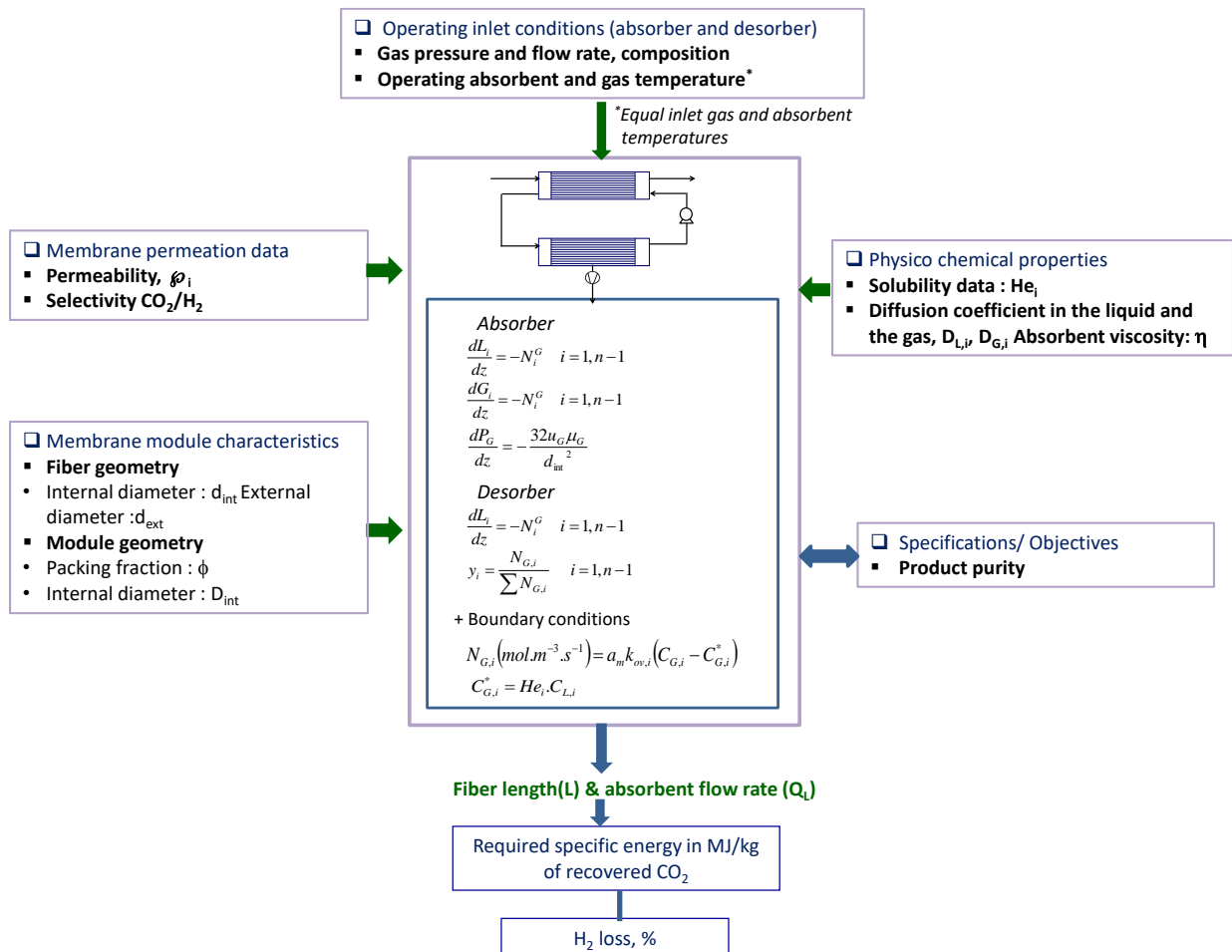


Figure 6 : Scheme of the simulation methodology

For all simulations, the liquid circulates in the shell side of the fiber while the gas flows in the lumen side. The 1D model takes into account the evolution of the local mass transfer coefficients, the evolution of gas velocity (due to CO₂ absorption) and fluid pressure through the axial coordinate (z). In the absorber, the flow is counter-current with plug flow assumed in both gas and liquid phases. In the

desorber, cross plug flow is considered with plug flow assumed for the liquid phase and free flow (perfect mixing) in the gas phase. Moreover, absorption and desorption processes are assumed to be isothermal. In **Appendix C**, details on model assumptions, gas and liquid mass transfer coefficient calculation as well as the equation system solved using Matlab software are presented.

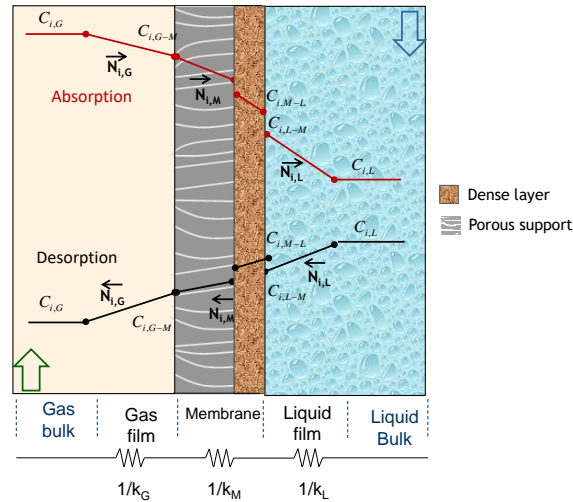


Figure 7: A schematic representation of the resistance in series based on film theory

5.2. Characteristics of the HFMC module

Geometrical characteristics of the hollow fiber membrane module (HFMC) are illustrated in **Figure 8**. In the simulation, the fiber geometry of commercial PPO (Parker P-240) is considered. The packing density and the module internal diameter were set at 0.5 and 36 cm respectively, which is typical of industrial modules. The characteristics of the membrane module are summarized in **Table 3**.

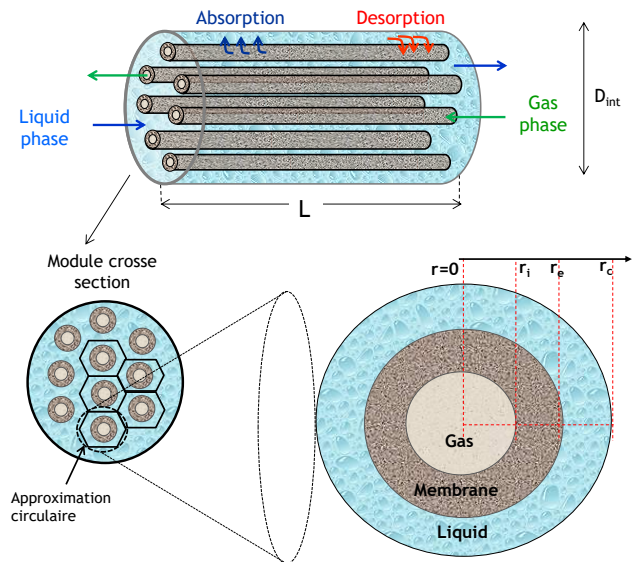


Figure 8: Geometrical characteristics of the hollow fiber membrane module (HFMC)

Table 3: Characteristics of the membrane module for all simulations.

	Characteristics	Value
Module	Inner diameter (m), D_{int}	0.36
	Packing ratio (-), ϕ	0.50
	Fiber number (-), N	$2.39 \cdot 10^5$
	Mean log specific interfacial area (m^{-1}), a	3260
Fiber	Inner diameter(μm), d_{int}	370
	Outer diameter(μm), d_{ext}	520

5.3. Physico-chemical data and operating conditions

In the simulation the gas is considered to be a binary CO₂/H₂ mixture, composed of 40% CO₂ and 60% H₂ (typical composition of a shifted syngas). Water is supposed to be available at 15°C. The gas feed is considered to be at 36 bar and 35°C [Kapetaki *et al.*, 2015, Padurean *et al.*, 2012, Dave *et al.*, 2016] according to typical relevant industrial conditions for syngas separation. The vacuum pressure for CO₂ stripping was set at 300 mbar.

The operating conditions considered in the simulations are summarized in **Table 4**. The simulation is achieved considering typical available polymeric membrane such as PDMS based membranes with $k_{M,CO_2}=5 \cdot 10^{-4}$ m/s and CO₂/H₂ selectivity of 4, for both absorber and desorber. The physico-chemical properties and phase equilibria of the system at 35°C are shown in **Table 5**.

Table 4: Operating conditions of all simulations

	Absorber	Desorber
Gas inlet composition	62% H ₂ , 38% CO ₂	Vacuum pumping
Temperature (°C)	35	35
Gas inlet flowrate (Nm ³ /h)	116.9	-
Gas inlet pressure (bar)	36	0.3
Gas interstitial velocity (m/s)	0.04	-

Table 5 : Physico-chemical properties and phase equilibria data of the system at 35 °C

	CO ₂	H ₂
Henry's constant (-) (C_G/C_L) _{eq} ^a	0.404	25.79
Diffusion coefficient in liquid phase (m ² /s) ^b	$2.6 \cdot 10^{-10}$	$3.6 \cdot 10^{-10}$
Diffusion coefficient in gas phase (m ² /s) ^c	$1.38 \cdot 10^{-5}$	$6.35 \cdot 10^{-5}$
Absorbent solubility selectivity CO ₂ /H ₂ (-)	63.83	
Absorbent viscosity (10 ⁻³ Pa.s) ^b	4.37	

^a Kapeteki *et al.*, 2015, ^b Heintz, 2011, ^c Chapman and Enskog theory

5.4. Process performances and energy requirement

The main performance indicators to be evaluated for gas-liquid HFMC for CO₂ removal from syngas are:

- The average overall CO₂ mass transfer coefficient k_{ov,CO_2} in m/s
- The product of $k_{ov,CO_2} \times a$ in s⁻¹, with a the specific membrane surface area in m⁻¹
- Average CO₂ specific absorbed flux in mol/m³.s
- CO₂ removal efficiency, η_{CO_2} (-)

- Process specific energy requirement in MJ/Kg of recovered CO₂

By writing a mass balance across a differential section of the membrane contactor, then integrating over the length of the contactor, the average overall CO₂ absorbed flux and overall mass transfer coefficient K_{ov} is calculated.

The CO₂ removal efficiency η_{CO_2} can be calculated as:

$$\eta_{CO_2} = \frac{G_{abs,in} \times y_{CO_2,in} - G_{abs,out} \times y_{CO_2,out}}{G_{abs,in} \times y_{CO_2,in}} \quad (1)$$

With y , mole fraction in the gas phase and G , molar gas flow rate.

For the HFMC process, the energy requirement for the HFMC based depicted in **Figure 5** is the summation of different contributions:

- Absorbent pumping power requirement for the recirculation of absorbent (selexol) in closed loop, $P_{L,p}$
- Power required for vacuum pumping in the desorber to strip CO₂ from CO₂-loaded absorbent, P_{vacuum}

The required energy demand for absorbent pumping is calculated from the solvent flow rate, Q_L , and total liquid pressure drop ΔP_L by :

$$P_{L,p} = \frac{1}{\eta_p} Q_L \cdot \Delta P_L \quad (2)$$

η_p is the pump efficiency, set to 0.6.

To estimate the power requirement of the vacuum pump for absorbent regeneration, isentropic compression was assumed:

$$P_{vacuum} = \frac{1}{\eta_v} G_{des} \frac{\gamma RT}{\gamma - 1} \left[\left(\frac{P_{atm}}{P_{G,des}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (3)$$

G_{des} and $P_{G,des}$ are the molar flow rate and pressure of the stripped gas in the desorber, respectively. η_v , set to 0.74, is the vacuum pump efficiency. γ is the adiabatic expansion factor of the gas mixture.

6. Results and discussion

Figure 9 shows the simulation results of the investigated process. Streams flow rates and concentrations are also indicated. **Figures 10a and 10b** show the axial profile of CO₂ and H₂ transmembrane flux in the absorber and desorber respectively. H₂ flux increases from the gas inlet as the driving force between the two phases increases. An inverse profile is observed for CO₂. CO₂ flux is minimal at the gas outlet where CO₂ content is low (near 3%) and where the driving force between the two phases is minimal. In the desorber CO₂ and H₂ follow the same trend as the CO₂ in the absorber. Fluxes are maximal at the liquid inlet (CO₂ and H₂ loaded solvent) and decreases as the gaseous species are desorbed from the liquid phase.

The energy requirement, overall mass transfer coefficient of both absorber and desorber are shown in **Table 6**. The proposed dense HFMC was able to recover up to 94% of CO₂ with 92.4% purity. The recovered H₂ purity is of 96.6%. The corresponding energy requirement is of 0.19 MJ_{el}/kg CO₂, which is approximately over 2 times lower than that reported under comparable gas inlet conditions and separation specifications as can be seen in **Table 8**.

However, the obtained H₂ loss is of 4.8% which is significantly higher than that reported for conventional packed column based process (less than 1%) (**Park et al., 2015**). In the latter, first flash

thank is used to recover H₂ from rich absorbent. The recovered H₂ is then recycled to the inlet of the absorber (**Figure 2**). In order to limit H₂ loss using the concept of membrane contactor proposed in this work, a configuration using a flash at medium pressure to recover a portion of H₂ before entering the desorber contactor need to be investigated.

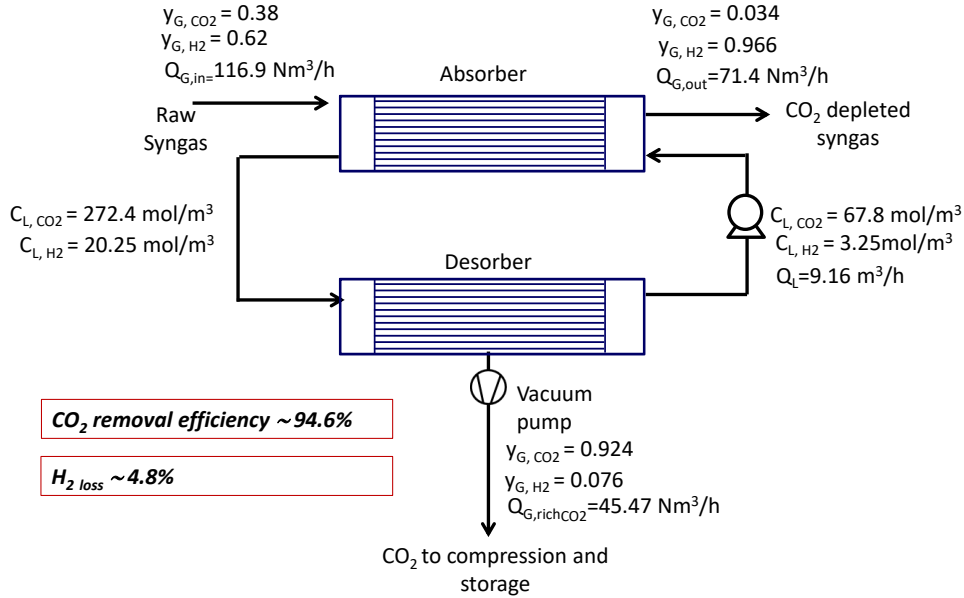


Figure 9: Simulation results of the HFMC process for CO₂ removal from syngas using Selexol as physical absorbent. Partial regeneration of the absorbent. $k_{M,CO_2}=5 \cdot 10^{-4}$ m/s, CO₂/H₂ selectivity of 4.

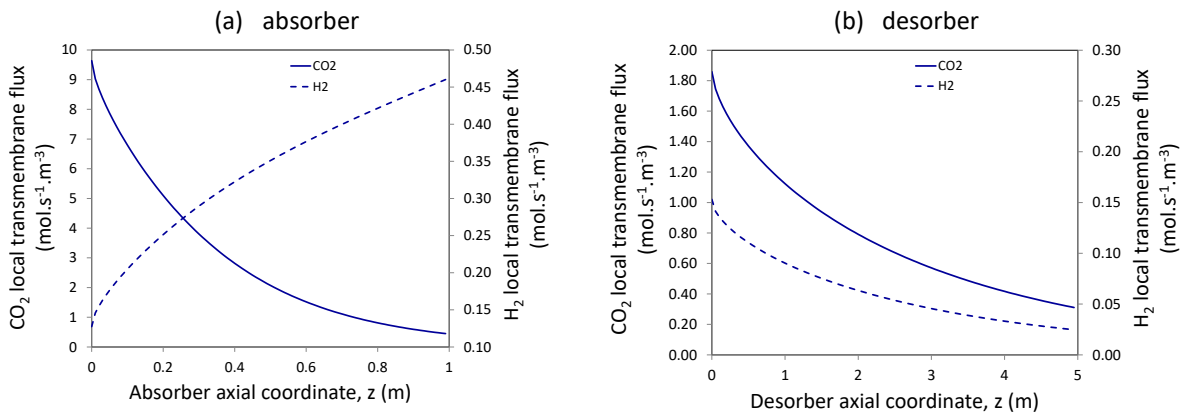


Figure 10: CO₂ and H₂ transmembrane flux profiles along the absorber. (a) absorber (b) desorber. z=0 corresponds to the gas inlet.

The $k_{ov, CO_2} \cdot a$ values obtained in this work are of 0.04 and 0.02 s⁻¹ for the absorber and the desorber respectively. The average CO₂ specific absorbed flux is of 5 mol/m³.s. These values can be used for comparison to packed Column technology under the same operating conditions allowing volume reduction potential calculations.

Table 6: Summary of simulation results

Absorber liquid pressure drop (bar)	0.63
Desorber liquid pressure drop (bar)	3.15
Absorber length	1
Desorber length	5
Liquid flow rate (m ³ /h)	9.16
Interstitial liquid velocity (m/s)	0.05
Liquid recirculation (pumping) (MJ/kg recovered CO ₂)	0.0709
Vacuum pump regeneration (MJ/kg recovered CO ₂)	0.119
Total specific energy requirement (MJ/kg recovered CO ₂)	0.19
k_{ov} (m.s ⁻¹) abs/des	1.2.10 ⁻⁵ /6.8.10 ⁻⁶
k_{ov} . a (s ⁻¹) abs/des	0.0388/0.022
Average CO ₂ specific absorbed flux (mol/m ³ .s)	5.10
Average CO ₂ specific stripped flux (mol/m ³ .s)	1.02
CO ₂ recovery ratio (%)	94.6
H ₂ purity (%)	96.65
H ₂ loss %	4.8%

Process selectivity analysis

Applying the resistance in series based on film theory (Equation 10) and considering flat membrane with neglecting gas side mass transfer resistance, overall mass-transfer coefficient of specie i can be expressed as follows:

$$\frac{1}{k_{ov,i}} = \frac{1}{k_{m,i}} + \frac{He_i}{k_{L,i}} \quad (4)$$

Overall process selectivity can be determined as the ratio of the overall mass transfer coefficient of the species to be separated i and j (Kerber et al., 2016):

$$S_{ov,ij} = \frac{k_{ov,i}}{k_{ov,j}} = \left(\frac{1}{k_{m,j}} + \frac{He_j}{k_{L,j}} \right) / \left(\frac{1}{k_{m,i}} + \frac{He_i}{k_{L,i}} \right) \quad (5)$$

The selectivity of the solvent, $S_{Abs, ij}$ is mainly given by the ratio of gaseous species solubility in the absorbent as liquid mass transfer coefficient of species i and j does not differ significantly in physical absorbent [Kerber et al., 2016]:

$$S_{Abs,ij} = \frac{He_j}{He_i} \quad (6)$$

The selectivity of the membrane, $S_{M, ij}$ is defined as the ratio of membrane mass transfer coefficient of species i and j :

$$S_{M,ij} = \frac{k_{M,i}}{k_{M,j}} \quad (7)$$

Membrane selectivity is also referred to as ideal selectivity α defined as a ratio of species permeabilities or permeance $J_{M,i}$ in mol/(m².s.pas):

$$\alpha_{ij} = \frac{\wp_i}{\wp_j} \quad (8) \text{ With:}$$

$$k_{M,i} = J_{M,i} RT = \frac{\rho_i}{e} RT \quad (9)$$

With e is the dense skin thickness of the membrane.

Integrating the two last equations in Equation 3 gives:

$$S_{ov,ij} = \frac{\alpha_{ij} + He_i \times S_{Abs} / (k_L / k_{M,i})}{1 + He_i / (k_L / k_{M,i})} \quad (10)$$

The overall selectivity of the process is expressed as a function of both the selectivity of the membrane and that of the liquid as well as solubility of specie i and the ratio $k_L / k_{M,i}$.

Considering laminar regime and developed concentration profile ($Gr > 0.03$), Sherwood number is constant and so is k_L for a given hydraulic diameter (Equation 1 and 2). Considering typical hydraulic diameter of 520 μm used in this study, the k_L value for CO_2 at 35°C in Selexol is of $2.2 \cdot 10^{-6}$ m/s.

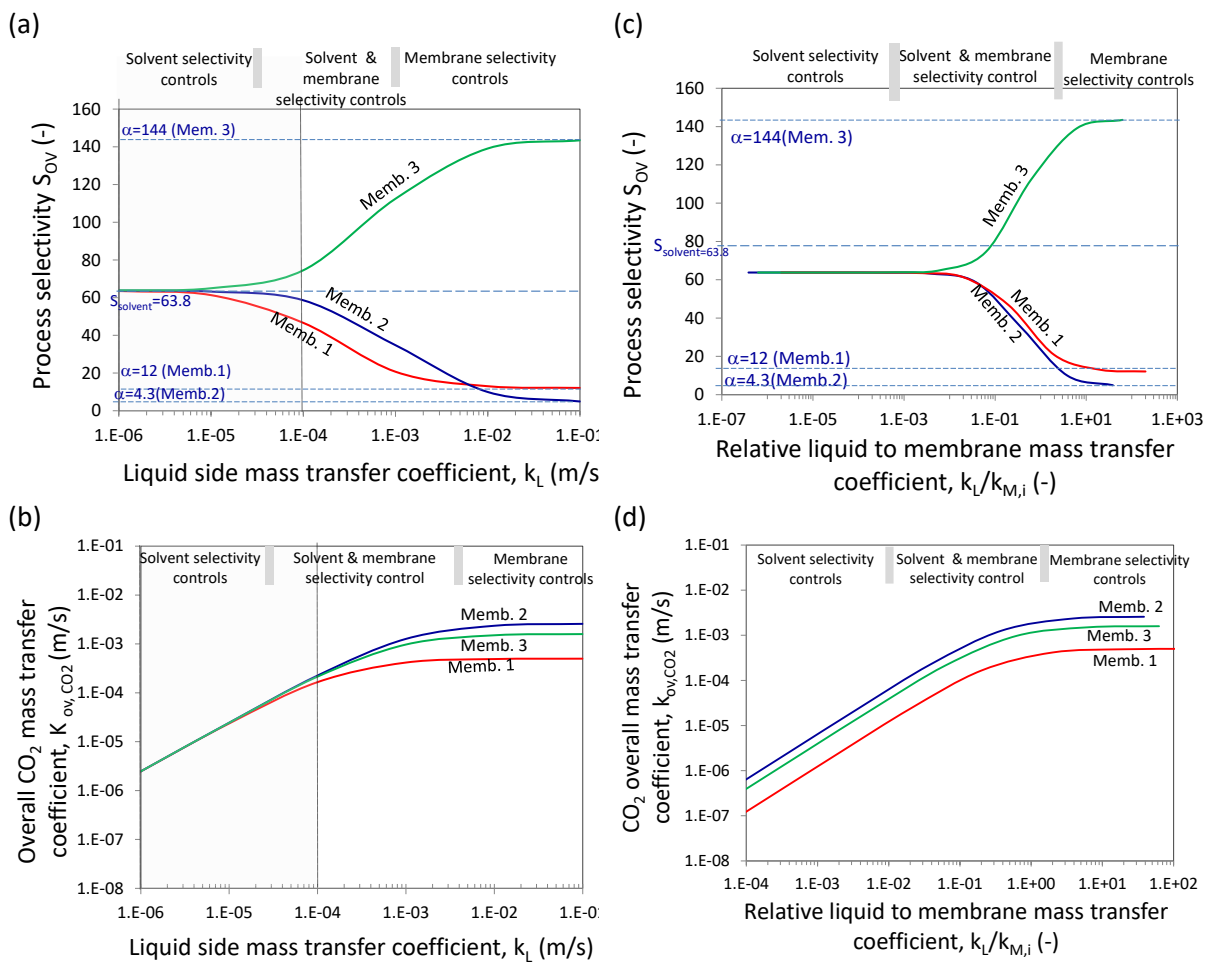


Figure 11: Process selectivity (a) and overall CO_2 mass transfer coefficient (b) as function of liquid mass transfer coefficient. Figures (c) and (d), represent the same plots than (a) and (b) with the absciss corresponding to relative liquid to membrane mass transfer coefficient. Memb.1: $k_{m,CO_2} = 5 \cdot 10^{-4}$ m/s, $\alpha_{CO_2/H_2} = 12$. Memb.2: $k_{m,CO_2} = 2.6 \cdot 10^{-3}$ m/s, $\alpha_{CO_2/H_2} = 4.3$. Memb.3: $k_{m,CO_2} = 1.6 \cdot 10^{-3}$ m/s, $\alpha_{CO_2/H_2} = 144$. Selexol as absorbent, $T = 35^\circ\text{C}$. $k_{L,CO_2} = 2.2 \cdot 10^{-6}$ m/s.

Figure 11 shows process selectivity and overall CO₂ mass transfer coefficient as function of liquid mass transfer coefficient and relative liquid to membrane mass transfer coefficients. Results are shown for three membranes noted Mem1, Mem2 and Mem3 (see Table B2).

When reporting, in **Figure 11a**, the k_l value for CO₂ at 35°C in Selexol is of $2.2 \cdot 10^{-6}$ m/s, it can be seen that process selectivity is mainly controlled by the selectivity of the solvent. However as liquid to membrane mass transfer increases (i.e. decreased membrane mass transfer), membrane selectivity starts to control progressively the overall process selectivity. Thus, theoretically, membrane mass transfer lower or at most comparable to that of absorbent mass transfer coefficient combined with higher CO₂/H₂ selectivity than that of the absorbent is required to increase the CO₂/H₂ process selectivity.

According to this discussion, we have achieved simulations considering membrane CO₂ mass transfer coefficient of $2 \cdot 10^{-6}$ m/s while keeping constant all other operating conditions at the same value than in the first set of simulations (temperature, pressure, inlet gas concentration, fluid flow rates). The results are shown in **Figure 12**. The energy requirement, overall mass transfer coefficient of both absorber and desorber are shown in **Table 7**. The proposed dense HFMC was able to recover up to 93.8% of CO₂ with 93.8% purity. The recovered H₂ purity is of 96.3%. Interestingly, H₂ loss is reduced to 1.3%. In order to attain these performances, membrane CO₂/H₂ selectivity of 300 was required. Such high selectivity has been reported experimentally for facilitated transport membranes (See Table B1). Indeed, facilitated transport fixed site carrier membranes (FSCM) have been reported to show high CO₂ permeability and selectivity for low CO₂ pressures prevailing in post-combustion capture applications. However, their ability to perform under high pressure pre-combustion capture application is very questionable due to carrier saturation under high CO₂ partial pressure [Rafiq et al., 2016]. High performances for this type of membranes have not been evidenced under relevant industrial conditions in pre-combustion application.

Compared to the first set of simulations, the required absorber and desorber length increased about 5 times. The corresponding energy requirement is of 0.446 MJ_{el}/kg CO₂, which is approximately over 2.3 times higher than that in the first set of simulations. Moreover, it can be seen that achieving lower H₂ loss is at the expense of increased contactor size and liquid energy pumping energy.

A systematic and detailed parametric analysis is of interest in order to evaluate the HFMC absorption/desorption loop process for a wide range of operating conditions and achieve parametric and process design optimizations. This important work will be presented in a forthcoming paper.

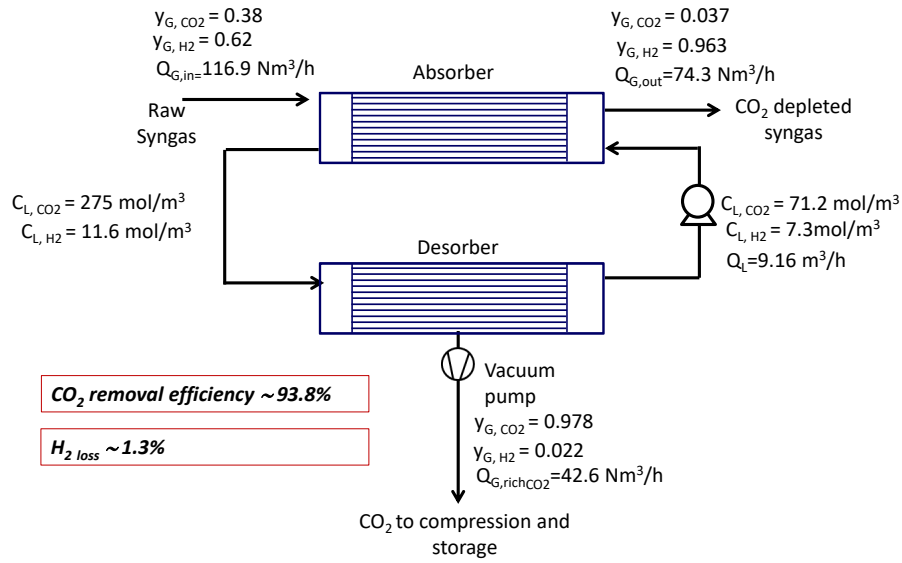


Figure 12: Simulation results of the HFMC process for CO_2 removal from syngas using Selexol as physical absorbent. Partial regeneration of the absorbent. $k_{M, CO_2} = 2 \cdot 10^{-6} \text{ m/s}$, CO_2/H_2 selectivity of 300.

Table 7: Table 12: Simulation results of configuration 2, membrane A in the absorber. Hypothetic membrane in the desorber: k_{m, CO_2} value of $1 \cdot 10^{-6} \text{ m/s}$, membrane CO_2/H_2 selectivity : 520.

Absorber liquid pressure drop(bar)	3.78
Desorber liquid pressure drop (bar)	13.86
Absorber length	6
Desorber length	22
Liquid flow rate (m^3/h)	9.16
Interstitial liquid velocity (m/s)	0.05
Liquid recirculation (pumping) (MJ/kg recovered CO_2)	0.334
Vacuum pump regeneration (MJ/kg recovered CO_2)	0.112
Total specific energy requirement (MJ/kg recovered CO_2)	0.446
k_{ov} ($\text{m} \cdot \text{s}^{-1}$) abs/des	$1.9 \cdot 10^{-6} / 1.5 \cdot 10^{-6}$
$k_{ov, a}$ (s^{-1}) abs/des	0.006/0.005
Average CO_2 specific absorbed flux ($\text{mol}/\text{m}^3 \cdot \text{s}$)	0.84
Average CO_2 specific stripped flux ($\text{mol}/\text{m}^3 \cdot \text{s}$)	0.23
CO_2 recovery ratio (%)	93.8
H_2 purity (%)	96.32

Table 8: Comparison with literature data

Solvent/process	CO ₂ and H ₂ Feed gas content	H ₂ loss %	Operating conditions	CO ₂ capture %	Total specific power consumption MJ _{el} /kg CO ₂
This study (simulation 1)	38% CO ₂ 62% H ₂	4.8	T =35°C P =36 bar	94.5	0.19
This study (simulation 2)	38% CO ₂ 62% H ₂	1.3	T =35°C P =36 bar	93.8	0.446
Kapetaki <i>et al.</i> , 2015	37.76% CO ₂ 56.33% H ₂	1%	T =35°C P =36 bar	90	0.4638
Mohammed <i>et al.</i> , 2014	-	-	-	90-91	0.389 (0.1080 kwh/kg CO ₂)

7. Conclusions and perspectives

This study intended to evaluate the potentialities of dense skin membrane contactors for shifted syngas purification using Selexol as physical absorbent considering absorption/ desorption loop. This topic has been indeed surprisingly unexplored, compared to CO₂ absorption into chemical solvents.

Through simulations, the following conclusions have been obtained:

- (i) Using commercially available membrane performance, the novel HFMC process is able to recover up to 92.4% of CO₂ with 96.6% H₂ purity. The energy requirement is of 0.19MJ_{el}/kg CO₂, this value is approximately over 2 times lower than that reported under comparable gas inlet conditions and separation specifications. It shows the possible potential of the concept for improved energy efficiency processes. However, this should be balanced regarding the total wide IGCC system energy requirement. H₂ loss is of 4.8% which is higher than that reported for conventional packed column based process (less than 1%). This result from the fact that no pressure flash is used with the HFMC process.
- (ii) The overall mass transfer coefficient is of $1.2 \cdot 10^{-5}$ m/s and $6.8 \cdot 10^{-6}$ m/s in the absorber and desorber respectively. The $k_{ov, CO_2} \cdot a$ values obtained in this work are of 0.04 and 0.02 s⁻¹ for the absorber and the desorber respectively.
- (iii) Membrane mass transfer lower or at most comparable to that of absorbent mass transfer coefficient combined with higher CO₂/H₂ selectivity than that of the absorbent is required to increase the CO₂/H₂ process selectivity.
- (iv) Lower H₂ loss is achieved at the expense of increased contactor size and liquid energy pumping energy.

A systematic and detailed parametric analysis (liquid and gas velocity, temperature, pressure, material permeation properties and module geometry) is needed in order to examine the interest of the HFMC loop process for a wide range of operating conditions. The potential of novel fiber geometry such as waves, helices or the addition of baffles to enhance the local mass transfer in the liquid phase could also be evaluated. These issues will be investigated in forthcoming papers.

The first simulation results of the proposed process raise several questions and the following perspectives can be proposed:

- (i) In order to limit H₂ loss, a configuration using a flash at medium pressure to recover a portion of H₂ before entering the desorber contactor need to be investigated.

- (ii) Isothermal 1D model is used to simulate the proposed process. Given the mass transfer limitation of the liquid phase, 2D model should be used in the simulation and compared to 1D simulation.
- (iii) Experimental validation of the concept would be also of interest. The potential permeation of Selexol through the dense membrane skin should be evaluated in order to ensure stable absorption performances over long time scales.

APPENDICES

Appendix A

Table A1: Data of gas solubility and absorbent selectivity for CO₂/H₂ and CO₂/CH₄, at 25°C.

	He' CO ₂ =1/He CO ₂ et 25°C (C _L /C _G) _{eq}	Selectivity CO ₂ /H ₂	Selectivity CO ₂ /CH ₄	Selectivity H ₂ S / CO ₂
DMEPG	2.59 ^f	76.9 ^a	14.92 ^{a c e}	8.93 ^a
	2.88 ^e	63.8 ^e 76 ^d	15.2 ^d	7.56 ^e
NMP	4.56 ^b	156.25 ^a	13.88 ^{a,b}	10.2 ^a
PC	3.50 ^b	128.2 ^a	26.31 ^{a,b}	3.29 ^a
Water	0.82 ^b		23.5 ^{a,b}	
	0.84 ^c		24.3 ^c	

^a Bucklin and Schebdel, 1984, ^b Dindore et al., 2004b ^c Sander, 1999, ^d Kohl and Nielsen, 1997, ^e Kapetaki et al., 2015, ^f Rayer et al., 2011.

Table A2: Physico-chemical properties of some physical absorbents including Selexol, at 25°C.

	Viscosity (Pa.s) ×10 ³ at 25°C	Vapor pressure(Pa) at 25°C	Freezing point (°C)	Molecular weight (g/mol)	Boilin g point (°C)	Density at 25°C Kg/m ³	Surface tension mN/m
DMEPG	5.80 ^{a,f}	0.097 ^f	-28 ^a	280 ^a	240 ^b	1030	33.5 ^f
	5.88 ^h						32 ⁱ
Methanol	0.6 ^b	-	-92 ^b	32.04	65 ^b	785	22.07 ^d
	0.55 ^d						22.2 ^e
NMP	1.65 ^a	52 ^a 53.33 ^f	-24 ^a	99 ^a	202 ^{b,d}	1027	40.7 ^d
	1.68 ^c						
	1.69 ^d						
	1.7 ^f						
PC	3 ^a	11 ^a 11.33 ^f	-48 ^a	102 ^a	240 ^b	1195	41.5 ^f
	2.5 ^f						
Water	1 ^f	3167.2 ^f	0 ^f	18 ^f	100 ^f	1000	72.5 ^d 72.3 ^f

^a Bucklin and Schebdel, 1984, ^b Kohl and Nielsen, 1997, ^c Tian et al, 2012, ^d Wang 1996, ^e Yong, 1981, ^f Dindore, 2004b, ^g Sander, 1999, ^h Heintz, 2011, ⁱ Siefert et al., 2016.

APPENDIX B

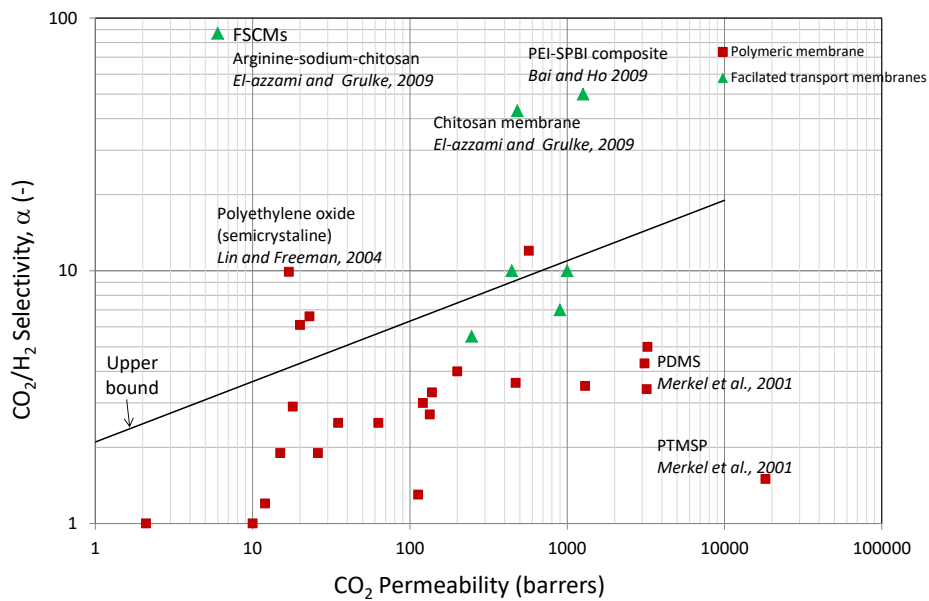


Figure B1: Data of polymeric membranes and advanced facilitated transport membrane for CO₂/H₂ separation (Scholes *et al.*, 2010, Elazzami and Grukle, 2009, Bai and Ho, 2009, Lin and Freeman, 2004, Merkel *et al.*, 2001). Contrary to H₂/CO₂ upper bound, that for CO₂/H₂ separation shows a positive slope.

Table B2: Example of polymeric membrane for CO₂/H₂ separation [1].

Membrane	CO ₂ permeability (barrer)	CO ₂ /H ₂ selectivity (-)	K _{M CO2} (for a 1μm thick membrane) m/s	T (°C)	P (bar)	Reference
Cross-linked Poly(ethylene glycol) acrylate (XLPEO)	570	12	4.89.10 ⁻⁴	35	1	Lin and freeman, 2004
PDMS	3100	4.3	2.6.10 ⁻³	35	5	Merkel et al., 2000
FSTM (arginine, sodium, Chitosan)	1500	144	1.6.10 ⁻³	110	1.5	El-Azzami and Grukle, 2009
PEBAX	20	6.1	1.65.10 ⁻⁵	25	4	Kim et al., 2001
PTFEP	470	3.6	4.03.10 ⁻⁴	35	13.6	Nagai et al., 2000
PTMSP	18200	1.5	1.56.10 ⁻²	35	1.4	Merkel et al., 2001

Appendix C

Resistances in series approach based on film theory is classically used for membrane contactors simulation purposes (**Gabelman and Hwang, 1999**). The local overall mass transfer coefficients can be expressed according to the resistance- in series model as follows:

The local absorbed CO₂ molar flux of specie *i* is expressed as:

$$N_{G,i} \left(\text{mol.m}^{-3} . \text{s}^{-1} \right) = a_m k_{ov,i} \left(C_{G,i} - C_{G,i}^* \right) \quad (\text{C1})$$

Where:

$$\frac{1}{k_{ov,i}} = \frac{He_i . d_{ml}}{d_e . k_{L,i}} + \frac{1}{k_{m,i}} + \frac{d_{ml}}{d_i . k_{G,i}} \quad (\text{C2})$$

$$C_{G,i}^* = He_i . C_{L,i} \quad (\text{C3})$$

a is the specific membrane module interfacial area (m⁻¹).

C_i^{}* is the hypothetical local gas-phase concentration in equilibrium with the liquid phase.

k_{ov,i} is the local global mass transfer coefficient of specie *i*. *k_{L,i}*, *k_{M,i}*, *k_{G,i}* are the local effective membrane mass transfer coefficients of the liquid, the membrane and the gas phase respectively.

d_{int}, *d_{ext}*, *d_{ml}* are the inner, outer and log mean diameters of the hollow fiber membrane. *He* is the Henry constant of the gas compound with water (defined as : *He* = *C_G* (mol/m³)/*C_L* (mol/m³)).

In this model, the film theory (diffusion in boundary layer) is applied in the liquid and gas phases. The key assumptions of the 1D model are:

- Constant membrane mass transfer (*k_{m,i}*) coefficient
- Thermodynamic equilibrium at the gas–liquid interface

In laminar flow through a cylindrical pipe, gas and liquid mass transfer coefficient, *k_G* and *k_L* respectively can be estimated by integrating the Graetz equation (**Beek, 1999, Skelland, 1985, Levêque, 1928**) for suitable boundary conditions.

The Sherwood number in each phase is estimated by:

$$\text{if } Gz < 0.03 \text{ then } Sh = 1.3Gz^{-1/3} \quad (\text{C4})$$

$$\text{if } Gz > 0.03 \text{ then } Sh = 4.36 \quad (\text{C5})$$

With Graetz and Sherwood numbers defined as follows (*z* is the axial coordinate):

$$Gz = \frac{D . z}{u_G . d_h^2} \quad (\text{C6})$$

$$Sh = \frac{k d_h}{D} \quad (\text{C7})$$

With *d_h* the hydraulic diameter.

For the gas phase, flowing in the lumen side, *d_h* corresponds to the internal fiber diameter (*d_i*).

The 1D model takes into account the evolution of the local mass transfer coefficients, the evolution of gas velocity (due to CO₂ absorption) and fluid pressure through the axial coordinate (*z*). Liquid velocity is supposed to be constant along the membrane length (i.e. negligible change in liquid molar flow due to gas absorption or desorption).

The differential equation system which is solved is detailed hereafter (*n* is the components number):

For the absorber:

- Gas differential molar balance:

$$\frac{dG_i}{dz} = -N_{G,i} \quad i = 1, n-1 \quad (C8)$$

- Liquid differential molar balance:

$$\frac{dL_i}{dz} = -N_{G,i} \quad i = 1, n-1 \quad (C9)$$

- Gas momentum balance (Hagen-Poiseuille) :

$$\frac{dP_G}{dz} = -\frac{32u_G\mu_G}{d_{int}^2} \quad (C10)$$

$$u_G = \frac{RT}{P_G} \frac{1}{S_G} \sum_{i=1}^n G_i \quad (C11)$$

With S_G , the gas flow section (m^2)

The boundary conditions are:

$$G_{G,i,z=0} = G_{z=0} \times y_{i,z=0}, \quad i = 1, n-1 \quad (C12)$$

$$C_{L,i,z=Z} = C_{L,i,0} \quad i = 1, n-1 \quad (C13)$$

$$C_{L,i,z=0} = C_{L,i,z=0}(\text{initialisation}) \quad i = 1, n-1 \quad (C14)$$

For the desorber:

- Liquid differential molar balance:

$$\frac{dL_i}{dz} = -N_{G,i} \quad i = 1, n-1 \quad (C15)$$

$$y_i = \frac{N_{G,i}}{\sum N_{G,i}} \quad i = 1, n-1 \quad (C16)$$

The gas mass transfer resistance was supposed negligible.

The boundary conditions are:

$$C_{L,i,z=0} = C_{L,i,z=0}(\text{initialisation}) \quad i = 1, n-1 \quad (C17)$$

$$C_{L,i,z=Z} = C_{L,i,0} \quad i = 1, n-1 \quad (C18)$$

With

$$L_i = u_L C_{i,L} \quad (C19)$$

$$G_i = u_G C_{i,G} \quad (C20)$$

G_i , L_i , is the molar flow rate of compound i in the gas phase and in the liquid phase respectively.

For the liquid phase flowing in the shell side in laminar regime, Happel equation is used:

$$\Delta P_L = \frac{\kappa \mu_L}{d_{ext}} \frac{\phi^2}{(1-\phi)^2} u_L Z \quad (C21)$$

κ is the Kozeny factor expressed by :

$$\kappa = 150\phi^4 - 314.44\phi^3 + 241.67\phi^2 - 83.039\phi + 15.97 \quad (C22)$$

With ϕ the packing ratio and Z the contactor length.

Equations system is numerically solved with the appropriate boundary conditions through a Matlab computer code.

NOMENCLATURE

Latin symbols

a	: Specific gas-liquid interfacial area (m^{-1})
d_h	: Hydraulic diameter (m)
d_{int}	: Internal fiber diameter (m)
d_{ext}	: External fiber diameter (m)
d_{ml}	: Log mean fiber diameter (m)
S_G	: Gas flow section (m^2)
D_{int}	: Internal membrane module diameter (m)
Z	: Total contactor length (m)
Sh	: Sherwood number (-)
Re	: Reynolds number (-)
Sc	: Schmidt number (-)
Gz	: Graetz number (-)
C	: Molar concentration ($mole \cdot m^{-3}$)
C_G^*	: Hypothetical local gas-phase concentration in equilibrium with the liquid phase ($mol \cdot m^{-3}$)
D_i	: Diffusion coefficient ($m^2 \cdot s^{-1}$)
Gz	: Graetz number (-)
k	: Mass transfer coefficient ($m \cdot s^{-1}$)
k_{ov}	: overall mass transfer coefficient ($m \cdot s^{-1}$)
N_i	: Molar flux ($mol \cdot m^{-2} \cdot s^{-1}$)
P	: Pressure (Pa)
ΔP	: Fluid pressure drop (bar)
ΔP_m	: Transmembrane pressure difference (bar)
Q	: Fluid volumetric flow rate ($m^3 \cdot s^{-1}$)
G	: Gas molar flow rate ($mol \cdot s^{-1}$)
L	: Liquid molar flow rate ($mol \cdot s^{-1}$)
T	: Temperature (K)
y	: Molar fraction in the gas (-)
u	: Interstitial fluid velocity ($m \cdot s^{-1}$)
He	: Henry constant (C_G/C_L) (-)
z	: Axial coordinate (m)

G_{des} : Molar flow rate the stripped gas in the desorber
 $P_{G,des}$: Vacuum pressure in the desorber (Pa)
 $P_{L,p}$: Pumping power requirement for the recirculation of the absorbent (W)
 P_{vacuum} : Power required for vacuum pumping in the desorber for CO₂ stripping (W)

Greek symbols

φ : Module packing fraction (-)
 μ : Viscosity (Pa·s⁻¹)
 ρ : Density (kg·m⁻³)
 η_{CO_2} : CO₂ removal efficiency (-)
 Ω : Contactor cross section (m²)
 η_V : Vacuum pump efficiency (-)

Subscripts/ Exponents

i : Compound
G : Relative to gas
L : Relative to liquid
m : Relative to the membrane
in : Relative to fluid inlet
out : Relative to fluid outlet
abs : Relative to the absorber
des : Relative to the desorber

Abbreviations

HFMC : Hollow Fiber membrane contactor
PTMSP : Poly[1-(trimethylsilyl)-1-propyne]
PTMGP : Poly[1-(trimethylgermyl)-1-propyne]
PMP : Poly[4-methyl-2-pentyne]
PDMS : Polydimethyl siloxane
PTMSP : Poly[1-(trimethylsilyl)-1-propyne]
PTFE : Polytetrafluoroethylene
PP : Polypropylene
NMP : N-Methyl-2-pyrrolidone
PC : Propylene carbonate,
MEA : Monoethanolamine
DEA : Diethanolamine
MDEA : N-methyldiethanolamine
AMP : 2-amino-2-methyl-1-propanol
DEAE : 2-diethylaminoethanol
PZ : Piperazine
[Bmim][TCM] : 1-Butyl-3-methylimidazolium tricyanomethanide

References

- Albarracin Zaidiza, D., Belaissaoui, B., Rode, S., Favre, E., 2017. Intensification Potential of Hollow fiber Membrane Contactors for CO₂ Chemical Absorption and Stripping using Monoethanolamine solutions, *Separation and Purification Technology*, 188, 38-51.
- Albarracin Zaidiza, D., Wilson, S. G., Belaissaoui, B., Rode, S., Castel, C., Roizard, D., Favre, E., 2016. Rigorous modelling of adiabatic multicomponent CO₂ post-combustion capture using hollow fiber membrane contactors, *Chemical Engineering Science*, 145, 45-58.
- Albarracin Zaidiza, D., Billaud, J., Belaissaoui, B., Rode, S., Roizard, D., Favre, E., 2014. Modeling of CO₂ post-combustion capture using membrane contactors, comparison between one- and two-dimensional approaches, *Journal of Membrane Science*, 455, 64-74.
- Bai, H. and Ho, W. S. W., 2009. New Carbon Dioxide-Selective Membranes Based on Sulfonated Polybenzimidazole (SPBI) Copolymer Matrix for Fuel Cell Applications, *Ind. Eng. Chem. Res.* 48, 2344–2354.
- Beek W.J., Muttzall K.M.K., Heuven J.W., 1999. *Transport Phenomena*, Wiley.
- Bucklin, R. W. and Schendel, R. L., 1984. Comparison of Fluor Solvent and Selexol Processes: Physical solvent processes can be very useful for acid gas removal applications. *Energy Progress*, 4, 137-142
- Casero, P., García Pena, F., Coca, P., Trujillo, J., 2014. ELCOGAS 14 MWth pre-combustion carbon dioxide capture pilot. Technical & economical achievements. *Fuel* 116, 804–811.
- Chabanon, E., Belaissaoui, B., Favre, E., 2014. Gas–liquid separation processes based on physical solvents: opportunities for membranes, *Journal of Membrane Science*, 459, 52-61.
- Cui, Z. and deMontigny, D., 2013. “Part 7: A review of CO₂ capture using hollow fiber membrane contactors,” *Carbon Manag.*, 4 (1), 69–89.
- Dai, Z., Ansaloni, L., and Deng L., 2016. Precombustion CO₂ Capture in Polymeric Hollow Fiber Membrane Contactors Using Ionic Liquids: Porous Membrane versus Nonporous Composite Membrane, DOI: 10.1021/acs.iecr.6b01247. *Ind. Eng. Chem. Res.*, 55, 5983–5992.
- Dave, A., Dave, M., Huang, Y., Rezvani, S., Hewitt, N., 2016. Process design for CO₂ absorption from syngas using physical solvent DMEPEG, *International Journal of Greenhouse Gas Control* 49, 436–448
- Davidson, O., Metz, B., 2005. Special Report on Carbon Dioxide Capture and Storage, International panel on climate Change, Geneva, Switzerland /[http:// www.ipcc.chS](http://www.ipcc.ch/S).
- Drioli, E., Curcio, E., Di Profio G., 2005. State of the Art and Recent Progresses in Membrane Contactors, *Chemical Engineering Research and Design*, 83 (3) , 223-233.
- Dindore, V.Y., Brillman, D.W.F., Geuzebroek, F.H., Versteeg, 2004a. G.F., Membrane–solvent selection for CO₂ removal using membrane gas–liquid contactors, *Separation and Purification Technology*, 40, 133–145.
- Dindore, V.Y., Brillman, D.W.F., Feron, P.H.M., Versteeg, G.F., 2004b. CO₂ absorption at elevated pressures using a hollow fiber membrane contactor, *J. Membr. Sci.*, 235, 99–109.

El-Azzami, L. A., Grulke, E. A., 2009. Carbon dioxide separation from hydrogen and nitrogen Facilitated transport in arginine salt–chitosan membranes, *Journal of Membrane Science* 328, 15–22

Falk-Pedersen, O., Dannstroem, H., Methods for Removing Carbon Dioxide from Gases, WO 98/04339 Kvaerner ASA, Norway.

Jansen, D., Gazzani, M., Manzolini, Van Dijk, G., E., Carbo, M., 2015. Pre-combustion CO₂ capture, *International Journal of Greenhouse Gas Control* 40, 167–187.

Gottlicher, G. and Pruschek, R., 1997. Comparison of CO₂ removal systems for fossil-fuelled power plant process, *Energy Convers. Mgmt*, 38, S173-S178.

Gabelman, A., Hwang, S-T, 1999. Hollow fiber membrane contactors, *Journal of Membrane Science*, 159 (1-2), 61-106.

Heintz, Y. J., 2011. carbon dioxide capture from fuel gas streams under elevated pressures and temperatures using novel physical solvents, Doctor of Philosophy dissertation, November 29, the Swanson School of Engineering

Heile, S., Rosenberger, S., Parker, A., Jefferson, B., McAdam E.J., 2014. Establishing the suitability of symmetric ultrathin wall polydimethylsiloxane hollow-fibre membrane contactors for enhanced CO₂ separation during biogas upgrading, *Journal of Membrane Science* 452, 37-45

Kerber, J., Repke, J-U, 2016. Mass transfer and selectivity analysis of a dense membrane contactor for upgrading biogas, *Journal of Membrane Science*, 520, 450-464.

Kapetaki Z., Brandani, P., Brandani, S., Ahn, H.g, 2015. Process simulation of a dual-stage Selexol process for 95% carbon capture efficiency at an integrated gasification combined cycle power plant, *International Journal of Greenhouse Gas Control* 39, 17–26.

Kohl, A. L. and Nielsen, R. B., 1997. *Gas Purification*, 5th ed., Gulf Publishing Company, Houston, Texas.

Kwak, D-H., Yun, D., Binns, M., Yeo, Y-K. and Kim, J-K, 2014. Conceptual Process Design of CO₂ Recovery Plants for Enhanced Oil Recovery Applications, [dx.doi.org/10.1021/ie502110q](https://doi.org/10.1021/ie502110q), *Ind. Eng. Chem. Res.* 53, 14385–14396.

Lévêque A., 1928. *Les Lois de la transmission de chaleur par convection*, Dunod, Paris, France.

Lin, H., Freeman, B.D., 2004. Gas solubility, diffusivity and permeability in poly(ethylene oxide), *Journal of Membrane Science*, 239 (1), 105-117.

Mohammed, I. Y., Samah, M., Mohamed, A., Sabina, G., 2014. Comparison of SelexolTM and Rectisol[®] Technologies in an Integrated Gasification Combined Cycle (IGCC) Plant for Clean Energy Production, *International Journal of Engineering Research*, 3 (12), 742-744.

Merkel, T.C, Gupta, R.P, Turk, B.S, Freeman, 2001. B.D, Mixed-gas permeation of syngas components in poly(dimethylsiloxane) and poly(1-trimethylsilyl-1-propyne) at elevated temperatures, *Journal of Membrane Science*, 191 (1–2), 85-94.

Merkel, T.C., Bondar, V.I., Nagai, K., et al., 2000. Gas sorption, diffusion, and permeation in poly(dimethylsiloxane), *Journal of polymer science part b-polymer physics*, 38 (3), 3415-434.

Kim, J.H., Ha, S.Y., Lee, Y.M., 2001. Gas permeation of poly(amide-6-b-ethylene oxide) copolymer, *Journal of membrane science*, 190 (2), 179-193.

Nagai, K, Freeman, BD, Cannon, A, et al., 2000. Gas permeability of poly(bis-trifluoroethoxyphosphazene) and blends with adamantane amino/trifluoroethoxy (50/50) polyphosphazene, *Journal of membrane science*, 172 (1-2), 167-176.

Nguyen, P.T., Lasseguette, Medina-Gonzalez, E., Y., Remigy, J.C., Roizard, D., Favre, E., 2011. A dense membrane contactor for intensified CO₂ gas/liquid absorption in post-combustion capture, *Journal of Membrane Science*, 377, 261-272.

Ozturk, B. and Hughes, R., 2012. Evaluation of mass transfer characteristics of non-porous and microporous membrane contactors for the removal of CO₂, *Chemical Engineering Journal*, 195–196, 122-131

Padurean, A., Cormos, C.-C., Agachi, 2012. P.S., Pre-combustion carbon dioxide capture by gas–liquid absorption for Integrated Gasification Combined Cycle power plants, *International Journal of Greenhouse Gas Control* 7, 1–11.

Park, S., Lee, S., Wook Lee, J., Chun, S. N., Lee, J. B., 2015. The quantitative evaluation of two-stage pre-combustion CO₂ capture processes using the physical solvents with various design parameters, *Energy* 81, 47-55.

Rayer, A.V., Henni, A. and Tontiwachwuthikul, P., 2012. High Pressure Physical Solubility of Carbon Dioxide (CO₂) in Mixed Polyethylene Glycol Dimethyl Ethers (Genosorb 1753), *the canadian journal of chemical engineering*, 90, 576-583

Scholes, C. A., Smith, K.H., Kentish, S. E., Stevens G. W., 2010. CO₂ capture from pre-combustion processes—Strategies for membrane gas separation, *International Journal of Greenhouse Gas Control* 4, 739–755.

Scholes A. C., Simioni, M., Qader, A., Stevens, G. W., Kentish, S. E., 2012. Membrane gas–solvent contactor trials of CO₂ absorption from syngas, *Chemical Engineering Journal* 195–196, 188–197.

Siefert, N.S., Agarwal, S., Shi, F., Shi, W., Roth, E.A., Hopkinson, D., Kusuma, V.A., Thompson, R.L., Luebke, D.R., Nulwala, H.B., 2016. Hydrophobic physical solvents for pre-combustion CO₂ capture: Experiments, computational simulations, and techno-economic analysis, *International Journal of Greenhouse Gas Control* 49, 364–371.

Skelland A.H. P., 1985. *Diffusional Mass Transfer*, R.E. Krieger Pub. Co.

Sander R., 1999. *Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry*. <http://www.mpch-mainz.mpg.de/~sander/res/henry.html>

Theo, W. L., Lim, J. S., Hashim, H., Mustafa A. A., Ho W. S., 2016. Review of pre-combustion capture and ionic liquid in carbon capture and storage, *Applied Energy* 183, 1633–1663.

Trusov, A., Legkov, S., Van den Broeke, L. J.P., Goetheer, E., Volkov, A., 2011. Gas/liquid membrane contactors based on disubstituted polyacetylene for CO₂ absorption liquid regeneration at high pressure and temperature. *Journal of Membrane Science*, 383 (1-2), 241-249.

Tian, S., Hou, Wu, Y. W., Ren, S. and Pang K., 2012. Physical Properties of 1-Butyl-3-methylimidazolium Tetrafluoroborate/N-Methyl-2-pyrrolidone Mixtures and the Solubility of CO₂ in the System at Elevated Pressures, *American Chemical Society* 756 dx.doi.org/10.1021/je200886j, *J. Chem. Eng. Data*, 57(2012) 756–763.

Wang, D., Li, K., Teo, W.K., 1996. Polyethersulfone hollow fiber gas separation membranes prepared from NMP/alcohol solvent systems, *Journal of Membrane Science* 115, 85-108.

Yong S. Won, Dong K. Chung, and Mills, A. F., 1981. Density, Viscosity, Surface Tension, and Carbon Dioxide Solubility and diffusivity of Methanol, Ethanol, Aqueous Propanol, and Aqueous Ethylene Glycol at 25 °C, *J. Chem. Eng. Data*, 26, 141-144.