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## 3.9 Membranes Contactors for Intensified Gas–Liquid Absorption Processes

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# MEMBRANES CONTACTORS FOR INTENSIFIED GAS-LIQUID ABSORPTION PROCESSES

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## **SYNOPSIS**

The absorption of a gaseous solute in a liquid is a classical unit operation with a large number of applications in numerous industrial sectors. A direct contact between the gas and liquid phase in order to promote mass transfer is classically applied for industrial equipment (trays, packings, stirred tanks, Venturi scrubbers...). The concept of membrane contactor for gas-liquid absorption (or stripping, i.e. gaseous solute removal from a liquid), which makes use of a gas permeable membrane interposed between the gas and liquid phase, has been recently proposed and shows several advantages: possibility to independently control the gas and liquid flow rates, no sensitivity to orientation, no foaming or entrainment problems and larger compactness. The latter characteristics, also named intensification, is of major interest. It is potentially achievable due to the very large specific gas-liquid interfacial area provided by membranes modules, but it also requires the membrane mass transfer resistance to be as low as possible. The different types of membrane materials (microporous hydrophobic, dense skin composite) are detailed and the associated properties and mechanisms which govern mass transfer properties are presented. Wetting, fouling and degradation issues are more specifically discussed, with the associated impact on membrane mass transfer performances. The different levels of modelling which can be proposed for the simulation of a membrane contactor module are shown, with a gradual complexity approach. The key role of the membrane mass transfer coefficient is highlighted. The different applications of membrane contactors are finally presented: blood oxygenators, oxygen removal (food, microelectronics, pharma), carbonated beverages, aromas or volatile compounds recovery, effluent treatment, bioreactors... Post combustion carbon capture and natural gas treatment could generate important new markets, for which process intensification is of key interest. The challenges and perspectives of membrane contactors, with a particular emphasis on process intensification framework are finally discussed.

## **KEYWORDS**

Absorption; Stripping; Intensification; Microporous membrane; Mass transfer; Wetting; Composite; Dense skin; Hollow fibers; Module; Modelling; Degassing; Oxygenators; Carbon capture.

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## GLOSSARY

i	:	Gaseous species
j	:	Reactive species from the liquid phase
MEA	:	Monoethanolamine
PDMS	:	Polydimethylsiloxane
PP	:	Polypropylene
PTFE	:	Polytetrafluoroethylene
PTMSP	:	Poly(1-trimethylsilyl)-1-propyne
PVDF	:	Poly(vinylidene) fluoride
SPEEK	:	Sulfonated Poly(ether ether)ketone

## NOMENCLATURE

a	:	Specific membrane area ( $\text{m}^2 \text{m}^{-3}$ )
B	:	Pore geometry coefficient (-)
C	:	Concentration of i or j ( $\text{mol m}^{-3}$ )
$C_p$	:	Thermal capacity ( $\text{J K}^{-1} \text{kg}^{-1}$ )
D	:	Diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$D_k$	:	Knudsen diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$D_{\text{micro}}$	:	Diffusion coefficient in a microporous support ( $\text{m}^2 \text{s}^{-1}$ )
d	:	Diameter (m)
$d_{\text{pmax}}$	:	Maximum pore diameter (m)
e	:	Dense skin layer thickness (m)
E	:	Enhancement factor (-)
$E_{\infty}$	:	Infinite enhancement factor (-)
H	:	Henry's law constant ( $\text{Pa m}^3 \text{mol}^{-1}$ )

Ha	:	Hatta number (-)
H <sub>i</sub>	:	Enthalpy of reaction (J mol <sup>-1</sup> )
k	:	Local mass transfer coefficient (m s <sup>-1</sup> )
K	:	Global mass transfer coefficient (m s <sup>-1</sup> )
K <sub>ov</sub>	:	Overall mass transfer coefficient (m s <sup>-1</sup> )
k <sub>B</sub>	:	Boltzmann constant (1.381 10 <sup>-23</sup> J K <sup>-1</sup> )
k <sub>max</sub>	:	Maximal mass transfer coefficient (m s <sup>-1</sup> )
k <sub>m,dense</sub>	:	Dense membrane mass transfer coefficient (m s <sup>-1</sup> )
k <sub>m,porous</sub>	:	Microporous membrane mass transfer coefficient (m s <sup>-1</sup> )
k <sub>m,dry</sub>	:	Membrane mass transfer coefficient in dried pores (m s <sup>-1</sup> )
k <sub>m,wet</sub>	:	Membrane mass transfer coefficient in wetted pores (m s <sup>-1</sup> )
k <sub>r</sub>	:	Kinetic constant (units depends of the order of reaction, i.e. 2 <sup>nd</sup> order: m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> ; 3 <sup>rd</sup> order: m <sup>6</sup> mol <sup>-2</sup> s <sup>-2</sup> ...)
J	:	Molar Flux (mol m <sup>-2</sup> s <sup>-1</sup> )
L	:	Effective fiber length (m)
LEP	:	Liquid Entry Pressure also called Breathrough pressure (Pa)
m	:	Partition coefficient (-)
M	:	Molecular weight (g mol <sup>-1</sup> )
N	:	Flux density (mol s <sup>-1</sup> )
n <sub>fib</sub>	:	Fiber number (-)
NUT <sub>g</sub>	:	Number of transfer units (-)
P	:	Pressure (Pa)
ΔP	:	Pressure drop (Pa)
Q	:	Flowrate (m <sup>3</sup> s <sup>-1</sup> )
R	:	Ideal gas constant (8.314 J K <sup>-1</sup> mol <sup>-1</sup> )
R <sub>i</sub>	:	Reaction rate (mol m <sup>-3</sup> s <sup>-1</sup> )

$r$	:	Radius or spatial coordinate (m)
$r_p$	:	Pore radius (m)
$r_{mod}$	:	Internal module radius (m)
$S$	:	Solubility coefficient ( $\text{mol m}^{-3} \text{ Pa}^{-1}$ )
$S_{lumen}$	:	Membrane surface area in the lumen side ( $\text{m}^2$ )
$S_{shell}$	:	Membrane surface area in the shell side ( $\text{m}^2$ )
$S_{ml}$	:	Logarithmic mean membrane surface area ( $\text{m}^2$ )
$S_{ext}$	:	Cross-section of the empty module, i.e. without hollow fibers ( $\text{m}^2$ )
$Sh$	:	Sherwood number (-)
$T$	:	Temperature (K)
$u_g$	:	Interstitial gas velocity ( $\text{m s}^{-1}$ )
$y$	:	Volume fraction (-)
$z$	:	Axial coordinate (m)

### **Greek Letters**

$\alpha$	:	Solvent loading (-)
$\beta$	:	Wetting pore ratio (-)
$\delta$	:	Membrane thickness (m)
$\varepsilon$	:	Membrane porosity (-)
$\gamma$	:	Surface tension ( $\text{N m}^{-1}$ )
$\eta$	:	Capture ratio (-)
$\varphi$	:	Packing ratio (-)
$\kappa$	:	Kozeny coefficient (-)
$\lambda$	:	Mean free path (m)
$\mu$	:	Viscosity ( $\text{Pa s}$ )
$\theta$	:	Contact angle (rad)

$\rho$	:	Density ( $\text{kg m}^{-3}$ )
$\tau$	:	Membrane tortuosity (-)
$v$	:	Superficial gas velocity ( $\text{m s}^{-1}$ )
$\omega$	:	Stoichiometric coefficient (-)
$\psi$	:	Thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ )
$\wp$	:	Permeability ( $\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ )

### Subscripts

g	:	Gas phase, gas bulk or gas molecule
g-m	:	Gas-membrane interface
i	:	Inner of the hollow fiber or gas solute
j	:	Solvent part
mem	:	Membrane
m-l	:	Membrane-liquid interface
lum	:	Lumen side
l-m	:	Liquid-membrane interface
l	:	Liquid phase or liquid bulk
o	:	Outer of the hollow fiber
sh	:	Shell side

### Superscript

in	:	At the inlet of the membrane module
p	:	$p^{\text{th}}$ order in i
q	:	$q^{\text{th}}$ order in i



## INTRODUCTION

Gas separation operation is a process of major importance for a large number of industries and can be basically operated through five main techniques: absorption (i.e. liquid auxiliary phase), adsorption (i.e. solid auxiliary phase), permeation (i.e. membrane separation), chemical conversion and condensation [1]. Amongst these, gas absorption is considered as the most important and is often referred as one of the key unit operations of chemical engineering [2]. The first industrial application of a gas-liquid absorption process can be dated back to 1830, by William Gossage, a chemical manufacturer who wanted to absorb hydrochloric acid vapor from the manufacture of alkali [3]. Nevertheless, it is known that the use of gas to liquid transfer techniques has been more empirically practiced much before (e.g. oxygenation for waste water treatment or fisheries). Generally speaking, gas absorption can be defined as a process in which one or more soluble components (solute) are removed from a gas phase by contact with a liquid phase (solvent) into which the target component(s) dissolve. In a great number of cases, the absorbed gas is further removed from the solvent, and the solvent liquid stream is subsequently returned to the system. This strategy results in an internal liquid loop between two units (i.e. absorption and regeneration), and enables solvent recycling. The solvent-regeneration process is called stripping. Stripping is also employed when volatile components have to be removed from a liquid mixture. The stripping agent is either a gas (e.g. air) or a superheated vapor (e.g. superheated steam). Moreover, depending on the molecular mechanism taking place in the liquid phase (solvent), a distinction is made between physical and chemical (or reactive) absorption; furthermore, chemical absorption can be reversible or irreversible [4,5].

Since its first application, a very large number of gas-liquid absorption units have been installed in industry and are operated for different purposes. Table 1 summarizes some typical large scale applications, with the different type of processes detailed above.

**Table 1: Industrial applications of gas-liquid absorption, from [1–4,6], adapted.**

		<b>Solute</b>	<b>Solvent</b>	<b>Absorption</b>	<b>Stripping</b>	<b>Application &amp; industry</b>
<b>Physical</b>	<b>Aqueous solvent</b>	Ethylene oxide	H <sub>2</sub> O	+	+	Chemical production
		VOC's	H <sub>2</sub> O	-	+	Effluent treatment
		O <sub>2</sub>	H <sub>2</sub> O	-	+	Ultrapure water (pharma, electronics)
		CO <sub>2</sub>	H <sub>2</sub> O	+	+	Biogas purification (PWA)
	<b>Organic solvent</b>	H <sub>2</sub> O	TEG	+	+	Gas industry (drying)
		C <sub>4</sub> H <sub>10</sub>	Oil	+	+	Petrochemistry
		Fatty acids	Hexane	+	+	Food
		CO <sub>2</sub>	Glycols, MeOH	+	+	Energy (IGCC coal gasification)
<b>Chemical</b>	<b>Reversible</b>	Cl <sub>2</sub>	H <sub>2</sub> O	+	+	Pulp & paper
		CO <sub>2</sub> H <sub>2</sub> S	MEA, MDEA	+	+	Natural gas
		CO	Cu NH <sub>4</sub> salt	+	+	Syngas
	<b>Irreversible</b>	HCl, HF, SO <sub>x</sub> , NO <sub>x</sub>	NaOH	+	-	Exhaust air scrubbing
		O <sub>2</sub>	H <sub>2</sub> O	+	-	Wastewater treatment
		CO <sub>2</sub>	NaOH	+	-	Chemical
		Triethylamine	H <sub>2</sub> O	+	-	Steel

Beyond the various equipment options listed in Table 2, which make use of a direct contact between the gas and liquid phase, a completely different strategy has been more recently explored. The basic concept, commonly referred as membrane

contactor technology and sketched on Figure 1, makes flow the gas and liquid phases into separate compartments, thanks to a gas permeable solid material (membrane). The concept was first proposed for wastewater treatment, VOC stripping and oxygenators [7–9], but the first practical use of membrane contactor for gas-liquid application is usually dated in the 70's [10]. In a membrane contactor, the direct gas-liquid contact is prevented and there is no hydrodynamic limitation like weeping, entrainment, frosting, channeling or flooding, typical of the classical direct contact systems. A very large range of gas to liquid flow volume, which is a very important variable for maximizing separation performances, can thus be applied. This unique flexibility of gas and liquid flows and independent pressure control of gas and liquid phase is of major interest. Moreover, the membrane contactor process can take advantage of the very large specific interfacial area ( $a$ ) of membrane modules [11]. In terms of mass transfer characteristics, the mechanism of the membrane contactor process is essentially the same as it is with a conventional contacting column. The membrane is however a barrier to direct contact of the two phases, and it is thus of primary importance to impart little additional resistance from the membrane to the transport of the gaseous species. The solute transport rate can still be expressed through an overall mass transfer coefficient ( $K$  in  $\text{m s}^{-1}$ ), taking into account the three mass transfer resistances, namely gas, membrane and liquid. Typical values of  $a$  and  $K$  for membrane contactors are indicated in the last row of Table 2, for sake of comparison to other absorption equipment. The possibility to achieve significantly larger  $K.a$  values, leading to more compact units (i.e. process intensification), is highlighted.

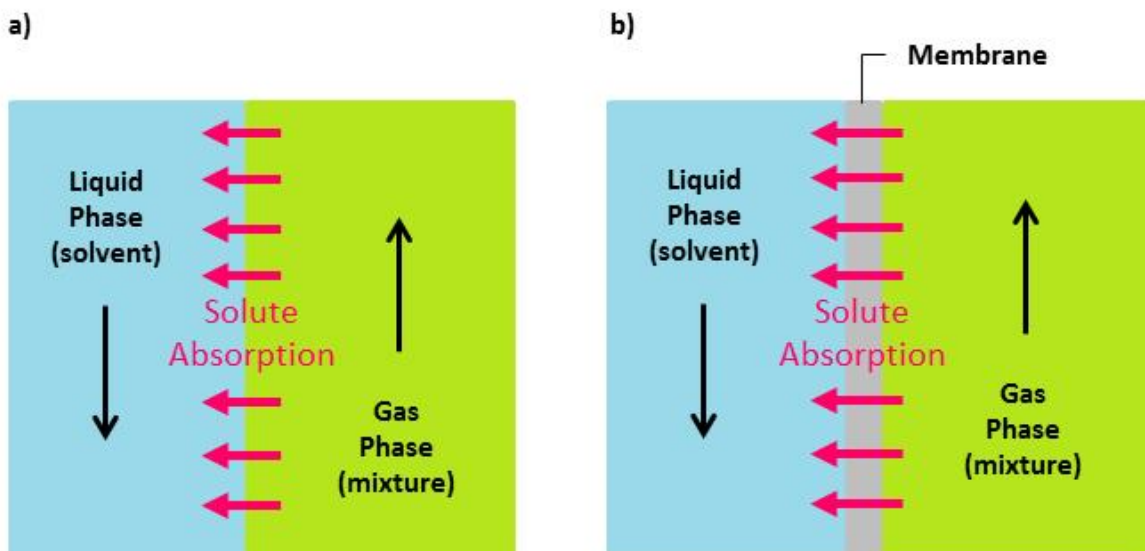
Additional advantages of membrane technology such as highly modularity, ease of scale-up, smaller size and lower weight can be expected. The system is also orientation and motion insensitive, at the contrary to tray or packed columns; this peculiarity is of interest for off-shore applications for instance. More generally, the membrane contactor concept is usually presented to support "green chemistry" and "process intensification" initiatives.

In summary, membrane contactors may offer improved performance and value over current unit operations, mainly absorption and gas stripping processes. The different aspects underlying the development of this technology are exposed and discussed in the next sections, with a specific focus on gas-liquid absorption processes and a

particular emphasis on intensification possibilities, which are often considered as one of their most attractive feature [12,13].

In a first step, an illustrative example of membrane contactor vs conventional packed column technology, for post combustion CO<sub>2</sub> capture by chemical gas-liquid absorption will be described. The framework is of interest because of the exceptional application potential [14], including very large scale units, but also because it shows several challenges for membrane, module and process developments.

The mass transfer, membrane material, module design and process (modelling and simulation) development framework will be more specifically detailed in the subsequent sections. An overview of industrial applications and prospects will finally be proposed.



**Figure 1: Schematic representation of a direct gas-liquid contact system for absorption processes (a) and a membrane contactor system (b)**

**Table 2 : Different types of gas-liquid absorption equipment and corresponding mass transfer performances. The comparison to membrane contactors performances, which are not based on a direct gas-liquid contact concept, is shown on the last row.**

Contact type	Examples of equipment	Surface area / volume (m <sup>2</sup> m <sup>-3</sup> )	Mass transfer K.a (s <sup>-1</sup> ) x 10 <sup>-2</sup>	Gas/Liquid Volume flow (-)
Gas and liquid continuous phases	Packed columns Thin film contactors	10 – 500	0.04 – 7	2% - 25%
Dispersed gas phase and continuous liquid phase	Bubble columns Plate columns (trays) Stirred tanks	50 - 600	0.5-12	60% – 98%
Dispersed liquid phase and continuous gas phase	Venturi scrubber Spray column	160 – 2500	8 - ~25	5% - 30%
<i>Membrane contactor</i>		<i>1000 – 10 000</i>	<i>5 – 50</i>	<i>1% - 99%</i>

## **MEMBRANE ABSORPTION VS CONVENTIONAL ABSORPTION: OVERALL FRAMEWORK AND ILLUSTRATIVE EXAMPLE (CO<sub>2</sub> ABSORPTION)**

Until now, CO<sub>2</sub> capture remains one of the main target application of gas-liquid absorption process due to the collective awareness regarding the greenhouse gases issue. Indeed, nature continually produces greenhouse gases such as carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), water vapor (H<sub>2</sub>O) or nitrous oxide (NO<sub>x</sub>) and which are fundamental to the equilibrium responsible of the life development on Earth. However, the increase of the anthropic CO<sub>2</sub> emission, since the beginning of the XX<sup>th</sup> century, is commonly accepted to depict an issue because it is responsible of a global climate change. In this context, the Kyoto protocol in 1997, followed more recently the COP21 in Paris in 2015, aims to reduce the emission of greenhouse gases including CO<sub>2</sub> in order to limit the temperature increase. It is important to note that the largest sources of CO<sub>2</sub> emissions worldwide are coming from the combustion of fossil fuels, e.g. in power plants.

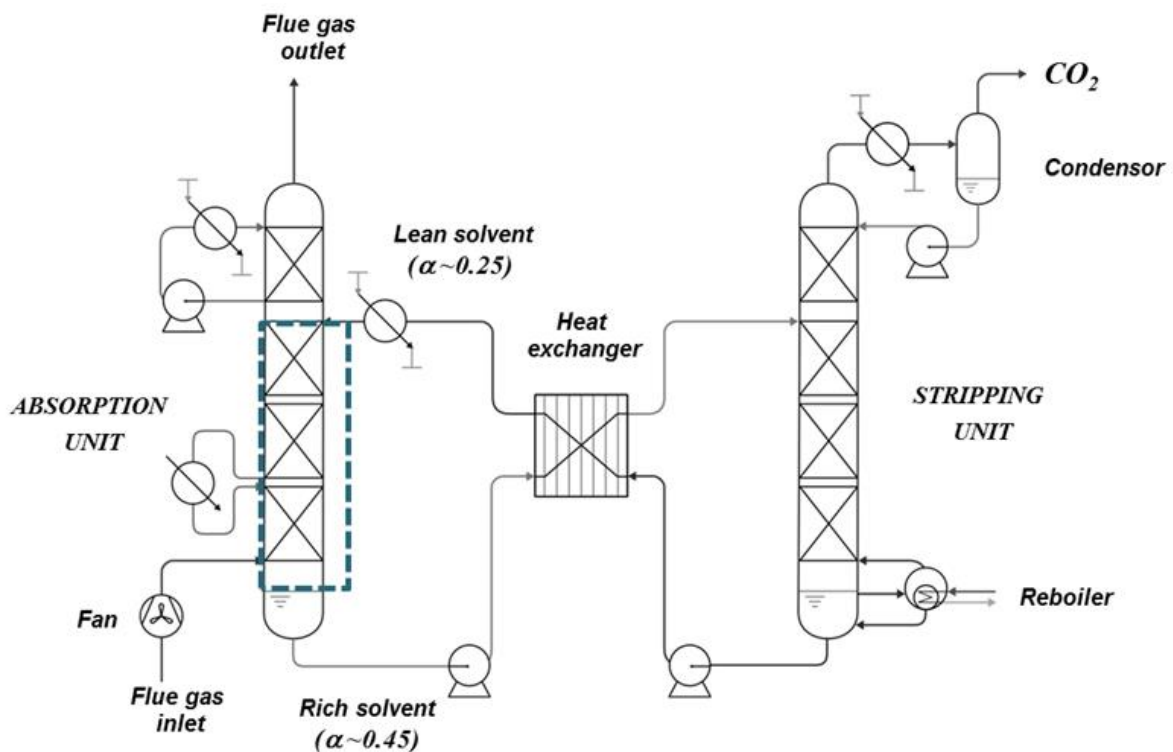
Several approaches are available to remove CO<sub>2</sub> from the flue gas:

- i. Post-combustion capture (PCC), i.e. after the combustion of the fossil fuels;
- ii. Pre-combustion capture, i.e. before the the combustion of the fossil fuels by replacing the fossil fuels with syngas;
- iii. Oxy-combustion capture, i.e. by using pure oxygen for combustion in order to produce a highly concentrated CO<sub>2</sub> flue gas.

Post-combustion capture is the approach allowing the best retrofit of the power plants already existing. But, CO<sub>2</sub> capture is quite challenging due to the properties of the flue gas: a low CO<sub>2</sub> volume fraction ranging ranging from 3 to 15%vol, a low gas pressure (around 1 bar) and the presence of some unwanted gas species (SO<sub>x</sub>, O<sub>2</sub>, H<sub>2</sub>O...). These properties reduce the current performances of the separation technologies and increase the costs [15].

A typical post-combustion capture unit is illustrated in Figure 2. The flue gas is flowing in an absorption unit where 90% of CO<sub>2</sub> is removed by chemical absorption in the liquid phase flowing counter-currently on the packed. The flue gas temperature should be around 45-50°C in order to minimize the loss of solvent due to evaporation

and maximize the CO<sub>2</sub> absorption rate [16]. The scrubbed gas is then generally washed with water and vented to the atmosphere; while the enriched solvent is then preheated in a heat exchanger by the lean solvent outgoing of the stripping unit before being pumped to the top of the desorber where it is regenerated. Carbon dioxide is thermally released in the stripping unit and dried. The CO<sub>2</sub> flux is highly pure (around 90%vol) and is ready to be compressed and stored [10]. The lean solvent is reused for a new absorption-desorption cycle, as explained in the introduction section.



**Figure 2: A typical post-combustion CO<sub>2</sub> capture unit based on gas-liquid absorption using monoethanolamine (MEA) as chemical solvent [10]**

Currently, amine-based solvents are considered for CO<sub>2</sub> capture because of their high reactivity with acid gases. Hence, the reference solvent is a 30%wt monoethanolamine (MEA) aqueous solution [10,17]; MEA has the highest reactivity ( $\Delta H_r = 84.4 \text{ kJ mol}^{-1}$ ) for CO<sub>2</sub>. In order to minimize the energy requirement of the stripping unit, the CO<sub>2</sub> concentration in the liquid phase also named the solvent loading, noted  $\alpha$  and expressed in mol CO<sub>2</sub>/mol MEA, is approximately 0.25 and 0.45 respectively at the inlet and the outlet of the liquid phase in the absorption unit [10,18,19]. However, the continuous use of the liquid phase induces solvent, i.e. MEA, degradations due to the secondary reactions occurring between oxygen or sulfur dioxide and MEA. The salts obtained are resistant to the operating conditions

of the stripping unit, so an important add of fresh MEA is required in order to limit the decrease of the process performances. The losses, due to chemical reaction but also to entrainment by steam in absorption and in stripping units, have been estimated to around 6.5 kg of MEA per ton of removed CO<sub>2</sub> [20], which represents about 10% of the capture cost [21]. Furthermore, some other products coming from MEA degradation are volatile and potentially dangerous [22]. These issues could be solved by using another liquid phase, but the reaction enthalpy should be equal or higher to 84.4 kJ mol<sup>-1</sup> in order to be interesting. Several studies are looking for new solvents.

A volumetric CO<sub>2</sub> absorption capacity of 1 mol m<sup>-3</sup> s<sup>-1</sup> is usually considered for post-combustion capture by using packed columns [18] having an interfacial area of 500 m<sup>2</sup> m<sup>-3</sup>, even if some better packings are commercially available (1000 m<sup>2</sup> m<sup>-3</sup>). However, the same issues are always reported whatever the packing selected; i.e. the packed columns are subjected to flooding, unloading, foaming or emulsion formation [23]. These issues can result from a change in the operating conditions such as the CO<sub>2</sub> volume fraction in the flue gas. Yet, the CO<sub>2</sub> volume fraction will directly depend on the power plant production which depends on the electricity consumption. Hence, the control of the absorption unit is scarcely easy.

Membrane contactors have received growing interest since 1985 and the first publications of Qi and Cussler about CO<sub>2</sub> gas-liquid absorption using membrane contactor [24,25]. Membrane contactors make use of a physical and non-selective barrier between the two phases. They are a non-dispersive contacting system providing a very high, known and constant interfacial area, up to 30 times higher than conventional packed columns [23]. The increase of the interfacial area offers several advantages: the increase of the mass transfer performance and thus the reduction of the absorber size by a factor which could be up to 10 [26,27]. Hence, the absorption unit is intensified [10]. By avoiding dispersion, membrane contactors allow avoiding unloading, flooding, foaming, channelling and entrainment which are issues of absorber columns. Moreover, the fact to have independent flows because of the physical separation due to the membrane also allows offering a high operational flexibility and modularity of the process to each modification of the flue gas composition and/or flowrate. Because of the high modularity, membrane contactor processes are expected to be easy to scale-up.



A large number of studies is available in the literature regarding CO<sub>2</sub> gas-liquid absorption using a membrane contactor; amongst them the work of Falk-Pedersen et al. [28] is noticeable. The authors reported results about CO<sub>2</sub> capture from a flue gas coming from a gas turbine on a offshore installation. The liquid phase is a 30%wt. MEA aqueous solution. The authors confirmed that the use of membrane contactors eliminated or at least significantly reduced the risk of foaming and corrosion (membrane contactors only use polymeric materials up to now). They also quantified few benefits:

- i. capital cost reduction of 35-40%
- ii. operating cost reduction of 38-42%
- iii. dry equipment weight reduction of 32-37%
- iv. operating equipment weight reduction of 34-40%
- v. total dry weight reduction of 44-47%
- vi. total operating weight reduction of 44-50%
- vii. footprint requirement reduction of 40-50%

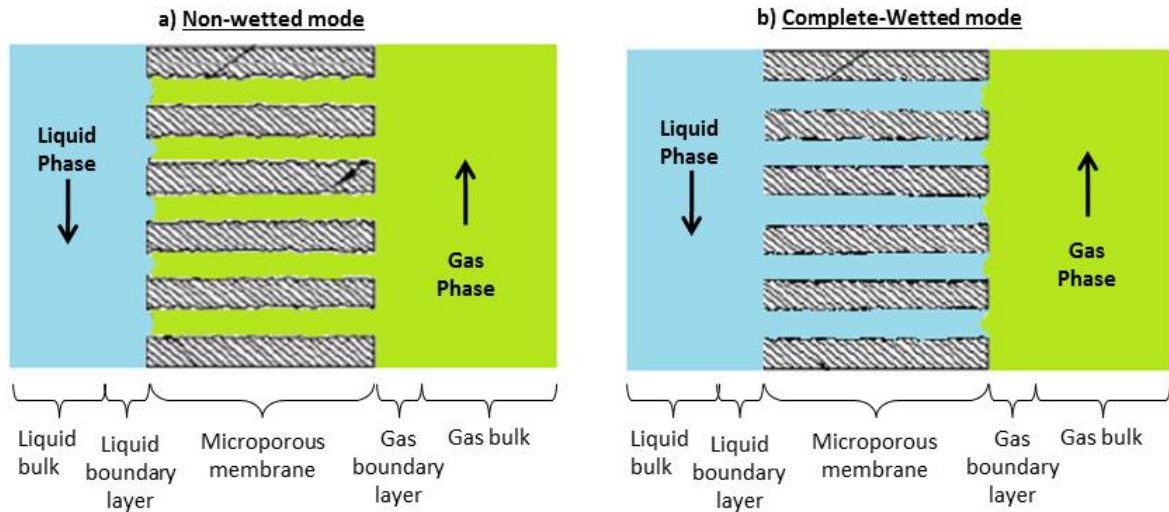
However, and these are the reasons why CO<sub>2</sub> gas-liquid absorption process using membrane contactors are not developed at industrial scales, membrane contactors by physically separating the two phases add a supplementary mass transfer resistance. Moreover, the polymer materials selected are sensitive to wetting, fouling and degradation which can significantly decrease the process performances and the process lifetime (see section Major challenges for membrane).

### **Mass transfer fundamentals**

In gas-liquid absorption processes using membrane contactors, the gas and the liquid phases are separated by a physical and non selective barrier, i.e. the membrane. The membrane can be microporous or dense but, in order to minimize the membrane mass transfer resistance, microporous membranes are generally used.

According to the membrane nature and the liquid phase, the membrane pores of the microporous material can be filled by the liquid phase, i.e. the membrane is in a wetted mode, or by the gas phase, i.e. the membrane is in a non-wetted mode, (cf. Figure 3). However, the non-wetted mode is generally preferred as the diffusion of a

species  $i$  in the gas phase is about 10 000 times higher than in the liquid phase. Thus hydrophobic polymer materials are recommended (see section Membrane materials and membrane structure) for gas-liquid absorption units using aqueous solution. The gas-liquid interface is then located at the membrane-liquid interface when non wetting conditions apply otherwise it takes place at the gas-membrane interface.



**Figure 3: Two operating mode of a microporous hollow fiber membrane contactor**

Phenomena ruling the mass transfer are classically referred to convection or diffusion, but the two mechanisms are often coupled.

In the case where the mass flux is strictly of diffusion type, Fick's law is applied (cf. Eq. (1)). It expresses that the diffusion flux in steady state is proportional to the concentration gradient (driving force).

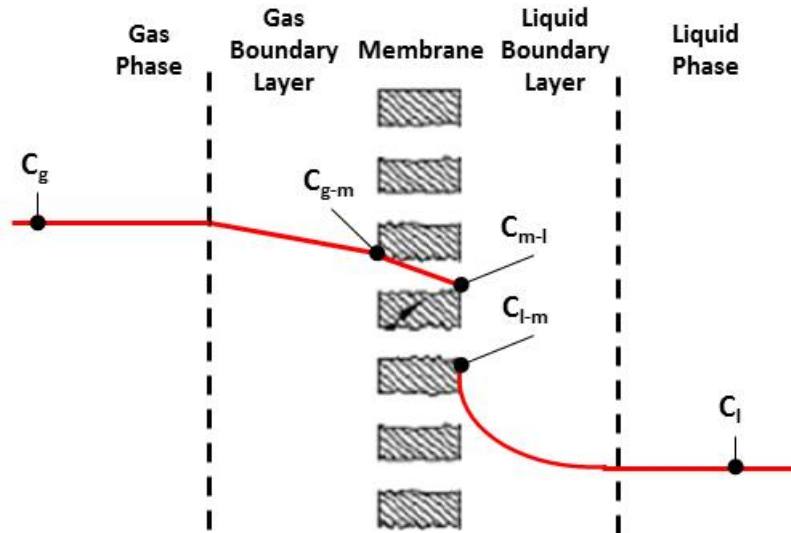
$$J = -D \frac{\partial C}{\partial r} = k \Delta C \quad (1)$$

Where  $J$  is the molar flux ( $\text{mol m}^{-2} \text{s}^{-1}$ ),  $D$  is the diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ ),  $C$  is the concentration of the diffusing species ( $\text{mol m}^{-3}$ ),  $r$  is the spatial coordinate (m), which corresponds to the radial axis for a cylindrical (i.e. hollow fiber) geometry and  $k$  is the mass transfer coefficient ( $\text{m s}^{-1}$ ).

Considering that the liquid phase is flowing in the shell side of the membrane contactor, the mass transfer of  $i$  from the gas phase into the liquid phase includes three consecutive steps (cf. Figure 4):

1. Diffusion of  $i$  from the gas bulk to the gas-membrane interface (gas side);

2. Diffusion of  $i$  from the gas-membrane interface to the liquid-membrane interface, through the membrane pores;
3. Dissolution of  $i$  into the liquid phase and diffusion to the liquid bulk, which can be associated to a chemical reaction, i.e. chemical absorption, or not, i.e. physical absorption (see Introduction).



**Figure 4: Mass transfer mechanism through a porous membrane**

Thus, the resistance in serie approach is commonly used and the solute flux density  $i$ ,  $N$  ( $\text{mol s}^{-1}$ ), for the three regions can be expressed by:

$$N = S_{lum}k_g(C_g - C_{g-m}) = S_{ml}k_m(C_{g-m} - C_{l-m}) = S_{sh}E k_l(C_{l-m} - C_l) = S_{sh}E K (C_g - C_l) \quad (2)$$

Where  $k_g$ ,  $k_m$  and  $k_l$  are the local mass transfer coefficients respectively in the gas phase, in the membrane and in the liquid phase ( $\text{m s}^{-1}$ ).  $C_g$ ,  $C_{g-m}$ ,  $C_{m-l}$ ,  $C_{l-m}$  and  $C_l$  are the concentration of  $i$  respectively in the gas bulk, at the gas-membrane interface, at the membrane-liquid interface (membrane side), at the liquid-membrane interface (liquid side) and in the liquid bulk ( $\text{mol m}^{-3}$ ). For cylindrical geometry,  $S_{lum}$ ,  $S_{ml}$  and  $S_{sh}$  are respectively the lumen, the logarithmic mean and the shell membrane surfaces ( $\text{m}^2$ ); while for a flat system  $S_{lum}$ ,  $S_{sh}$  and  $S_{ml}$  are equivalent and correspond to the planar surface of the membrane ( $\text{m}^2$ ).  $E$  is the local enhancement factor (-). If the species  $i$  is physically absorbed, then  $E=1$ ; but, if a chemical reaction occurs between  $i$  and at least one component of the liquid phase, i.e. chemical absorption, then  $E>1$ . The increased solute absorption rate provided by the chemical reaction is thus explicitly obtained.

The membrane pores are ideally filled by the gas phase. This reference configuration allows minimizing the mass transfer resistance of the membrane. Hence, there is no concentration discontinuity between the gas-membrane interface and the gas concentration inside the membrane pores.

The thermodynamic equilibrium, expressed by the Henry's law, is assumed to be reached at the membrane liquid interface:

$$C_{g-m} = \frac{1}{m} C_{l-m} \quad (3)$$

With  $m$  the partition coefficient (-) defined by:

$$m = \frac{RT}{H_i} \quad (4)$$

Where  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature (K) and  $H_i$  is the Henry's law constant of  $i$  in the liquid phase ( $\text{Pa m}^3 \text{ mol}^{-1}$ ).

Based on equations (2) and (3), and according to the resistance-in-series approach, the global mass transfer resistance ( $1/K$ ) in hollow fiber membrane contactor can be expressed from the local mass transfer resistances:

$$\frac{1}{K} = \frac{d_o}{d_i} \frac{1}{k_g} + \frac{d_o}{d_{ml}} \frac{1}{k_m} + \frac{H_i}{RT E} \frac{1}{k_l} \quad (5)$$

Where  $d_o$ ,  $d_i$  and  $d_{ml}$  are respectively the outer, the inner and the logarithmic mean diameters of the hollow fibers (m). For a flat geometry, Eq. (5) becomes:

$$\frac{1}{K} = \frac{1}{k_g} + \frac{1}{k_m} + \frac{H_i}{RT E} \frac{1}{k_l} \quad (6)$$

Theoretically, it is possible to estimate the local mass transfer coefficient based on correlations. For  $k_g$ , and  $k_l$ , expressions based on the Sherwood number have been reported in the literature [23,29]:

$$k_g = Sh_g \frac{D_g}{d_i} \quad (7)$$

$$k_l = Sh_l \frac{D_l}{d_h} \quad (8)$$

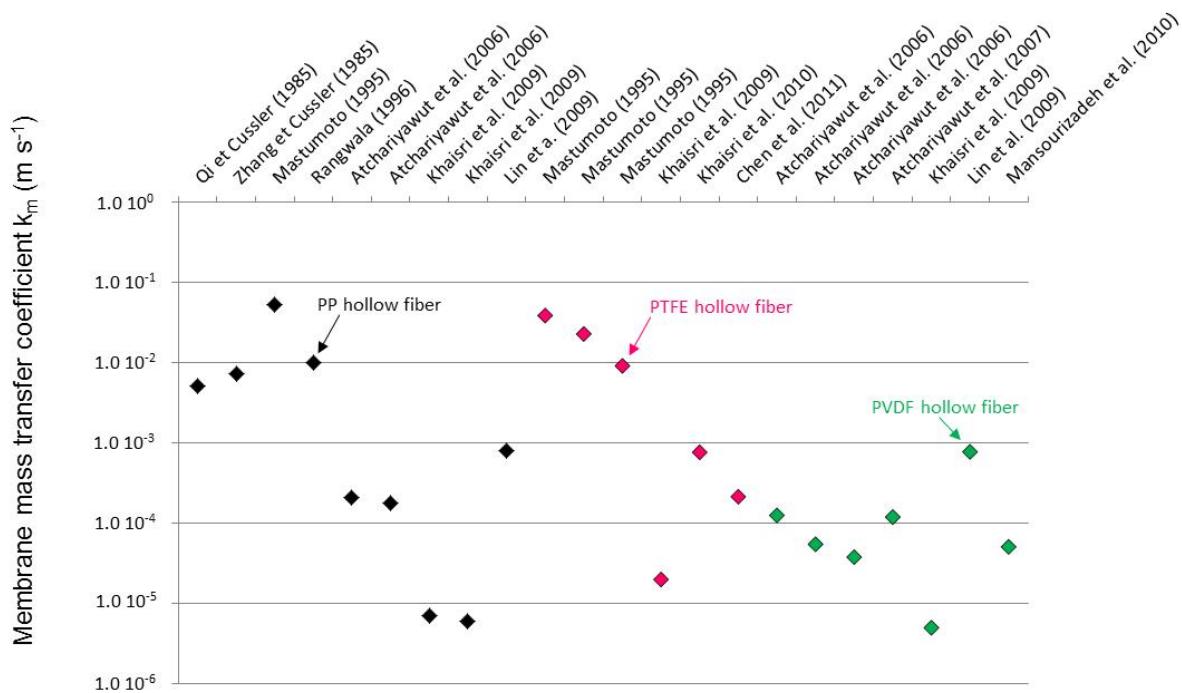
Where  $Sh_g$  and  $Sh_l$  are the Sherwood number respectively in the gas phase and in the liquid phase (-),  $D_g$  and  $D_l$  are the diffusion coefficient of  $i$  respectively in the gas and in the liquid phase ( $\text{m}^2 \text{ s}^{-1}$ ) and  $d_h$  is the hydraulic diameter (m).

Generally, the membrane mass transfer coefficient is supposed to be constant and can be calculated, for a microporous membrane, by:

$$k_m = \frac{\varepsilon D_m}{\tau \delta} \quad (9)$$

With  $D_m$  the diffusion coefficient of  $i$  in the membrane ( $m^2 s^{-1}$ ),  $\varepsilon$  is the membrane porosity (-),  $\tau$  is the membrane tortuosity (-) and  $\delta$  is the membrane thickness (m).

According to Eq. (9), the membrane mass transfer is governed by the material structure and by the gas diffusion mechanism that takes place inside [30]. However, it has to be noted that the estimation of the membrane mass transfer coefficient is usually very difficult to achieve due to the impossibility to exactly know the properties of the porous network. In fact, membrane porosity can range from 20 to 90% while the tortuosity is generally included between 2 and 3 [23]. Hence, the membrane mass transfer coefficient is very difficult to determine and several orders of magnitude of the  $k_m$  value are reported in the literature (cf. Figure 5) depending on membrane type (polymer, pore size and distribution, porous material production process...).



**Figure 5: Membrane mass transfer coefficient reported in the literature for CO<sub>2</sub> capture using membrane contactor [31]**

Considering an aqueous solution of j in which the gas species is dissolved, the local enhancement factor (E), due to the reaction occurring in the liquid phase between i and j, can be determined by the Hatta number (Ha) and the infinite enhancement factor ( $E_{\infty}$ ):

$$Ha = \frac{\sqrt{\frac{2}{p+1} D_l \text{kr} C_i^p C_{j,l}^q}}{k_l} \quad (10)$$

$$E_{\infty} = \left(\frac{D_l}{D_j}\right)^{1/3} + \frac{C_{j,l}}{2C_{l-m}} \left(\frac{D_l}{D_j}\right)^{-2/3} \quad (11)$$

Where Ha is the Hatta number (-),  $D_j$  is the diffusion coefficient of j in the liquid phase ( $\text{m}^2 \text{s}^{-1}$ ), p and q are respectively the reaction order of i and j (-), kr is the kinetic constant (units are function of the reaction order, e.g. 1<sup>st</sup> order  $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ ),  $C_{j,l}$  is the j concentration in the liquid phase ( $\text{mol m}^{-3}$ ),  $E_{\infty}$  is the infinite enhancement factor (-).

Regarding the case of  $\text{CO}_2$  capture by an aqueous solution of monoethanolamine (MEA), Eq. (10) and (11) become [32,33]:

$$Ha = \frac{\sqrt{D_l \text{kr} C_{\text{MEA},l}}}{k_l} \quad (12)$$

$$E_{\infty} = \left(\frac{D_l}{D_{\text{MEA}}}\right)^{1/3} + \frac{C_{\text{MEA},l}}{2C_{l-m}} \left(\frac{D_l}{D_{\text{MEA}}}\right)^{-2/3} \quad (13)$$

Where  $C_{\text{MEA},l}$  is the MEA concentration in the liquid bulk ( $\text{mol m}^{-3}$ ) and  $D_{\text{MEA}}$  is the MEA diffusion coefficient in the liquid phase ( $\text{m}^2 \text{s}^{-1}$ ).

However, according to the reaction regime, the expression of the enhancement factor can be simplified as follows [34]:

- The j diffusion is not the limiting step:

$$\frac{E_{\infty}}{Ha} > 50, \text{ then} \quad E = \sqrt{1 + Ha^2} \approx Ha \quad (14)$$

- The j diffusion is the limiting step:

$$\frac{E_{\infty}}{Ha} < 0.02, \text{ then} \quad E = E_{\infty} \quad (15)$$

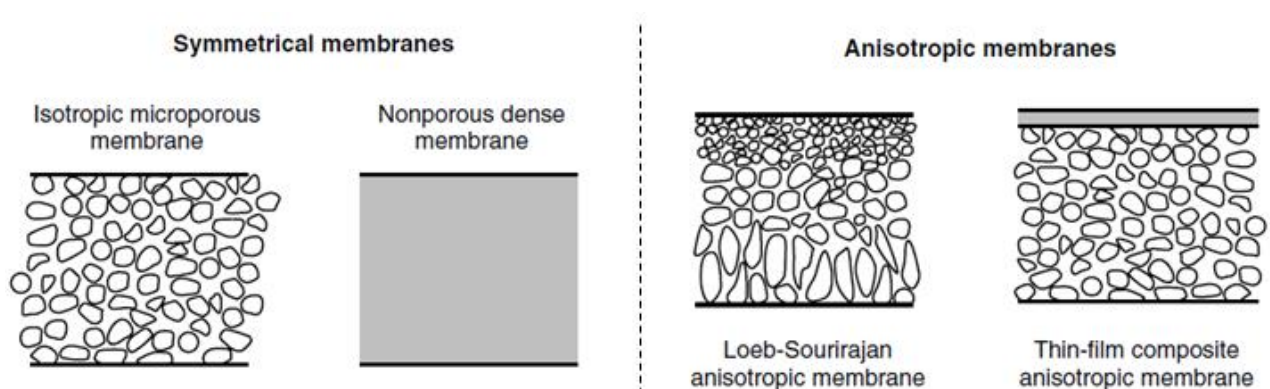
- The j diffusion is a partial limiting step:

$$0.02 \leq \frac{E_{\infty}}{Ha} \leq 50, \text{ then} \quad E = \frac{Ha \sqrt{\frac{E_{\infty}-E}{E_{\infty}+1}}}{\tanh\left(Ha \sqrt{\frac{E_{\infty}-E}{E_{\infty}+1}}\right)} \quad (16)$$

## MEMBRANE MATERIALS AND MEMBRANE STRUCTURE

Regarding the field of application referred, i.e. gas-liquid absorption, polymer materials are usually used to make membrane contactors up, as less expensive. Different membranes morphologies are available, and can be divided into two groups (cf. Figure 6):

- Symmetric, also named isotropic, membranes:
  - Microporous membranes made of only one polymer material.
  - Homogeneous dense membranes
- Asymmetric, i.e. anisotropic, membranes :
  - Homogeneous asymmetric membranes are made of only one porous polymer material, but the porosity is varying with the membrane thickness. The membrane is divided into two sections: the skin, which is the thinner part of the material, and the mechanical support. The porosity of the dense part is much lower than the porosity of the support section.
  - Composites membranes are made of at least two different materials. A macroporous section, ensuring the mechanical support, is coated by a dense layer from a different polymer material. Generally speaking, in gas-liquid absorption process using membrane contactor, the polymer selected for the dense skin is highly permeable in order to minimize the mass transfer resistance of the membrane because the process selectivity is due to the liquid phase.



**Figure 6: Schematic diagram of the main membranes morphologies [35]**

The choice of the polymer material is a key issue of the unit operation as it is straight responsible of the process lifetime. Hence, the selection of a polymeric material is preliminary driven by the necessity to achieve a high chemical (any reaction of the liquid and/or the gas phases with the polymer material), thermal and mechanical stability.

Then, the polymer material is also selected according to:

- Its permeability: i.e. its ability to be permeated by a gaseous species. This property is considered only for dense membranes or composite membranes having a dense skin. The permeability is defined for a pair polymer material-crossed species.
- Its wetting resistance: i.e. its ability to avoid the entering, even partially, of the liquid phase inside the membrane pores (see membrane wetting subsection).

### **Hydrophobic microporous material**

As defined by Baker [35], a microporous membrane has “a rigid, highly voided structure with randomly distributed, interconnected pores”. Hence, Baker [35] highlights that microporous membranes are closed in structure but also in function to a conventional filter, the main difference coming from the pores diameter which are extremely small compared to those of a filter, on the order of 0.01 to 10 $\mu$ m [35]. Hence, according to the pore diameters and the particles size, three scenarios are worth considering [35]:

- i. If the particles are larger than the largest pores, then they are completely rejected by the membrane;
- ii. If the particles are smaller than the smallest pores, then they passed through the membrane;
- iii. If particles are smaller than the largest pore but larger than the smallest pores are partially rejected according to the pore size distribution of the membrane.

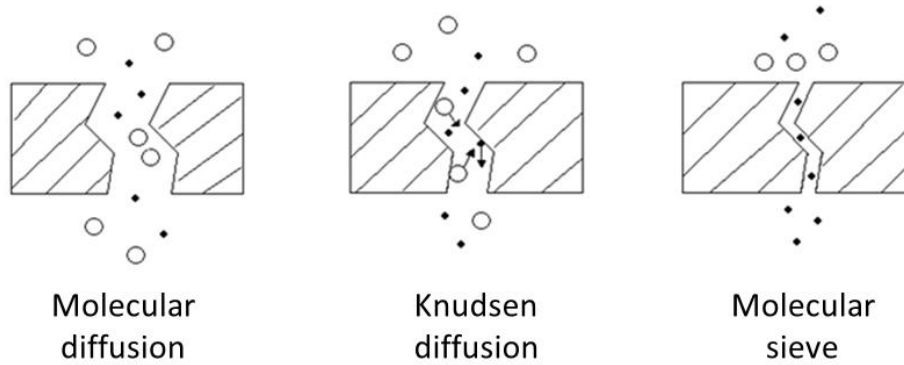
The gas transport through the microporous membrane can be described according to a diffusion mechanism in the porous network. In fact, the low gas pressure allows neglecting the convective mechanism of Poiseuille type. The nature of the gas flow, i.e. the nature of the diffusion mechanism, depends on the pore size (cf. Figure 7). The flow regime is defined by comparing the mean free path ( $\lambda$  in m), which



corresponds to the mean distance crossed between two collisions, to the pore radius,  $r_p$  (m) and defined by:

$$\lambda = \frac{k_B T}{\pi d_g^2 P \sqrt{2}} \quad (17)$$

Where  $k_B$  is Boltzmann constant ( $1.381 \cdot 10^{-23} \text{J K}^{-1}$ ),  $d_g$  is the diameter of the gas molecule of the species  $i$  flowing inside the pores (m),  $P$  is the pressure (Pa).



**Figure 7: Gas transport through the membrane pores**

If  $r_p$  is much higher than  $\lambda$ , then the gas molecules will preferentially collide to each other. The gas transport occurs according to a molecular diffusion mechanism and the separation is not selective. In the opposite case, i.e.  $r_p$  is lower or equal to  $\lambda$ , the collisions between the gas molecules and the wall of the membrane pores are dominating, the separation occurs then according to a Knudsen diffusion mechanism defined by:

$$D_k = \frac{2 r_p}{3} \sqrt{\frac{8 R T}{M_i}} \quad (18)$$

Where  $D_k$  is the Knudsen diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ ) and  $M_i$  is the molecular weight of the gas molecule  $i$  ( $\text{g mol}^{-1}$ ).

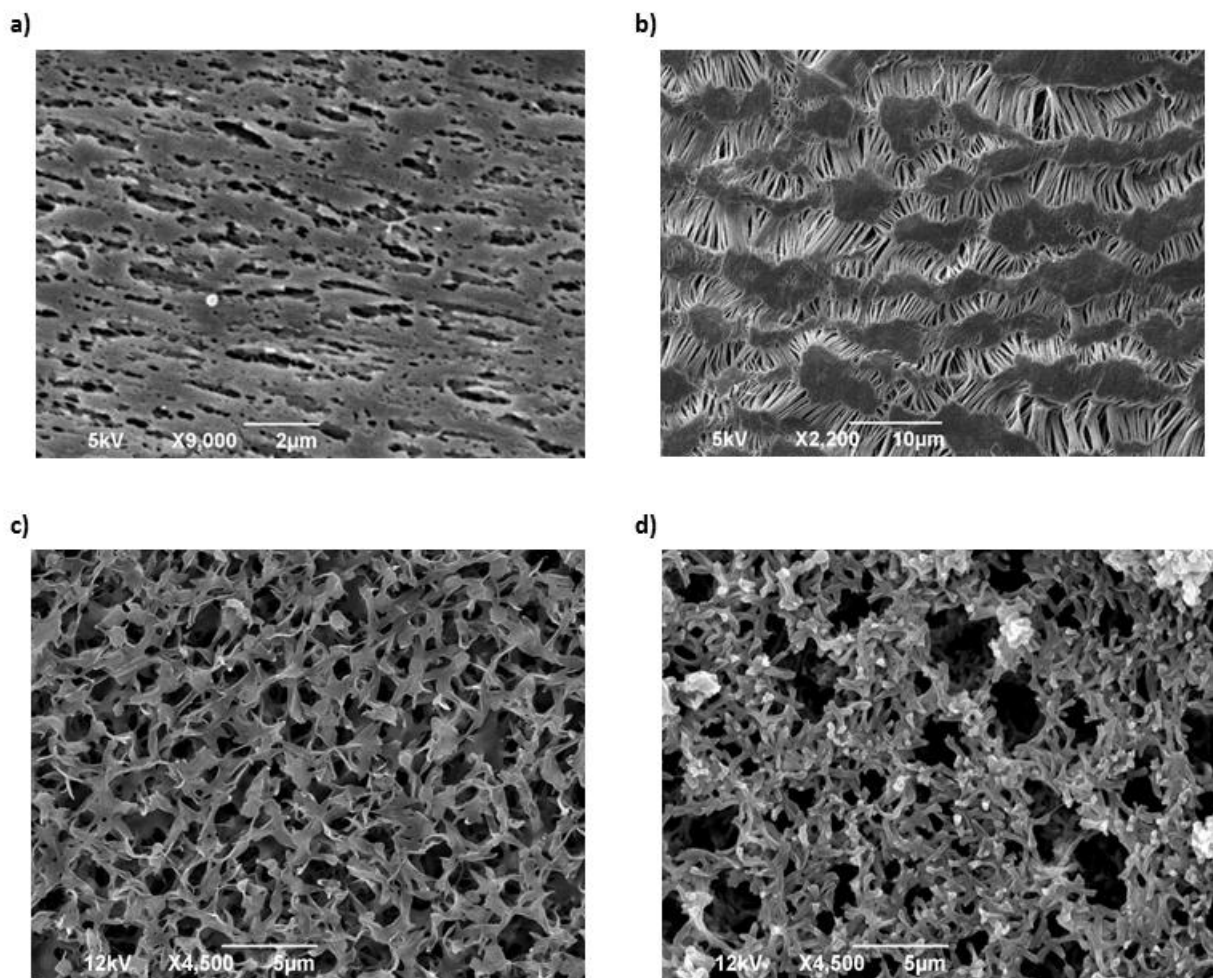
Hence, in order to be thorough, the membrane diffusion coefficient must consider both contributions, i.e. the molecular diffusion mechanism (close to the gas diffusion in the gas bulk) and the Knudsen diffusion mechanism, according to:

$$\frac{1}{D_m} = \frac{1}{D_{\text{micro}}} + \frac{1}{D_k} \quad (19)$$

Finally, molecular sieving may also occur when the pore size is comparable to the molecular dimension, i.e. 3-5 Å. The smallest molecule can flow through the

membrane while the larger are retained. This mechanism generally occurs in dense membrane and will not be more detailed.

Several hydrophobic microporous polymer materials are commercially available as membrane contactors but only three of them are regularly used: polypropylene (PP) [29,36–41], polyvinylidene fluoride (PVDF) [29,40–46] and polytetrafluoroethylene (PTFE) [36,39,41,47,48]. Figure 8 shows typical structures of microporous polymeric membrane used for membrane contactor applications.



**Figure 8: Examples of microporous membrane materials used for membrane contactors applications: a) PP b) PTFE c) PVDF d) Nylon[10]**

The performances of these three polymers have been compared amongst others by Khaisri et al. [41] who highlighted that the more hydrophobic polymer material allowed achieving the highest absorption rate. Hence, in water, the authors compared PVDF and PP showing that the best performance are obtained with PVDF; while in chemical absorption, with a MEA aqueous solution, the comparison of PVDF and PTFE to PP showed that the performances ranked as PTFE>PVDF>PP. It has to

be noted that amongst all the microporous polymer material available, PTFE is the polymer showing the higher long-term stability compared to other hydrophobic microporous polymer materials [36,39,49] (see section Major challenges for membrane). The performances differences can be explained by the wetting resistance, i.e. the ability of the polymer material to resist to the entering of the liquid phase in the membrane pores, but also by the chemical stability of the polymer. Indeed, Barbe et al. [50] and Wang et al. [51] reported some changes in the membrane structure due to a swelling or to a chemical reaction between the polymer and the liquid phase.

### **Composite membrane with a dense skin layer**

As reported above, a composite membrane is an assymetric membrane exhibiting a thin dense layer (typically less than 1 $\mu$ m), that may provide in some cases a selectivity amongst the gas species, on the top of a highly porous sub-layer. The porous substructure supplies the necessary mechanical properties and offers the advantage of a low resistance to the mass transport through the membrane. Both the skin layer and the porous sub-structure and porous support are manufactured from two differents materials. The opposite situation, i.e. same material for the dense skin layer and the porous sub-structure, characterizes homogeneous asymmetric membranes.

These different types of membranes have been developed further to the recurring observation of the wetting by the liquid phase of the membrane pores of severals hydrophobic polymer materials [36]. The idea was initially proposed and validated by Kreulen et al.[52]. They reported in this study that their membrane contactors, made of a microporous membrane covered by a thin silicone rubber layer (0.7 $\mu$ m) at the inside of the fibers, allowed achieving similar performances regarding the absorption rate than the uncoated membranes.

However, to be interesting, the dense skin of composite membranes should:

- be as thinner as possible in order to minimize the mass transfer resistance.
- be as permeable as possible to minimize the mass transfer but also because in a gas-liquid absorption process, the selectivity is connected to the affinity of the liquid phase for the absorbed gaseous component.

- have high thermal and chemical stabilities, as microporous polymer materials.

Hence, the most studied membrane materials for the skin layer are polydimethylsiloxane (PDMS) and poly(1-trimethylsilyl)-1-propyne (PTMSP). The first one is a rubbery polymer ( $T_g = -125^\circ\text{C}$ ) while the second is a glassy polymer ( $T_g \geq 250^\circ\text{C}$ ) [53–55]. However few other polymer materials have been explored as dense skin layer on a porous polymer material in membrane contactors: ethylene propylene terpolymer, butadiene rubber, styrene butadiene and Teflon AF 2400 [53,56]. The use of composite membrane having a thin dense skin layer has confirmed the new opportunities for achieving membrane contactors able to offer a high wetting resistance over long time scales [36].

Some studies are also available in the literature about the use of dense membranes, i.e. non-porous membranes, in the place of microporous membranes in order to avoid the wetting phenomena. However, Scholes et al. [57] observed that the dense PDMS membrane had an overall mass transfer resistance which was two or three orders of magnitude higher than, respectively, PP and PTFE membranes. Their observations highlighted that the composite membrane with a dense layer is one of the best alternative to microporous membrane for gas-liquid absorption.

In the dense skin of a composite membrane, the phenomena governing mass transport are the same than in a dense membrane. As defined by Strathmann [58], the transport of a gas component is determined by two terms: its mobility and its concentration in the membrane matrix. Its mobility, i.e. its ability to diffuse in membrane material, is inversely proportional to its size while its concentration is directly proportional to its solubility in the membrane material. The combination of these two terms allows defining the permeability according to the solution diffusion model:

$$\phi = D.S \quad (20)$$

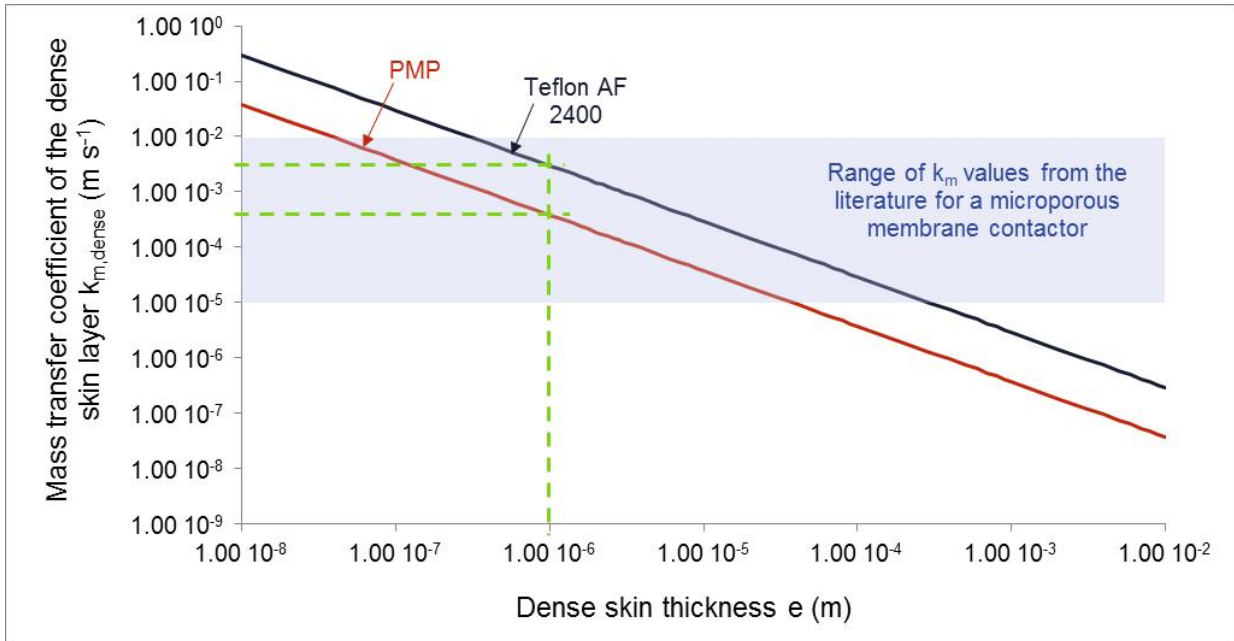
Where  $\phi$  is the permeability ( $\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ ) but commonly expressed in Barrer,  $D$  is the diffusion coefficient of the gas component in the dense skin ( $\text{m}^2 \text{s}^{-1}$ ) and  $S$  is the solubility ( $\text{mol m}^{-3} \text{Pa}^{-1}$ ).

So, the use of a composite membrane induces the addition of a supplementary and non negligible resistance to mass transfer due to the dense skin layer. Hence, the

membrane mass transfer coefficient in a composite membrane has to consider both contribution such as:

$$\frac{1}{k_m} = \frac{1}{k_{m,\text{porous}}} + \frac{1}{k_{m,\text{dens}}} = \frac{\delta\tau}{\varepsilon D_m} + \frac{e}{\phi RT} \quad (21)$$

Where  $e$  is the dense skin thickness (m). For more information about gas transport in dense membrane, the reader is invited to refer to the chapter entitled **Polymeric Membranes for Gas Separation**.



**Figure 9: Mass transfer coefficient of the dense skin layer as a function of the skin thickness ( $\phi_{PMP} = 500$  barrer and  $\phi_{Teflon\ AF\ 2400} = 3500$  barrer)[10]**

Figure 9 shows the evolution of the dense skin mass transfer coefficient as a function of the skin layer. The results highlight that the mass transfer resistance of the dense permeable layer can be neglected, compared to the non-wetted porous support, when a thin enough skin is used (typically  $0.1\ \mu\text{m}$ ). Thinner dense layer membranes are currently produced for gas separation applications for instance [53]. The objective of a very low mass transfer resistance generated by a dense polymeric layer is thus non systematic but realistic for membrane contactor applications and will be detailed afterwards.

## Nanoparticle incorporation

According to what has been stated above, microporous membranes offer lower membrane mass transfer resistance than dense composite membrane but are more

sensitive to wetting issue. In order to improve the membrane hydrophobicity and keeping the lowest mass transfer resistance as possible, new polymer materials are developed. Hence, the incorporation of fluorinated SiO<sub>2</sub> nanoparticles in polyetherimide polymer having a high porosity before performing a surface treatment was reported by Wang et Zhang in order to improve the polymer hydrophobicity [59,60]. Their results confirmed an increase of the hydrophobicity and a higher absorption flux, i.e. a lower membrane mass transfer resistance, and a long-term stability over 30 days [59] and 60 days [60]. Mixed matrix membranes (MMMs) are also reported [61,62]. In MMMs, clay particles, e.g. general montmorillonite or cloisite 15A, are incorporated in a porous polymer material such as PVDF still in order to improve the wetting resistance of the polymer material and increase the CO<sub>2</sub> absorption rates. Nevertheless, these membranes are not yet commercially available and their development remains at the investigation state so far.

### **Surface modification**

In order to improve the polymer material performance regarding its wetting resistance, its long term stability and its mass transfer coefficient, it is also possible to modify the membrane surface. Several techniques are investigated including non-solvent assisted deposition [63,64], plasma modification [38,65,66], ultraviolet photografting [67] or sol-gel coating [68].

These techniques are generally applied to microporous polypropylene material. Indeed, PP is the commercially most widespread polymer in the literature because of its low cost, availability, well-controlled pore size and porosity but also its relatively high thermal and chemical stabilities.

Hence, Lin et al. [38] used CF<sub>4</sub> plasma to modify PP hollow fibers. Their results highlighted that the absorption flux, the membrane lifetime and its mass transfer coefficient was significantly improved.

Franco et al. [65,66] covered PP hollow fiber with an ultrathin layer of PTFE by using plasma technique in order to obtain a composite membrane. PTFE is a higher hydrophobic and much expensive polymer than PP. The authors achieved to improve the absorption rate and to enhance the membrane resistance to wetting and chemical degradation. But the performances were not maintained on more than 45h.

Instead, Lv et al. [63] covered PP microporous membrane with a dense skin of PP by using cyclohexanone and methylethylketone (MEK) as non-solvent. By this method, the authors obtained a superhydrophobic polymer with a contact angle up to 158° and were able to maintain the process performances over 20 days.

More recently, Yu et al. [69] reported results about a superhydrophobic ceramic membrane with a modified surface and offering a water contact angle up to 153°, a high resistance to wetting and to fouling. Lin et al. [68] used sol-gel coating method to produce hydrophobic polymethylsilsesquioxane (PMSQ) aerogel membranes onto an Al<sub>2</sub>O<sub>3</sub> membrane support. The membranes obtained exhibit a good lifetime and are reusable.

It has to be noted that, at the industrial scale, membrane contactors are expected to be used preferably for years for gas-liquid absorption processes. So the stability of the membrane over long-time scale, in terms of performances but also thermal and chemical resistances, is of crucial interest.

## MODULE DESIGN

In mass transfer as in heat transfer exchangers, one of the most important parameter is the interfacial area ( $a$  in  $\text{m}^2 \text{m}^{-3}$ ), also named packing density, which corresponds to the surface exchange reported to the volume module. In both cases, the membrane should provide a sufficient and an efficient gas-liquid interface without allowing a convective flow through the membrane material. Hence, the membrane module design plays a key role on the process performances. The membrane can be manufactured as: flat sheet, tubes or capillaries and hollow fibers. However, the most suitable geometry for a membrane in a given separation process depends on the application and is determined by the technical performance as well as by manufacturing cost [58] (cf. Table 3).

**Table 3: Module design characteristics [30,35,58]**

	Flat sheet membranes	Spiral-wound membranes	Hollow fiber membranes	Capillary membranes	Tubular membranes
<b>Diameter (mm)</b>			0.05 – 0.5	0.25 – 2	5 – 25
<b>Packing Density (<math>\text{m}^2 \text{m}^{-3}</math>)</b>	100 – 400	300 – 1 000	$\leq 30\ 000$	600 – 1 200	< 300
<b>Concentration polarization fouling control</b>	Good	Moderate	Poor	Good	Very Good
<b>Pressure drop</b>	Low	Moderate	High	Moderate	Low
<b>Membrane substitution</b>	Flat membrane	Spiral wound module	Membrane module	Membrane module	Tubular membrane
<b>Manufacturing cost (US\$/<math>\text{m}^2</math>)</b>	50 – 200	5 – 100	5 – 20	10 – 50	50 – 200
<b>Material availability</b>	Large	Large	Limited	Limited	Limited

### Longitudinal flow module

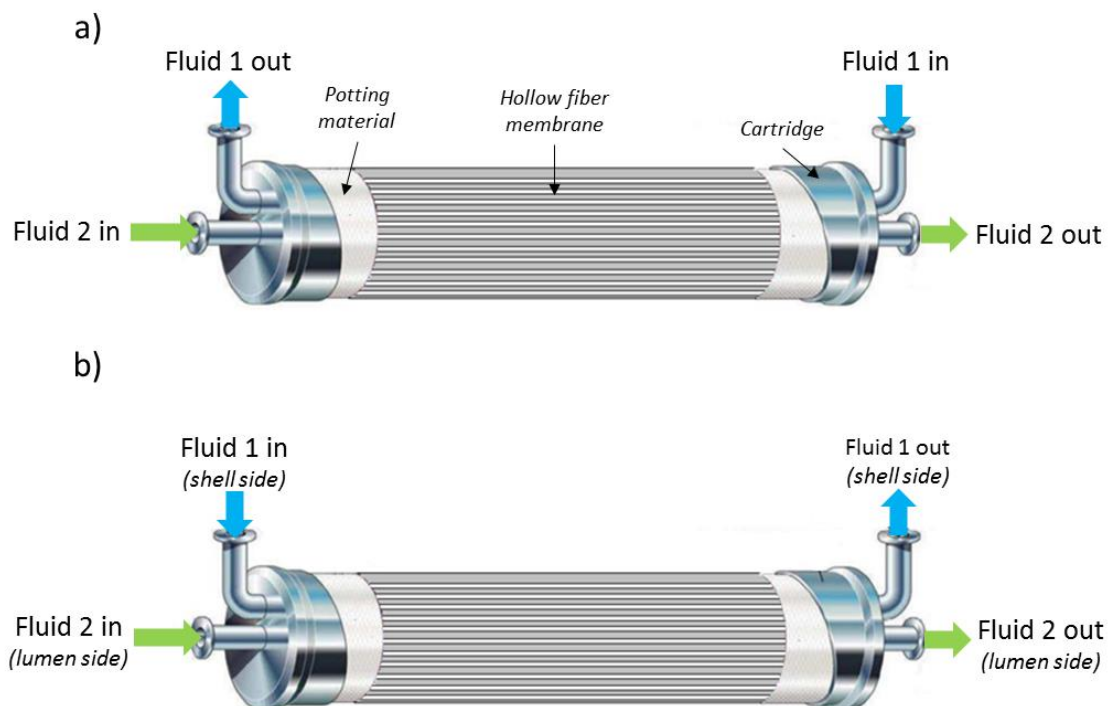
Longitudinal flow, or parallel flow, corresponds to membrane modules where both fluids are flowing parallel to each other on the opposite sides of the membrane. Fluid flows can be co-currently, i.e. in the same direction, or counter-currently, i.e. in



opposite direction (cf. Figure 10). This configuration corresponds to a membrane contactor containing hollow fiber membranes, tubular membranes or capillary membranes. Longitudinal flow modules develop the highest interfacial area among the different membrane types, which allows decreasing significantly the volume of the unit operation.

Both configurations have been studied in the last decades, but deMontigny et al. [39] highlighted that the counter-current mode achieved an increase of the mass transfer rate, on average, 20% higher to the mass transfer rate in co-current mode. Moreover, the authors [39] also showed that flowing the liquid phase in the lumen side of the membrane contactor allows improving the mass transfer. But, the pumping cost of the liquid phase in the lumen side becomes expensive when the hollow fibers have a small diameter, in the range of a few hundred microns.

However, Mansourizadeh and Ismail [42] underlined that, in most of the hollow fiber membrane contactors, the fibers are packed randomly which leads to non-uniform fiber distribution. Consequently, severe fluid channeling and/or by-passing may exist which will be responsible of a much lower mass transfer and may increase the pressure drop.

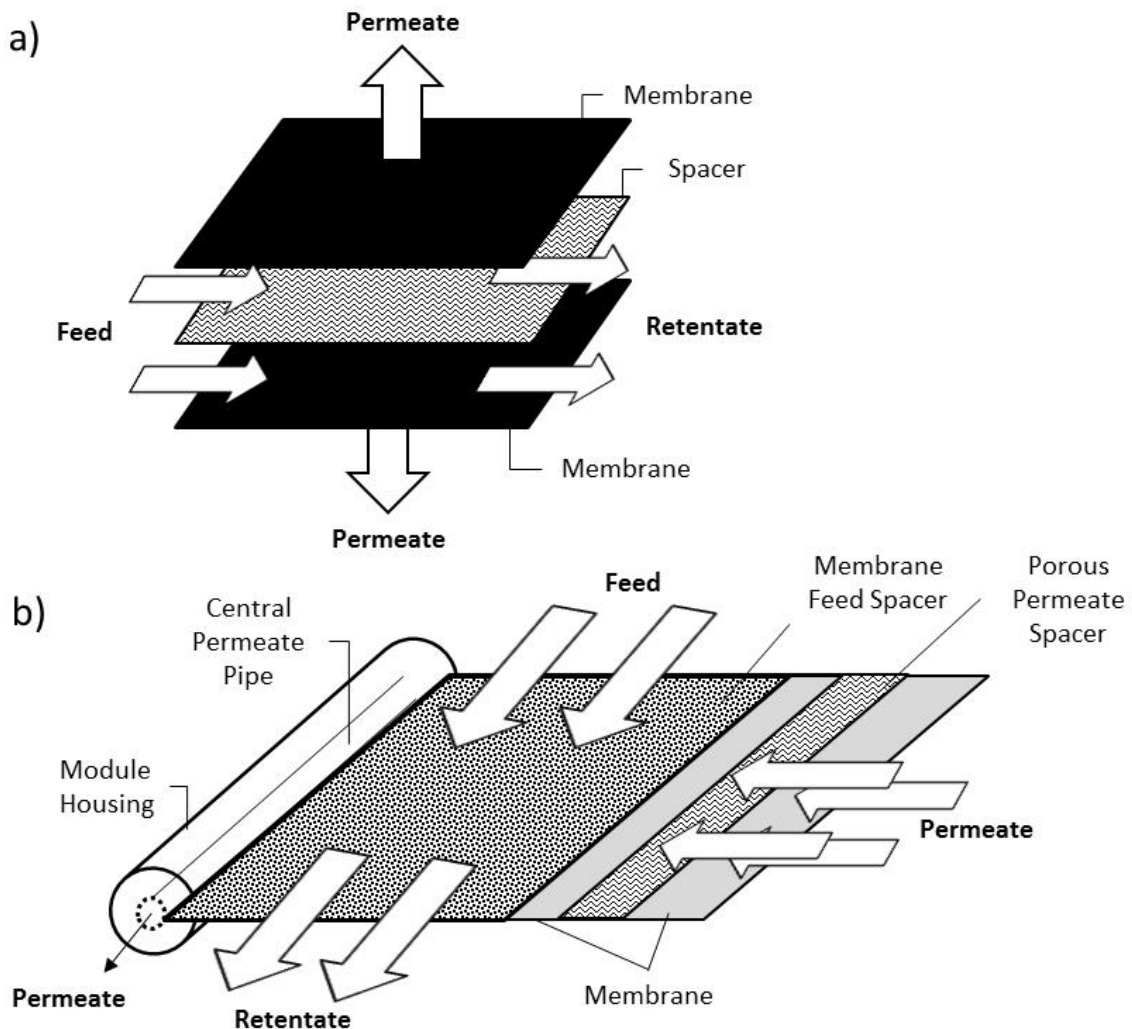


**Figure 10: Longitudinal flow module: a) counter-current flow; b) co-current flow**

It has to be noted that longitudinal flow modules are quite simple to manufacture, the fluid dynamics are well known on both sides, and the mass transfer easy to estimate [42].

### Cross flow module

As opposite to longitudinal flow modules, cross flow modules correspond to a contact mode where the permeate flows perpendicularly to the feed and the retentate flows. Two configurations are commercially available: flat sheet membrane modules (similar to plate cooler) or spiral-wound membrane modules (cf. Figure 11). In both cases, membranes are separated by spacers, the ensemble is then wound in a cartridge.



**Figure 11: Cross flow module: a) flat sheet module; b) spiral-wound module [30]**

Wickramasinghe et al. [70] compared several membrane contactors geometries and among them a longitudinal module, made of hollow fiber, and a cross flow module.

The membranes module performances have been compared at equal flow per membrane area and/or at equal flow per membrane volume for a model system (water/air). Their results, reported at equal flow per membrane area, highlighted that, in some cases, the counter-current cross flow membrane module was the most efficient.

## MAJOR CHALLENGES FOR MEMBRANE

The choice of the polymer material of a membrane contactor is of key importance as it plays a direct role on the process lifetime. Hence, whatever the application area, the polymer material selected should have the following properties:

- Good thermal resistance to degradation at elevated temperature;
- Excellent chemical stability to the absorbent;
- Low wetting tendency;
- High porosity to minimize the mass transfer resistance.

All these properties are required to face the main challenges of membrane contactors discussed below, which are membrane wetting, membrane fouling and membrane degradation.

### Membrane wetting

One of the main challenges to the use of microporous membrane contactors for gas-liquid absorption is to maintain the membrane pores dried, i.e. avoid the liquid entrance inside the pores. The phenomenon is also referred to membrane wetting (cf. Figure 3). In fact, membrane wetting is responsible of a significant increase of the mass transfer which leads to a large drop of the absorption performances.

Rangwala [71] reports that a low wetting (< 2%) of the membrane can result in a membrane mass transfer resistance which can represent 60% of the total mass transfer resistance of the process. Wang et al. [72] reports that the CO<sub>2</sub> absorption rate by an aqueous solution of DEA is six times higher if the membrane is in a non-wetted mode than those of the wetted mode. They also quantified that a 5% membrane wetted is responsible of the increase by 20% of the total mass transfer resistance.

Hence, the pair absorbent/membrane, as well as the operating conditions (pressures of the gas and the liquid phases), has to be cautiously chosen. The Laplace-Young equation allows making the link between these parameters by estimating the liquid entry pressure (LEP, also called the breakthrough pressure) which corresponds to the minimum pressure applied on the liquid to enter the membrane pores. This parameter defines the membrane wettability by a liquid absorbent.

$$LEP = - \frac{4 B \gamma \cos(\theta)}{d_{pmax}} \quad (22)$$

As reported by Eq. (22), the breakthrough pressure, LEP (Pa), depends on:

- The polymer material through the maximal pore diameter,  $d_{pmax}$  (m);
- The absorbent through its surface tension,  $\gamma$  (N m<sup>-1</sup>);
- The pair absorbent/membrane through the contact angle,  $\theta$  (rad);
- The pore geometry through the pore geometry coefficient, B (-): B = 1 for perfectly cylindrical pores otherwise  $0 < B < 1$ .

A high breakthrough pressure can be provided by combining a high polarity difference, between the membrane and the absorbent, with a small maximal pore diameter and a narrow pore size distribution.

It is commonly accepted that the membrane wetting gradually occurs. Hence, three modes of wetting have been reported [34]:

- a) Non-wetting mode
- b) Partial-wetting mode
- c) Complete-wetting mode

Most of the liquid absorbent reported in CO<sub>2</sub> capture process are aqueous solution of alkanolamine, ammonia, sodium hydroxide, etc. These aqueous solutions are polar, so the polymer material has to be hydrophobic in order to limit the membrane wetting. Amongst the large amount of polymer material commercially available, polytetrafluoroethylene (PTFE) and poly(vinylidene fluoride) (PVDF) are mainly used due to their contact angle higher than 90°. However, polypropylene (PP), less hydrophobic than PTFE and PVDF, is the most used polymer material in membrane process applied to CO<sub>2</sub> capture because of its low cost and its commercial availability as hollow fiber membrane contactors. Several studies, reported in the literature, have studied the membrane wetting, a state-of-the-art review is proposed in Table 4.

In practice, the applied liquid pressure on the membrane is systematically still slightly higher (e.g. few millibar), than the gas pressure. This pressure difference between the gas and the liquid phase, also named the transmembrane pressure, is different from the pressure drop in the membrane contactor (i.e. in the axial direction) and allows avoiding the gas dispersion in the liquid phase and thus permitting to maintain

the membrane pores dry. Some studies, mostly on short time scales (few hours) [40,52,73], confirm that the process performances are stable and reproducible. However, some results, achieved on long time scales (few days) [36,72,74,75], highlight that the membrane wetting is a recurring issue, whatever the microporous polymer material selected [36]. In fact, the entering, even limited, of the liquid phase in the membrane pores will quickly induce a significant decrease of the process performances by reducing the membrane mass transfer coefficient, and thus of the overall mass transfer coefficient [40,71,72].

Hence, a microporous membrane contactor with a highly hydrophobic polymer hollow fiber will undergo all three wetting modes over a prolonged operation: during the first few hours, the membrane contactor will maintain non-wetted conditions (cf. Figure 3.a)) and thus have the best absorption efficiency. After few days of use, the membrane pores will be gradually wetted by the liquid phase reducing the process performances by increasing the overall mass transfer resistance. Finally after few weeks or months, the membrane module can be completely wetted by the absorbent (cf. Figure 3.b).

The real causes of membrane wetting remain until now difficult to explain, mainly due to the numerous parameters influencing: the membrane properties (e.g. pores diameter, porosity, tortuosity and surface roughness), the absorbent property (e.g. surface tension), the membrane-absorbent interaction (e.g. contact angle) and the operating conditions (e.g. pressure drop, pressure on the liquid side). Moreover, several studies have reported that chemical reactions occurring between the membrane and the liquid phase are responsible of the membrane wetting by changing the membrane morphology (surface roughness, hydrophobicity, pore enlargement...) [46,71,72,75].

Atchariyawut et al. [45] reported that capillary condensation may cause membrane wetting by allowing the entrance of the water vapor in the membrane pores. Zhao et al. [34] assumed that capillary condensation would be a real issue in membrane desorption due to the significant water vapor flow occurring into the colder section of the fibre.

**Table 4: List of publications about membrane wetting applied for CO<sub>2</sub> capture process**

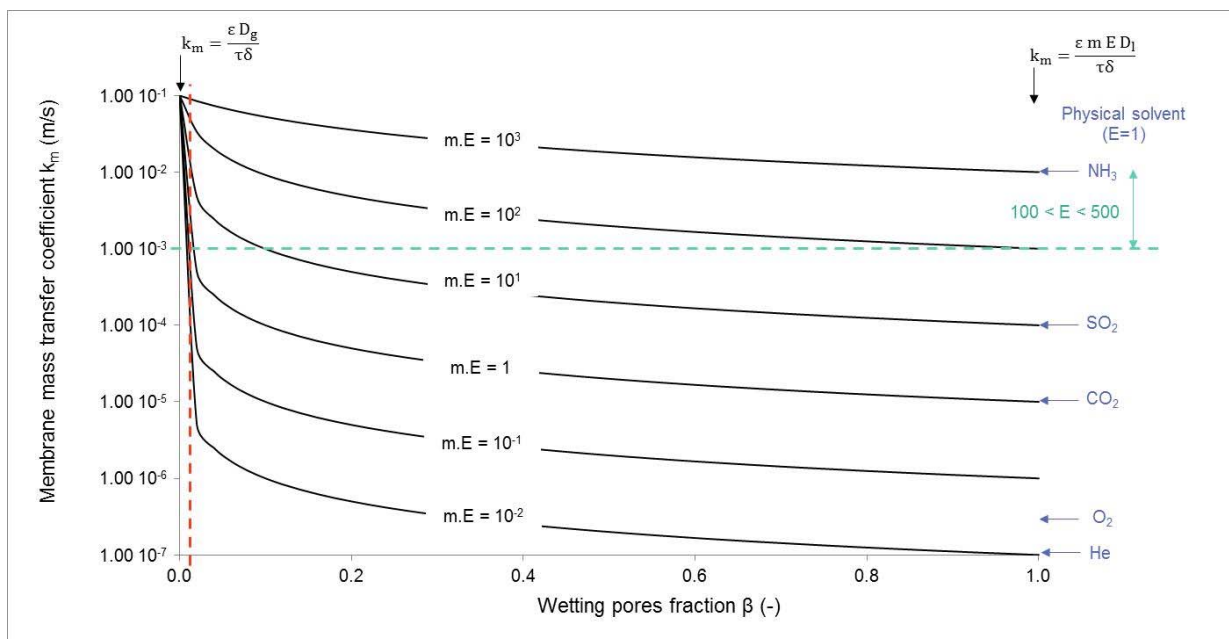
Reference	Polymer material	Liquid phase	Duration (days)	Observation
[50]	PP	Water	3	Increase of membrane porosity, pores diameter and pores size, internal and external surface
[75]	PP	MEA, MDEA, Water	90	Decrease of the contact angle faster with MEA and MDEA than with water. Stabilization after 60 days.
[72]	PP	DEA	106	21% flux decrease during 4 days then stabilization
[76]	PP	Potassium Glycinate	1.8	No wetting
[49]	PTFE, PP	MEA	275 & 42	No wetting of PTFE hollow fibers. Decrease of the process performances using PP hollow fibers
[40]	PVDF, PP	Water, DEA	Short time	10% of the membrane wetted = $k_m$ corresponds to 10 to 70% of $K_{ov}$
[77]	PP	MEA, Degraded MEA	2.92	Decrease of the flux by 70% Decrease of the flux by 22 to 31%
[41]	PVDF, PTFE	MEA	2.50	No wetting of PTFE hollow fibers
[74]	PP, PMP	PAMAM, MEA	55 & 70	No change on PP. Decrease of the performances after 54 days with PMP
[73]	PP	Water	Short	Wetting
[52]	PP, PS	MDEA	Short	Wetting
[36]	PP, PTFE, PP-Teflon AF2400, PP-PDMS	MEA	50	Significant decrease of the process performances after 6.2 days for PP and 16.7 days PTFE. No wetting of PP-Teflon AF2400 and PP-PDMS

In order to show the influence of the gradual wetting of a microporous polymer material on the mass transfer coefficient, a brief analysis is achieved. In this analysis, the physical absorption, i.e.  $E=1$ , of several gases in water is assumed. The mass

transfer coefficient of a wetting microporous polymer is estimated thanks to the resistance-in-serie approach: the membrane mass transfer coefficient is defined by the sum of the resistance of the wetted pores ( $k_{m,wet}$ ,  $m s^{-1}$ ) and the dried pores ( $k_{m,dry}$ ,  $m s^{-1}$ ) according to Eq. (23).

$$\frac{1}{k_m} = (1-\beta) \frac{1}{k_{m,dry}} + \beta \frac{1}{k_{m,wet}} = (1-\beta) \frac{\tau \delta}{\varepsilon D_g} + \beta \frac{\tau \delta}{\varepsilon m E D_l} \quad (23)$$

Where  $D_l$  is the gas diffusion coefficient in the liquid phase ( $m^2 s^{-1}$ ) and  $\beta$  the wetting pore ratio (-).



**Figure 12: Influence of the wetting pore fraction on the membrane mass transfer coefficient in a microporous polymer material, adapted from [10] (with  $D_g = 10^{-5} m^2 s^{-1}$ ;  $D_l = 10^{-9} m^2 s^{-1}$  and  $\frac{\varepsilon}{\tau \delta} = 10^{-4}$ )**

Figure 12 summarizes the results obtained through this approach and highlights that a small increase of the wetting fraction induces a significant decrease of the membrane mass transfer coefficient. However, the decrease is highly dependent on the gas solubility in the liquid phase: the high solubility of  $NH_3$  in water allows minimizing the decrease of  $k_m$  by only a factor of 10; while the solubilities of  $SO_2$  and  $CO_2$  in water are much lower and the decrease is much more significant, respectively by a factor of 1 000 to 10 000.

The use of a chemical reaction between the gas dissolved and the liquid phase also minimizes the decrease of the membrane mass transfer coefficient. As an example, the enhancement factor of the chemical reaction occurring between  $CO_2$  and MEA is



generally estimated around 100 [78]. In that case, the decrease of the membrane mass transfer coefficient will be limited to a factor of 100 instead of 10 000.

In order to avoid the membrane wetting, several strategies are available. The first one consists to maintain the transmembrane pressure below the breakthrough pressure. However, the control of the pressure gradients along the hollow fiber is a major operational issue. In fact, it is assumed that the pressure drop, in the gas and the liquid phases, remains unequal and uneven which can lead to localized area where the transmembrane pressure is higher than the breakthrough pressure [57]. This is the case in a counter-current configuration where wetting often occurs near the absorbent entry in the membrane module due to the pressure drop on the gas side.

The second is to increase the breakthrough pressure by using absorbent with a very high surface tension, by increasing the contact angle and/or by using membrane with small pore size. This strategy is mainly limited by the development of new superhydrophobic polymer materials and their commercial availability at small fiber diameter contrary to PTFE hollow fibers; but also by the availability of solvents having a high surface tension and able to be used in the process.

Finally, the third strategy aims to replace microporous hollow fibers by composite hollow fibers. These type of hollow fibers are made of a macroporous hollow fiber, used as mechanical support, covered by a dense skin from a different polymer. The dense skin polymer should be highly permeable as the process selectivity is usually assumed by the absorbent in gas-liquid processes. The studies reported on this type of materials highlight their ability to resist to membrane wetting [36].

## **Membrane fouling**

Solid formation or impact on a porous or dense surface is prone to generate unwanted phenomena such as particulate deposit accumulation leading to so called surface fouling [79]. This phenomenon is mainly reported on water treatment processes using reverse osmosis (RO) [80,81] because of the precipitation of mostly mineral ( $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{SiO}_2$ ...) but also organic matters on the polymer surface [79] generating particulate deposit accumulation. Hence, membrane fouling concerned every membrane processes [82–85] having at least one phase in contact

with the membrane. However, the reasons why, how, when and where fouling occurred are relatively unexplored. In fact, the deposit accumulation can take place on the membrane surface but also inside the membrane pores as a result of the wetting phenomenon. Studies, about membrane fouling of membrane contactors, are scarce. For carbon capture for instance, presence of fine particles in flue gas are also responsible of a significant increase of the mass transfer resistance [86,87]. In both cases, membrane fouling, due to particles from the liquid or the gas phase, the phenomenon stays a critical issue for the process and requires further investigations.

### **Membrane degradation**

As reported before, the key issue of membrane contactor is the lifetime and the stability of the performances over long time scale. Therefore, the polymer material should be thermally but also chemically inert in order to achieve the objectives. However, due to the low solubilities of most gases in water in normal pressure and temperature conditions, gas-liquid absorption often makes use of chemical absorption systems. In some cases, such as CO<sub>2</sub> or SO<sub>2</sub> absorption, the liquid phases are generally more corrosive after the absorption of the gases [20,88,89]. Thus, the products, outcoming from the chemical reaction between CO<sub>2</sub> and alkanolamine for example, are able to change the membrane hydrophobicity, the membrane morphology and the membrane chemical structure leading to membrane wetting and membrane degradation.

In addition to the chemical degradation, thermal degradation could also be another issue. It is commonly admitted that the temperature of the absorption step is close to the temperature of the gas phase at the inlet of the unit in order to minimize the energy cost. However, most of the studies reported in the literature are achieved under ambient temperature conditions. For CO<sub>2</sub> capture, ambient temperature is at least 20 to 40°C lower than in the reality. As the thermal stability of a polymer material (whatever its structure, i.e. dense or microporous) is a function of its glass transition temperature ( $T_g$ ) and its melting temperature ( $T_m$ ) compared to the operating temperature of the unit operation, the choice of the polymer is clearly of major importance. Hence, the  $T_g$  and the  $T_m$  of the polymer selected should be as far as possible from the operating temperature in order to avoid thermal degradation (cf.

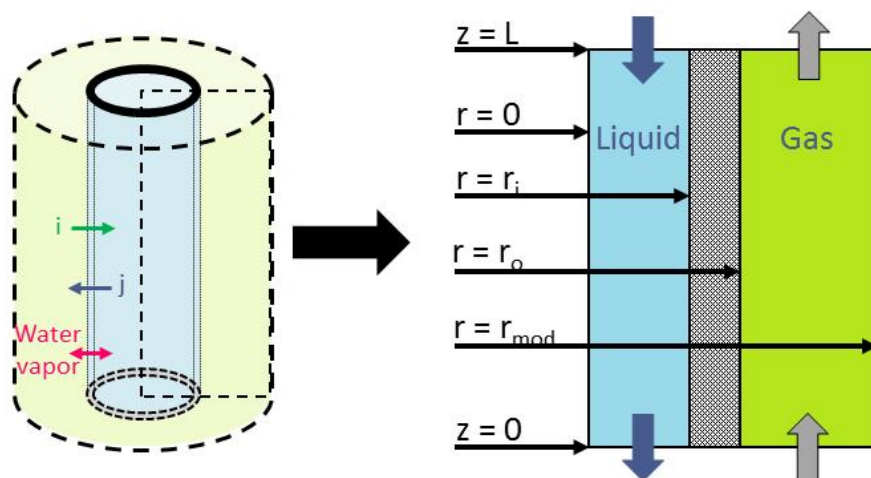
Table 5). It has to be noted that thermal degradation could also be located on the potting material used to maintain the hollow fiber in the cartridge (cf. Figure 10) [23].

**Table 5: Glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of the main polymer materials reported in the literature [90–94]**

<b>Polymer material</b>	<b>Structure</b>	<b><math>T_g</math> (°C)</b>	<b><math>T_m</math> (°C)</b>
Polypropylene (PP)	Semi-crystalline	-20	176
Polyvinylidene fluoride (PVDF)	Semi-crystalline	≈ - 30	≈ 170
Polytetrafluoroethylene (PTFE)	Semi-crystalline	127	327
Polydimethylsiloxane (PDMS)	Amorphous	-125	-40
Poly(1-trimethylsilyl)-1-propyne (PTMSP).	Amorphous	> 250	
Teflon AF 2400	Amorphous	239	≈ 340

## MASS TRANSFER AND PROCESS SIMULATION

In this section, the modelling conditions and/or the different notations used by researchers are defined in order to avoid confusion, and discuss the different types of approaches which are used for modelling gas-liquid absorption with membrane contactors. The case of stripping, which makes use of the same mechanisms will not be detailed. The modelling and simulation of membrane contactors has been extensively investigated for decades [10,23,95–98]. The modelling framework is basically similar to that used for absorption column simulation, but the membrane mass transfer description requires dedicated approaches. A general sketch of mass transfer of different compounds in membrane contactors is shown in Figure 13. It should be stressed that, for the sake of simplicity, solute absorption is almost systematically considered as the only mass transfer phenomenon in modelling approaches (i.e. water or non solute gaseous species absorption is not taken into account).

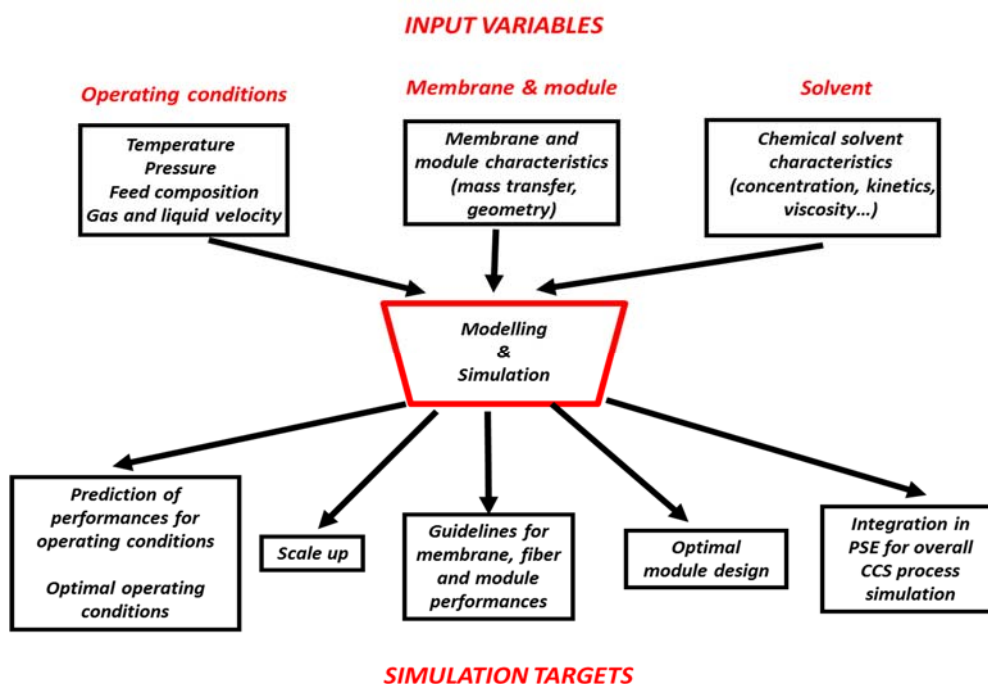


**Figure 13: Schematic diagram of the membrane contactor used in the mathematical models [31]**

A considerable amount of knowledge and experience can be gained from the literature dedicated to absorption into physical and chemical solvents in packed columns, including at industrial scale [2,18,99–102]. Many publications have addressed the modelling/simulation problem for the specific case of membrane contactors for absorption in a chemical solvent and a large portfolio of models has been reported. The ultimate target of these studies is to predict experimental results through a large range of operating conditions and systems with a minimal number of

adjustable parameters. A key problem with modelling is finding a balance between model complexity, numerical resolution and the possibility of precisely estimating the maximal number of variables in the simulation set, to completely predict process performances.

Figure 14 summarizes the key variables that must be defined when simulating the absorption performance of a membrane contactor and the different targets of modelling/simulation studies. Generally speaking, a large number of studies are limited to a comparison of a set of experimental data to the predictions of one type of model. Several publications make use of a given model for parametric sensitivity studies (e.g. prediction of the influence of gas or liquid velocity, or membrane mass transfer coefficient on absorption performances). Very few comparative studies evaluating different models have been published. Similarly, optimization and scale-up problems are largely unreported.



**Figure 14: General sketch of process modelling and simulation for membrane contactor applications [34]**

### Overall framework

Whatever the type of modelling approach developed, the first step must always correspond to the definition of the set of assumptions regarding the physico-chemical

properties of the selected system. Generally, the steady state condition is almost systematically assumed, as it is the case in the reference technology (absorption column). As reported by Zhao et al. [34], the input variables are classified into three main categories: (i) operating conditions, (ii) membrane and module properties, and (iii) solvent properties (cf. Figure 14).

Regarding the fluid flow conditions, two options are available:

- Liquid inside: the liquid phase is flowing on the lumen side while the gas phase is flowing on the shell side. This configuration is preferred for industrial applications when a very large gas flow rate is required (possibility to provide a larger cross-section area for gas flow). However, the flow of the most viscous fluid in the lumen side induces an increase of the lumen-side pressure which could favor the membrane wetting.
- Liquid outside: the liquid phase is flowing on the shell side while the gas phase is flowing on the lumen side. This option is also widely studied because it allows minimizing the flow resistance of the liquid in standard hollow fibers. Moreover, it offers a larger gas-liquid interfacial area. However, it induces an increase of the pressure drop on the gas phase and of the risk of fiber blocking by dust particles for some practical applications.

After defining the operating conditions, the membrane and module properties, the mass, and eventually the energy, balances and transfer equations are developed in accordance to the set of assumptions regarding the modelling approach selected.

## **State of the art**

Most publications about gas-liquid absorption using membrane contactors propose a specific mathematical approach. However, the different studies can more generally be gathered in four families of models with gradual complexity. These four models will be presented and discussed hereafter. The assumptions of each modelling strategy and a tentative analysis of the corresponding situation that best fits the set of hypotheses are summarized in Table 6.

Note that regardless of the level of complexity of the mathematical approach selected, the models are all developed based on a single hollow fiber representative approach, as shown in Figure 13 [103].

### *Model based on constant overall mass transfer coefficient ( $K_{ov}$ )*

The model based on a constant overall mass transfer coefficient has been historically reported in the first publications dedicated to membrane contactors [24,25,31,70,104]. This is also the simplest approach available which highlights the advantage to include the different mass transfer mechanisms into a single overall parameter:  $K_{ov}$  ( $m\ s^{-1}$ ). Thus, the process performances are easily and quickly assessed. More specifically, knowing the gas-liquid interfacial area ( $a$ ) and the overall mass transfer coefficient  $K_{ov}$ , the  $K_{ov}\cdot a$  performance can be easily obtained and compared to other technologies (cf. Table 2).

The constant  $K_{ov}$  model is based on the following set of assumptions:

- i. Constant gas velocity.
- ii. Isothermal conditions.
- iii. Constant total gas pressure, i.e. negligible pressure drop.
- iv. Plug flow of the gas phase in the membrane contactor.
- v. Negligible solute concentration in the liquid phase.
- vi. Constant overall mass transfer coefficient between the inlet and the outlet of the membrane contactor.

It is important to note that the assumption v. can be considered as acceptable if the solvent concentration in the liquid phase is in large excess throughout the membrane contactor. This assumption allows simplifying the expression of the local driving force for the solute as the solute  $i$  concentration in the gas phase ( $C_g$  in  $mol\ m^{-3}$ ).

Hence, according to the set of assumptions defined above, the solute mass balance on the gas phase can be expressed as:

$$u_g \frac{dC_g}{dz} = - K_{ov} a C_g \quad (24)$$

Where  $u_g$  is the interstitial gas velocity ( $m\ s^{-1}$ ) and  $z$  is the axial contactor coordinate (m).

Thus, for a membrane contactor with an effective length of  $L$  (m), the differential solute mass balance can be easily integrated. The effective solute capture ratio,  $\eta$  (-), which corresponds to the ratio of the inlet solute flux which is effectively absorbed by the solvent, is most often one of the key performance indicator of the process, and can be easily expressed as follows:

$$\eta = 1 - \exp\left(\frac{-K_{ov} a L}{u_g}\right) \quad (25)$$

It has to be noted that the product of  $K_{ov} \cdot a$  corresponds to the inverse of the solute transfer time in the process, which is a key parameter allowing comparison of gas absorption technologies and evaluation of scale-up possibilities. The term  $\frac{L}{u_g}$  (s) is indeed homogeneous to a gas-liquid contact time. Thus, the term  $\frac{K_{ov} a L}{u_g}$  allows determining the process mass transfer performance.

The model based on constant overall mass transfer coefficient offers the advantages to be very easy to use. Indeed, the evolution of the capture ratio ( $\eta$ ) with the gas velocity ( $u_g$ ) is easily determined experimentally. Consequently,  $K_{ov}$  is the only unknown parameter and is generally used to fit the data. Moreover, the set of hypotheses can be applied to a physical or chemical absorption process.

However,  $K_{ov}$  logically depends on the operating conditions (such as the fluid velocities, which directly impact the Reynolds number) and can by no means be considered as a constant for a given contactor type and absorption system. This is clearly the major limitation of the model, which hinders the extrapolation to a different set of operating conditions. Additionally,  $K_{ov}$  may also vary along the axial position. In such a case, Eq. (24) and (25) no longer apply and more rigorous models (e.g. the following ones) are required.

### *Resistance-in-series (1D) approach*

The resistance-in-series model was detailed in section Mass transfer fundamentals.

This modelling approach is based on the film theory. The local overall mass transfer coefficient ( $K$ ) is expressed for a flat geometry according to Eq. (6).

This approach considers the gas phase, the liquid phase and the membrane. However, the membrane mass transfer coefficient ( $k_m$ ) is generally supposed to be constant and used as the only adjustable parameter to fit the data.

If radial dispersion effects are neglected in the gas and the liquid phases, then a one dimensional approach can be developed. This approach has already been investigated for CO<sub>2</sub> absorption, by a 30%wt MEA aqueous solution, through a parametric study [33]. This approach is based on the following set of assumptions:



- i. Film theory (i.e. diffusion in the boundary layers) applies to the liquid and the gas phases.
- ii. Plug flow in the liquid and in the gas phases
- iii. Constant membrane mass transfer coefficient ( $k_m$ ).
- iv. Thermodynamic equilibrium at the gas-liquid interface.
- v. Isothermal conditions.

Contrary to the previous approach, i.e. the  $K_{ov}$  model, this modelling approach takes into account the evolution of the local mass transfer coefficients through the axial coordinate, and, from this, of  $K$ . Additionally, the absorption of solute  $i$  by the liquid phase induces a variation of the gas velocity, a variation of the concentrations of solvent and solute in both phases and a change of the total gas pressure (pressure drop). All these variations are taken into account in the following set of equations [33]:

- Solute mass balance in the gas phase:

$$d(Q_g C_g) = -K a C_g S_{ext} dz \quad (26)$$

- Global mass balance in the gas phase:

$$Q_g^{in} \frac{P_g^{in}}{RT} (1 - y_i^{in}) = Q_g \frac{P_g}{RT} (1 - y_i) \quad (27)$$

- Stoichiometric constraint due to the chemical reaction between solute  $i$  and solvent  $j$  :

$$d(Q_l C_j) = -\frac{\omega_j}{\omega_i} d(Q_g C_g) \quad (28)$$

In the lumen side, the pressure drop is usually estimated through the Hagen-Poiseuille equation [17]:

$$-\frac{\Delta P}{dz} = \frac{8 \mu}{r_o^2 \left(1 - \left(\frac{\delta}{r_o}\right)^4\right) \phi \nu} \quad (29)$$

While in the shell side, the pressure drop is often expressed according to the Kozeny equation [17]:

$$-\frac{\Delta P}{dz} = \frac{4\mu}{r_o^2} \frac{\varphi^2}{(1-\varphi)^2} \upsilon \quad (30)$$

$$\kappa = 150 \varphi^4 - 314.44 \varphi^3 + 241.67 \varphi^2 - 83.039 \varphi + 15.97 \quad (31)$$

Where  $P_g$  is the pressure of the gas phase (Pa),  $Q_g$  and  $Q_l$  are respectively the gas and the liquid flowrate ( $m^3 s^{-1}$ ),  $y_i$  is the solute  $i$  volume fraction in the gas phase (-),  $C_j$  is the  $j$  (solvent) concentration in the liquid phase ( $mol m^{-3}$ ),  $\omega_i$  and  $\omega_j$  are respectively the stoichiometric coefficients of the chemical reaction occurring between the absorbed solute  $i$  and the solvent  $j$ ,  $\Delta P$  is the pressure drop (Pa),  $\mu$  is the viscosity (Pa s),  $\upsilon$  is the superficial velocity ( $m s^{-1}$ ),  $r_o$  is the outer radius of the hollow fiber (m),  $S_{ext}$  is the cross-section module area without fibers ( $m^2$ ),  $\kappa$  is the Kozeny coefficient (-) and  $\varphi$  is the packing ratio (-) of the membrane contactor defined by  $\varphi = n_{fib} \left( \frac{r_o}{r_{mod}} \right)^2$ ,  $n_{fib}$  is the number of fiber in the membrane contactor (-) and  $r_{mod}$  is the internal module radius (m).

The differential equation system is then modified to become dimensionless by using the five following variables:  $C_g^* = \frac{C_g}{C_g^{in}}$ ;  $C_j^* = \frac{C_j}{C_j^{in}}$ ;  $P_g^* = \frac{P_g}{P_g^{in}}$ ;  $NUT_g = \frac{L k_{max,a}}{u_0^0}$  and  $z^* = \frac{z}{L}$ .

Where  $NUT_g$  is the number of transfer units (-) and  $k_{max}$  the maximal mass transfer coefficient ( $m s^{-1}$ ) defined by:

$$k_{max} = m E_{\infty} k_l = m Ha k_l \quad (32)$$

The characteristic boundary conditions of the system are then required in order to solve the resistance-in-series model.

- At  $z^* = 0$  :  $C_g^{*0} = 1$  and  $P_g^{*0} = 1$
- At  $z^* = NUT_g$  :  $C_j^{*L} = \text{Inlet solvent concentration}$

### *Convection-diffusion (2D) approach*

The two-dimensional model corresponds to a more general approach proposed by several authors [32,40,103,105,106], which takes into account the convection and diffusion contributions in the gas and in the liquid phases. This strategy leads to a more complex set of equations requiring the following set of assumptions:

- i. Constant membrane mass transfer coefficient ( $k_m$ ).
- ii. Thermodynamic equilibrium at the gas-liquid interface.

- iii. Isothermal conditions.
- iv. Constant total gas pressure.

Generally, the 2D modelling approach considers the solvent concentration gradient in the liquid phase and the solute concentration gradient in both liquid and gas phases, the chemical reaction between solute  $i$  and solvent  $j$  in the liquid phase and the decrease of the gas velocity due to solute absorption.

The set of differential mass balance equation system for solute in the gas and liquid phases, and solvent in the liquid phase in cylindrical coordinates are respectively defined by:

$$u_{z,g} \frac{\partial C_g}{\partial z} = D_g \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_g}{\partial r} \right) \right] \quad (33)$$

$$u_{z,l} \frac{\partial C_l}{\partial z} = D_l \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_l}{\partial r} \right) \right] + \omega_i R_{i-j} \quad (34)$$

$$u_{z,l} \frac{\partial C_{MEA}}{\partial z} = D_{MEA} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{MEA}}{\partial r} \right) \right] + \omega_j R_{i-j} \quad (35)$$

The stoichiometric constraint due to the chemical reaction between  $i$  and  $j$  is expressed as:

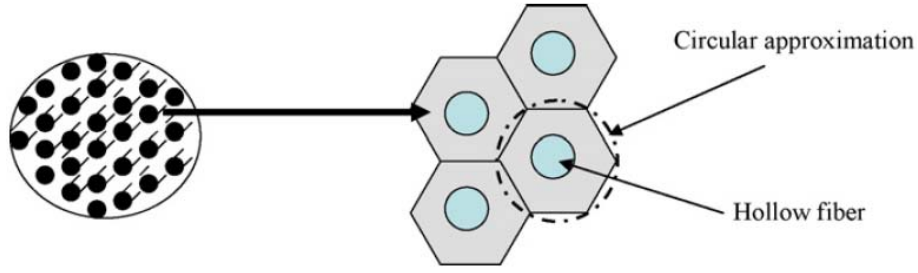
$$u_{z,l} \frac{\partial C_{MEA}}{\partial z} = -\frac{\omega_j}{\omega_i} u_g \frac{\partial C_g}{\partial z} \quad (36)$$

The gas solute,  $l$ , transfer in the membrane is assumed to result only from the contribution of diffusion. Consequently, mass balance in the membrane can be expressed through Fick's law:

$$D_m \frac{\varepsilon}{\tau} = \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_{i,m}}{\partial r} \right) \right] = 0 \quad (37)$$

With  $r$  the spatial coordinate (m),  $C_{i,m}$  the  $i$  concentration in the membrane ( $\text{mol m}^{-3}$ ) and  $R_{i-j}$  the reaction rate between  $i$  and  $j$  ( $\text{mol m}^{-3} \text{s}^{-1}$ ).

Based on the value of the term  $D_m \frac{\varepsilon}{\tau}$ , the  $k_m$  value is easily obtained through Eq. (9).



**Figure 15: Cross section of the membrane module and circular approximation of the fluid surrounding the fibers according to the Happel's free surface model [107]**

The flow on the lumen side of the membrane is assumed to be a fully-developed laminar parabolic flow, as confirmed by the low value of the Reynolds number:

$$u_{lum} = 2 \langle v \rangle \left[ 1 - \left( \frac{r_i}{r} \right)^2 \right] \quad (38)$$

The flow on the shell side of the membrane contactor is generally modelled using the Happel's free surface model (cf. Figure 15) [107,108]:

$$u_{sh} = 2 \langle v \rangle \left[ 1 - \left( \frac{r_o}{r} \right)^2 \right] \left[ \frac{\left( \frac{r}{r_c} \right)^2 - \left( \frac{r_o}{r_c} \right)^2 + 2 \ln \left( \frac{r_o}{r} \right)}{3 + \left( \frac{r_o}{r_c} \right)^4 - 4 \left( \frac{r_o}{r_c} \right)^2 + 4 \ln \left( \frac{r_o}{r_c} \right)} \right] \quad (39)$$

With

$$r_c = r_o \sqrt{\frac{1}{1-\phi}} \quad (40)$$

The boundary conditions required to solve the convection-diffusion approach are:

- Axial direction (assuming counter-current flow pattern)

$$z = 0, \quad c_{i,lum} = 0 \quad \& \quad c_{j,lum} = c_{j,lum}^{in}$$

$$z = L, \quad c_{i,sh} = c_{i,sh}^{in} \quad \& \quad c_{j,sh} = 0$$

- Radial direction

$$r = 0, \quad \frac{\partial c_{k,lum}}{\partial r} = 0 \quad \text{for } k = \text{all species,}$$

$$r = r_i, \quad \frac{\partial c_{k,lum}}{\partial r} = 0 \quad \text{for } k = \text{amine species} \quad \& \quad c_{i,lum} = m c_{i,mem}$$

$$r = r_o, \quad c_i^{mem} = c_{i,sh} \quad \& \quad c_{j,mem} = 0,$$

$$r = r_g, \quad \frac{\partial c_{i,sh}}{\partial r} = 0 \quad \& \quad c_{j,sh} = 0$$

Until now, for modelling approach developed considering isothermal conditions have been presented. Isothermal conditions are most often considered to apply for a physical absorption process. However, it is well known that, for reactive absorption systems, the chemical reaction between the gas and the liquid phase can be exothermic [100]. The temperature change has thus to be computed and requires a more sophisticated modeling framework.

### *Model for non-isothermal systems*

Only few authors [109,110] have reported a similar convection diffusion approach but under non-isothermal conditions. In this case, a set of differential energy balances has to be added to the mass balances:

$$\Psi_{sh} \left[ \frac{\partial^2 T_{sh}}{\partial r^2} + \frac{1}{r} \frac{\partial T_{sh}}{\partial r} \right] = \rho C_p u_{z,sh} \frac{\partial T_{sh}}{\partial z} \quad (41)$$

$$\Psi_{mem} \left[ \frac{\partial^2 T_{mem}}{\partial r^2} + \frac{1}{r} \frac{\partial T_{mem}}{\partial r} \right] = 0 \quad (42)$$

$$\Psi_{lum} \left[ \frac{\partial^2 T_{lum}}{\partial r^2} + \frac{1}{r} \frac{\partial T_{lum}}{\partial r} \right] + \rho \sum H_{i,lum} = \rho C_p u_{z,lum} \frac{\partial T_{lum}}{\partial z} \quad (43)$$

Where  $\rho$  is the density ( $\text{kg m}^{-3}$ ),  $C_p$  is the thermal capacity ( $\text{J K}^{-1} \text{kg}^{-1}$ ),  $\psi$  is the thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ ),  $H_i$  is the enthalpy of reaction of the species  $i$  with  $j$  ( $\text{J mol}^{-1}$ ).

In the non-isothermal approach, the mass balance equations are the same as those reported in the convection diffusion model, thus the same boundary conditions are used regarding the mass transfer. However, by adding the energy balance equations, the following boundary conditions are also required:

- Axial direction

$$z = 0, \quad T_{lum} = T_{lum}^{in}$$

$$z = L, \quad T_{sh} = T_{sh}^{in}$$

- Radial direction

$$r = 0, \quad \frac{\partial T_{lum}}{\partial r} = 0$$

$$r = r_i, \quad T_{\text{lum}} = T_{\text{mem}}$$

$$r = r_o, \quad T_{\text{mem}} = T_{\text{sh}}$$

$$r = r_c, \quad \frac{\partial T_{\text{sh}}}{\partial r} = 0$$

**Table 6: Summary of the four types of modelling approaches proposed in membrane contactor and the corresponding situation [34]. The specific case of CO<sub>2</sub> absorption in MEA is taken as a reference system.**

Modelling strategy	Assumptions	Remarks (pros/cons)	Ref.
Constant overall mass transfer coefficient ( $K_{ov}$ )	<ol style="list-style-type: none"> <li>1. T, P, K and <math>Q_g</math> are constants;</li> <li>2. Low <math>C_{CO_2,l}</math></li> <li>3. Plug flow in the gas phase;</li> <li>4. Adjusted parameter <math>K_{ov}</math></li> </ol>	<p>Fresh solvent at the inlet with a large excess (<math>\alpha_{in} \sim \alpha_{out} \sim 0</math>).</p> <p><u>Pros</u>: simplest approach; minimal information needed; enables comparison with literature data.</p> <p><u>Cons</u>: not rigorously applicable to industrial situations; lumped K variable combining solvent and membrane mass transfer performances.</p>	[24,25,70,104]
Resistance-in-series (1D)	<ol style="list-style-type: none"> <li>1. T, <math>k_g</math> and <math>k_l</math> are constants</li> <li>2. <math>C_{MEA}</math>, <math>\Delta C</math> and P are variables</li> <li>3. Plug flow in the gas and liquid phases</li> <li>4. Chemical reaction considered</li> <li>5. Adjusted parameter: <math>k_m</math></li> </ol>	<p>Classical approach for various inlet and outlet solvent conditions.</p> <p><u>Pros</u>: good prediction of mass transfer when <math>K_m</math> is known.</p> <p><u>Cons</u>: not rigorously applicable to industrial situations.</p>	[33,78]
Convection diffusion (2D)	<ol style="list-style-type: none"> <li>1. T and P are constants</li> <li>2. Axial convection and radial diffusion in the liquid and gas phases</li> <li>3. Chemical reaction considered</li> <li>4. Adjusted parameter: <math>k_m</math></li> </ol>	<p>Classical approach for various inlet and outlet solvent conditions; be equivalent to the resistance-in-series approach reported by some researchers.</p> <p><u>Pros</u>: applicable to real absorption situations (no assumption of fresh amine excess); roles of the membrane, solvent and hydrodynamic can be evaluated separately; probably the best compromise in terms of complexity and prediction efficiency.</p>	[32,40,103,105,106]
Non-isothermal system (2D)	<ol style="list-style-type: none"> <li>1. P is a constant</li> <li>2. Axial convection and radial diffusion in the liquid and gas phases</li> <li>3. Chemical reaction considered</li> <li>4. Adjusted parameter: <math>k_m</math></li> </ol>	<p>Complicated and rarely reported; many variables required; water and non-isothermal behaviors should be considered simultaneously; could be used for better prediction and/or pilot scale studies; experimental temperature profile remains difficult to predict.</p>	[109–111]

## INDUSTRIAL APPLICATIONS

Compared to conventional gas liquid absorption equipment (packed columns, trickle beds, stirred tanks, Venturi ejectors, sprays...cf. Table 2), membrane contactors are a recent technology and the number of suppliers is still extremely limited. Liqui-Cel Membrana, which proposes mostly microporous PP hollow fiber membrane contactors, is the historically first and largest equipment supplier. Membrane contactors based on dense layers (either self standing or anisotropic) are recently available with different polymeric materials such as Fluoropolymers (Compact Membrane Systems), Polydimethylsiloxane (Permselect) or SPEEK (Porogen). It is also important to note that several different companies have activities limited to medical applications such as artificial lungs. A significant number of industrial applications are confidential or have not been reported in the open literature. Consequently, it is difficult to report an exhaustive review of the existing applications of membrane contactors in industry and the associated market.

Table 7 proposes a summary of the major applications of membrane contactors, for gas absorption or desorption in different industrial sectors. Compared to the major applications of gas-liquid processes listed in the introductory part (cf. Table 1), several observations can be made:

- i) The large majority of applications of membrane contactors remain limited to aqueous systems with O<sub>2</sub> or CO<sub>2</sub> solutes. The high surface tension of water is indeed favorable for minimizing wetting problems and porous polymeric membranes do not show compatibility problems when in contact to O<sub>2</sub> and CO<sub>2</sub>.
- ii) Physical absorption and desorption cover the spectrum of applications, while chemical absorption is mostly limited to natural gas treatment, with very few installations reported up to now.
- iii) The industrial sectors and application framework correspond, generally speaking, to “clean and soft” systems: food, pharma, microelectronics, biotechnology, process water. Harsh environments with aggressive gases and media, or chemically reacting solvents, are scarce.
- iv) The size of the installations is not often reported but a number of applications are of limited scale compared to the large industrial units listed



in Table 1. Membrane contactors indeed show attracting compactness characteristics when size, weight and/or footprint constraints are of primary importance. Similarly, to other membrane processes, they do not enable however economy of scale characteristics. Specific costs remain essentially unchanged with an increase of scale, due to the numbering up property of modular separation processes. This fundamental difference to other unit operations explains why membrane contactors did not found up to now applications for very large feed flowrates. In terms of capacity, the largest installations are found for deoxygenating water but very few applications exceed  $1000 \text{ m}^3 \text{ h}^{-1}$ .

- v) In-vehicle (space, defense) and off shore applications are another favorable context for membrane contactors, which are not sensitive to gravity and orientation for ensuring mass transfer.
- vi) Finally, membrane contactors offer unique possibilities for single use applications and strong specifications such as blood oxygenators.

**Table 7: Industrial applications of membrane contactors for gas-liquid absorption or desorption**

<b>Process type</b>	<b>Solute (gas)</b>	<b>Solvent</b>	<b>Process</b>	<b>Application</b>
<b>Physical</b>	O <sub>2</sub>	Blood	Absorption	Blood oxygenators (medical)
	O <sub>2</sub>	Water	Desorption	Ultrapure water (< 1ppb O <sub>2</sub> ) in semiconductors or pharma Process water (corrosion protection for boilers)
	O <sub>2</sub>	Organic liquids	Desorption	Inks, photoresist, photographic products production
	O <sub>2</sub>	Water	Absorption	Bioreactors (cell culture, biotechnology)
	O <sub>2</sub>	Aqueous effluents	Absorption	Aerobic waste water treatment (bubble less aeration)
	CO <sub>2</sub>	Water	Absorption	Carbonated beverages (food)
	CO <sub>2</sub>	Water	Absorption	Photobioreactors for algae production Biogas purification (PWA)
	CO <sub>2</sub>	Water	Desorption	Process water (ion exchange beds protection, reverse osmosis units post treatment)
	Acids, O <sub>2</sub> , CO <sub>2</sub>	Wine	Gas exchange	Wine production
	EtOH	Fermentation broth	Desorption	Alcohol production (biotechnology)
	Aromas	Aqueous solutions	Desorption	Aromas recovery for food or perfumes
	VOc's	Water	Absorption or desorption	Gaseous and liquid effluent treatment
	NH <sub>3</sub>	Water	Absorption	Gaseous effluent treatment
	H <sub>2</sub> O	Glycol (TEG)	Absorption	Drying of gases
	H <sub>2</sub> O	Water	Desorption	Gas (air) humidification and moistening
	H <sub>2</sub> O	Oil	Desorption	Oil dehydrating
O <sub>3</sub>	Water	Absorption	Ozonation (water treatment, disinfection)	
<b>Chemical</b>	CO <sub>2</sub> , H <sub>2</sub> S	Aqueous amine (MEA)	Absorption	Natural gas treatment Post combustion carbon capture

The different applications listed in Table 7 are expected to correspond to existing units currently in operation in different industries. The market share among them is however largely unequal. The blood oxygenators and water degassing applications

are likely to represent a very large ratio, both in terms of number of installed units and market. A brief overview of the different types of uses of membrane contactors is proposed hereafter.

### **Blood oxygenators**

Blood oxygenators (artificial lungs) have been early identified as a promising application of membrane contactors [112]. The possibility to provide gas exchange without bubble formation is indeed absolutely necessary in order to prevent surgical problems. This application is often considered as the largest current market of membrane contactors, because of the large numbers of units which are needed for medical use and also because of the single unit usage specification. The oxygenator component serves as the lung, and is designed to expose the blood to oxygen and remove carbon dioxide. It is disposable and contains about 2–4 m<sup>2</sup> of a membrane permeable to gas but impermeable to blood, in the form of hollow fibers. Blood flows on the outside of the hollow fibers, while oxygen flows in the opposite direction on the inside of the fibers. Gas containing oxygen and medical air is delivered to the interface between the blood and the device, permitting the blood cells to absorb oxygen molecules directly. The design of blood oxygenators is specific, the materials have to show stringent characteristics in terms of compatibility for medical use and either porous hydrophobic or dense membranes are proposed. Each unit is of small size. Suppliers are specialized for this application and differ from the other technology providers.

### **Water degassing (pharma, microelectronics, process water, corrosion protection)**

The removal of dissolved gases (mostly oxygen but also carbon dioxide and nitrogen) from water is the second large market. Membrane contactors are widely used and have progressively displaced the vacuum tower, forced draft deaerator, and oxygen scavengers for over 20 years.

Numerous situations of interest can be listed: *ultrapure water* in the microelectronics and pharma sectors (WFI: Water For Injection) is one of the most often cited, with residual oxygen concentrations as low as 1ppb. Degassing can be performed by

vacuum, but an inert gas carrier can also be applied in some cases when the residual concentration is not too low. In the semiconductor and flat panel/TFT industries, high levels of oxygen can cause lower wafer and flat panel yields.

*Deionised and purified water* is another very large market. In many cases the CO<sub>2</sub> content in the raw water has effectively to be reduced to obtain purified water with a conductivity of < 1.3 μS/cm (at a temperature of 25°C). Historically, NaOH dosing has been used to control CO<sub>2</sub> content. With chemical dosing CO<sub>2</sub> is converted into a carbonate, which has further to be removed, for instance by Reverse Osmosis. The latest state of the art technology for this task is degasification by a membrane contactor where chemicals are not needed. A strip gas or vacuum used on the inside of the hollow fiber lowers the partial pressure of the gas phase which causes the gases to diffuse from the liquid phase through the membrane wall into the gas phase. The removed CO<sub>2</sub> is continuously swept out of the contactor by the air sweep.

*Boiler water treatment* is another large field of application. As steam is produced, dissolved solids become concentrated and deposit inside the boiler. This leads to poor heat transfer and efficiency reduction of the boiler. Dissolved gases such as oxygen and carbon dioxide will react with the metal surfaces inside the boiler promoting corrosion. Chemical treatment is often used to control the dissolved oxygen. Degassing, without adding chemicals, such as enabled by membrane contactors, is an important step for protecting the boiler.

Dissolved oxygen removal from water for injection is also common practice in water flooding, *Improved Oil Recovery (IOR)* and *Enhanced Oil Recovery (EOR)*. Traditionally, large vacuum towers and oxygen scavengers are used, but this is changing. Today's water flooding activities require lower dissolved oxygen specifications, minimal chemical use, and optimized use of available space and weight limits.

Another important use of degassing equipment is to *prevent bubble formation*. For instance, bubbles can be formed in water if excess nitrogen has been absorbed from a nitrogen blanketed storage tank. Once the water leaving the tank is pressurized, the nitrogen will come out of solution in the form of bubbles. The bubble and foaming problems may be solved by simply removing the nitrogen from the water as it exits the tank with membrane contactors degassing modules. In analytical and

measurement systems also, bubbles can negatively impact the readings of the equipment. Bubbles can be read as particles, for example, in particle monitors. Another important field of application is ink jet printers, which are adversely affected by bubbles in the fluid stream. These bubbles can create ink starvation to the print head. They can also cause foaming problems at the filler. Contactors, using only a single membrane contactor will be adequate to reduce the gas concentration to satisfactory levels. Polyolefin hollow fiber membrane with a denser outer membrane wall are used for this purpose. This denser outer wall forms a barrier between the vacuum phase and the ink or coating. The membrane maintains its gas permeability allowing the gasses to be removed from the ink or coating through the membrane wall. The gas will travel through the membrane into the hollow fiber lumens while ink and other aqueous fluids will stay on the outside of the membrane and continue on through the ink jet or coating system. A vacuum phase will be introduced to the lumen side (inside) of the hollow fiber membrane. Membrane contactors offer several distinct advantages over existing technologies: a small footprint first, allowing to be installed anywhere in the system (e.g. right at the print head for printers) or further upstream in the process: moreover, they are very simple to operate and the gas content in liquid process streams can be maintained very precisely.

The specific case of carbon dioxide removal from water is also achievable by membrane contactors. Carbon dioxide is commonly found in water supplies throughout the world. It is produced from the dissolution of  $MgCO_3$  and  $CaCO_3$  (magnesium and calcium carbonate). When carbonates dissolve in water, they form magnesium, calcium, carbonate and bicarbonate ions and carbon dioxide gas. The concentration of each depends on the pH of the water source. A Reverse Osmosis unit, very often used for water purification, will reject the ionic species, however, the carbon dioxide gas will freely pass through the membrane. The dissolved  $CO_2$  gas that passes through the membrane will again ionize. This will be a source of ions in the water that will increase the conductivity of the water. When adjusting the pH, chemicals can be added to the water. This adds however to the contamination of the reject water that needs to be treated. Water that has high alkalinity may also foul the RO membrane. In order to prevent this fouling, anti-scalants are typically used. This again increases the chemicals added to the water. A second alternative for  $CO_2$  removal from the water is to remove the gas from the water using a strip gas. This

has traditionally been accomplished by using a forced draft decarbonation tower. In a decarbonation tower, water flows over a packing material and air is blown into the tower. As the water flows over the packing material it forms a thin film that is in contact with the air. The carbon dioxide preferentially moves from the water into the air stream and it is removed or "stripped" from the water. In a water purification unit, classically combining Reverse-Osmosis and Electrode Ionization, a forced draft decarbonation tower is not practical due to its size and risk of adding contaminants back into the post water. Membrane contactors offer a compact, clean, low-cost alternative to the conventional decarbonation tower.

Other processes are also improved with the introduction of nitrogen into the water or fluid. Ultrasonic and megasonic cleaning, for example, is improved if the oxygen is removed and some nitrogen is added to the water.

### **Water carbon dioxide absorption (beverages)**

Membrane contactors offer an efficient means to carbonate a beverage or liquid. The addition of carbon dioxide gas to a beverage is what gives it its sparkle and a tangy taste. Adding carbon dioxide can also prevent spoilage and reduce bacteria in liquids. Rather than sparging CO<sub>2</sub> gas bubbles into a liquid through a direct contact equipment, membrane contactors diffuse the CO<sub>2</sub> into the liquid on a microscopic level. This produces a much more controlled level of carbonation in the end product. The process of dissolving CO<sub>2</sub> into the liquid is much more controlled and less CO<sub>2</sub> gas is required to get to the same level of carbonation as sparging systems that are very wasteful. In most cases, this reduces operating costs to the end user while producing a superior end product.

### **Aroma recovery, gas exchange in food industry**

Membrane contactors are used for the deoxygenation of water, beer and other liquids in the *food and beverage industry*. Oxygen can indeed negatively impact the shelf life, product quality, product consistency and taste.

Alternatively, different biomolecules can be recovered from fluids in the food industry thanks to a controlled stripping process performed by a membrane contactor. Aromas are a typical example but the same operation can be applied to small

molecules such as alcohols, ketones or organic acids. The volatility of the compound is the key property which will govern the efficiency of the extraction. Associated water losses can however be a problem. The membrane contactor solution is nevertheless often favored compared to stripping equipment based on columns or trickle beds.

The food and beverage industry also adds nitrogen to liquids in various processes. Nitrogenation is typically a step used in beverage processing if more bubbles or a thicker 'head' or foam layer on top of the beer is desired.

Membrane contactors are also used to remove gases from ice. Removing the dissolved gas produces cleaner, clearer ice because the gasses that produce a hazy effect are removed resulting in the clear appearance that people like to see in ice.

### **Effluent treatment**

The use of membranes for gas liquid transfer in waste water treatment is reported in numerous studies. Basically, the membrane sparging or bubbleless operation can be interesting for improved oxygen transfer processes. The specific case of oxygenation of wastewater containing VOC's without bubble formation has received particular attention; membrane contactors offer in that case the unique possibility to enable a biological aerobic degradation without an associated stripping mechanism (transfer of the pollutants to air due to bubble flow).

At the contrary, the absorption of a compound present in a gaseous effluent into a solvent (e.g. water) can also be achieved by membrane contactor. Ammonia recovery from a gas stream is a typical example with several units under operation.

### ***Bioreactors and algae production***

The gas liquid absorption of oxygen into bioreactors for bacteria, yeasts or animal cells production is classically performed by sparging air (or oxygen) into stirred bioreactors. Nevertheless, bubbles can generate problems such as foaming (particularly when proteins are present in the liquid) or shear forces with detrimental effects to the cells (e.g. animal cells). In that case, an internal bubble free oxygen transfer can be achieved thanks to a membrane contactor. An external loop, with controlled liquid and gas flowrates, is also possible. The same situation holds for algae production, with CO<sub>2</sub> in place of O<sub>2</sub>. Several studies report the use of

membranes for the dissolution of CO<sub>2</sub> in photo bioreactors. Among different arguments, the possibility to ensure a complete dissolution in a reactor of limited water height (typically 1m in open ponds, due to the drastic decrease of light transfer in the liquid below this level) is often mentioned. A bubbling gas transfer operation is effectively limited to a dissolution ratio around 30% when the liquid height does not exceed 1m.

## **Natural gas treatment and carbon capture**

Membrane contactors can be of major interest for off-shore gas treatment, because of their small weight and footprint. The absorption of CO<sub>2</sub> and H<sub>2</sub>S from natural gas is a very large market for absorption units (cf. Table 1) and numerous attempts have been reported in order to replace absorption columns by membrane contactors. This development has been mostly reported by Kvaerner company with off-shore units for natural gas purification. Membrane wetting and polymer degradation due to the chemical aggressive environment (concentrated amine solutions, such as MEA) generate specific problems. Teflon (PTFE) membranes have been proposed in that case, because standard PP hollow fibers are not stable in contact to MEA.

Gas drying thanks to water absorption in a glycol liquid (such as TriEthyleneGlycol, TEG) has been also occasionally attempted, but this application does not seem to be intensively applied.

The last, potential major market of chemical absorption by membrane contactors is the post combustion carbon capture (PCC), detailed in the introductory part of this chapter. The intensification effect expected, compared to packed columns, is a major advantage and has received considerable attention. An intensification factor around 4 seems to be achievable. The industrial deployment of PCC is however not realized yet. The materials and process challenges of absorption in chemical solvents, with CO<sub>2</sub> absorption in MEA as an illustrative example, have been discussed throughout this chapter (high mass transfer coefficient in the liquid which imposes a very high membrane mass transfer, wetting and membrane degradation issues, scale up needed to produce large modules...). More generally, the application of post-combustion carbon capture in industry (power plants, cement and steel factories, petrochemistry...) requires dedicated economic incentives and international



regulations before becoming a reality. The possibility for membrane contactors to find applications for this challenging problem would be undoubtedly a breakthrough in terms of market and in order to prove that the membrane contactor concept can compete to conventional chemical absorption technologies for very large capacities.

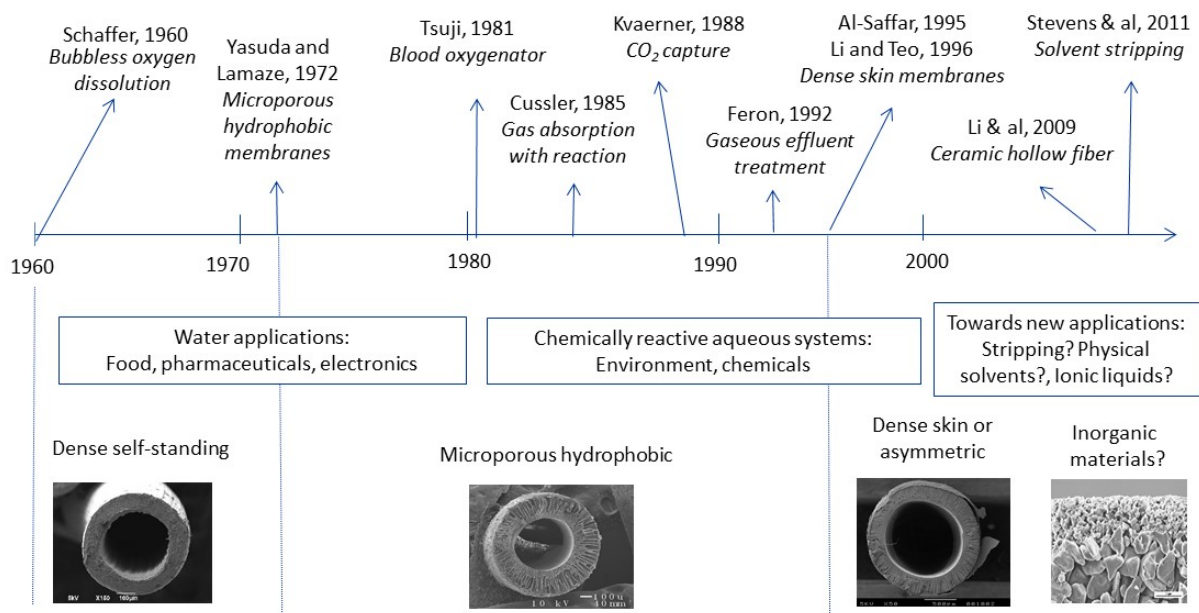
## CONCLUSION, FUTURE TRENDS AND PROSPECTS

The different previous sections on the state of the art and challenges of membrane contactors have shown that the novel concept of using a permeable membrane for gas-liquid absorption processes, suggested in the 60's, is gradually progressing for different industrial applications. The key advantages of membrane contactors, summarized in the introduction, effectively offer attractive potentialities, compared to conventional equipment. The possibility to achieve a significant unit volume reduction, so called process intensification, is one of the most appealing feature. Surprisingly, very few studies report a quantitative evaluation of the volume reduction factor offered by a given membrane contactor for a specific application. Theoretical arguments suggest impressive values of the intensification factor up to 30, while a very limited number of pilot studies end up with a value of 4, for post combustion carbon capture for instance. Whatever the level of the intensification provided by this new technology, a significant effort should be provided to better evaluate this indicator over a broad range of situations. The important problem of the energy requirement of a membrane contactor in order to attain a certain level of intensification is largely unexplored. This should be systematically investigated in order to identify the best trade-off between intensification and energy efficiency [17].

Coming back to the global mass transfer performance indicator  $K_a$  (cf. Table 2), the membrane contactor concept addresses a series of challenges, and important associated issues.

The *membrane material selection and production* clearly and logically correspond to an essential prerequisite. A large  $K$  value, corresponding to a negligible membrane mass transfer resistance is an absolute necessity. Interestingly, both porous hydrophobic and dense permeable membranes have been initially proposed for practical operation. Nevertheless, most of the current applications are based on PP hollow fibers, because of the too low permeability of dense polymers. Porous PTFE, dense skin Teflon-AF and SPEEK have been more recently developed with better wetting, thermal and chemical resistances. It is important to note however that the large ratio of industrial applications correspond to gas absorption or stripping in (from) aqueous fluids, in a clean environment (pharmaceutical, medical, food, electronics, process water). These systems indeed ensure a large surface tension

(thus limiting wetting problems) and a soft chemical and thermal environment. The extension of membrane contactor concept to low surface tension non aqueous solvents or chemically reacting systems or harsh environments (such as caustic, acid, high temperature, high pressure, aggressive gases such as Cl<sub>2</sub> or O<sub>3</sub>), which correspond to the most frequent industrial context (cf. Table 1) will necessitate further membrane developments. The same holds for stripping operation, be it by steam, depressurization or heat. Composite dense skin membranes or inorganic materials such as ceramics could offer a strong chemical and temperature resistance but the production of industrial inorganic membranes for contactor applications is far to be achieved. The tentative evolution of membrane materials discussed before is illustrated on Figure 16.



**Figure 16 : Membrane contactors material evolution since the 1960s [113]**

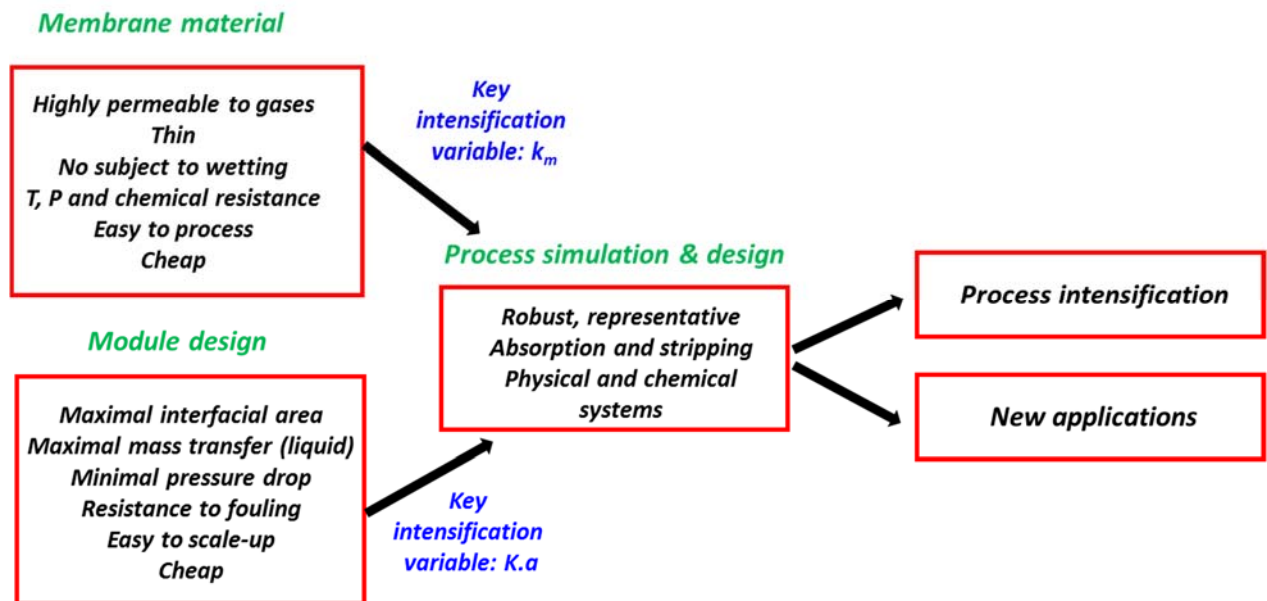
Module design and operation is another challenge, with hollow fiber modules being the preferred geometry. As soon as the membrane mass transfer performances are maximized (previous paragraph), the mass transfer resistance will be mostly located in the liquid phase. It is thus necessary to provide the maximal liquid mass transfer coefficient thanks to fluid flow and contactor design. Turbulence promoters, spacers or fluid flow restrictions can be of interest, but the impact in terms of pressure drop should absolutely be taken into account. The application of a similar strategy to packings has given impressive mass transfer improvements, such as structured

packings. It might be that advanced CFD studies offer novel and improved geometries for maximizing the liquid mass transfer coefficient, and from this the intensification potential. The specific case of viscous liquid solvents (such as physical solvents, glycols for drying operations or ionic liquids), requires dedicated studies. Apart from the mass transfer maximization, scale-up is a major challenge of membrane contactor modules. Given the modular characteristic of membrane operations, a significant module size is most often necessary for industrial applications, in order to limit the number of modules. Very few modules of industrial size are available today. The extrapolation of results obtained on lab scale modules, which correspond to the large majority of published results, to the industrial scale, addresses important issues. The fluid distribution of large hollow fiber modules is indeed complex and dispersion effects can significantly decrease the process performances. Solutions to this problem have been proposed for gas or liquid separations but the peculiarities of gas-liquid operation may call for tailor made designs. The very large range of liquid / gas volume flow, specifically applicable with membrane contactors (cf. Table 2), probably generate different situations in terms of gas and fluid distribution characteristics. These aspects are once more essentially unexplored in the open literature.

Finally, by analogy to conventional gas-liquid absorption equipment, rigorous and efficient simulation tools are of major importance in order to promote the use of membrane contactors in different industrial sectors. Interestingly, simulation approaches for the gas-liquid absorption processes based on packed columns in a Process Simulation Engineering software, usually make use of a predictive mass transfer coefficient method, while the interfacial area usually requires an empirical correlation. The modelling section overview detailed above has shown that a reverse situation is typical of membrane contactors: the interfacial area is usually expected to be precisely known from the module geometry, while the mass transfer coefficient, especially in the membrane domain, is usually taken as an adjustable parameter.

It is expected that the joined efforts in membrane materials, module design and process simulations challenges listed above will contribute to a significant deployment of membrane contactors for intensified, energy efficient and sustainable gas-liquid absorption processes. A synoptic diagram of the synergy between these different challenges is proposed on Figure 17. After trays, random packings and

structured packings, the membrane gas-liquid contactor concept could lead to the fourth generation of gas-liquid contacting equipment.



**Figure 17: Schematic interplay between membrane material, module design and process system engineering for membrane contactors intensification and extension to new industrial applications.**

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