



Norwegian University of
Science and Technology

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Chemical Engineering

Submission date: June 2016

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PREFACE

Here it is the work of my last six months. This work has required me hours and hours of experiments in the laboratory and more than one headache. I hardly remember someday in which I've been resting or doing other things instead of working in the lab. It probably won't be possible to appreciate how much work there is behind each point in a graphic or each phrase in the document. However, I think I've learned not only about membranes, but also about how to face some kinds of problems. And finally, I think I'm ready to face the world and try my best.

I would like to thank those persons who make this work possible in some way. First of all, I would like to thank to Professor May-Britt Hägg for giving me the chance to work in this group and accept me to do my Master Thesis. I also would like to thank Maria Teresa Guzman Gutierrez for teaching me how to manage most of the equipment in the beginning of my work. My most sincere gratitude to Arne Lindbråthen who was the person most helped me through all my work, giving me advices, solving a lot of my problems and trying to help me in every time he could. This work wouldn't be possible without him.

Thanks to my family, my parents and brother, who have been feeling as me in every moment and giving me strength to keep fighting. Thanks for making a big effort to allow me to be here, in Norway, for one year. And finally, thanks to my girlfriend for recharging my energy when I most needed, raising my self-esteem when everything was wrong and being positive to cheer me up.

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

ABSTRACT

Carbon dioxide needs to be separated from natural gas or biogas streams and membrane contactors can be a very good alternative for it. In this work a poly(1-trimethylsilyl-1-propyne) supported by a polyvinylidene fluoride membrane, also referred as composite PTMSP-PVDF membrane, was studied.

Firstly, a short review of membrane contactors in literature was made, finding out which materials and absorbents are mostly used and understanding which the most important parameters are. Mass transfer theory through a membrane contactor was briefly explained too.

Characterization techniques were used to study the permeability, contact angle and structure. The membrane showed a very high permeability, near to 28000 barrers for CO₂, as well as a nice hydrophobicity. However, it showed a not very good stability what should be studied in further works.

The mass transfer in a flat sheet composite PTMSP-PVDF membrane contactor was studied by running different experiments and measuring the CO₂ flux as well as the CO₂ removal efficiency. The effect of gas flow rate, inlet CO₂ concentration, gas pressure, liquid flow rate was studied both for distilled water and NaOH solution as absorbents. The results obtained were discussed to see if it was in agreement with the mass transfer theory and comparing them with literature.

Lastly, the conclusions and future recommendations were postulated. The mass transfer needs to be studied in a well-designed module and at more realistic conditions to ensure that the membrane is appropriate to the process is going to be used. And also, stability of the membrane needs to be improved with, for instance, crosslinking techniques that have shown good results in other works.

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LIST OF SYMBOLS

Symbol	Meaning	Units
Latin characters		
A	Area	m ²
b	Hole solubility coefficient	bar ⁻¹
c	Concentration	m ³ (STP)/m ³
c' _d	Saturation solubility coefficient	m ³ (STP)/m ³
c _d	Gas concentration based on Henry's law	m ³ (STP)/m ³
c _h	Gas concentration based on Langmuir sorption	m ³ (STP)/m ³
D	Diffusivity	m ² /s
D _k	Knudsen diffusion coefficient	m ² /s
d _h	Hydraulic diameter	m
E	Enhancement factor	-
H	Henry's law constant at ideal conditions	m ³ (STP)/m ³ bar
Ha	Hatta number	-
J	Flux	mol/m ² s
k	Constant reaction rate	m ³ /kmol s
k _d	Henry's law constant at non-ideal conditions	m ³ /m ³ bar
k _g	Gas mass transfer coefficient	m/s
k _{npm}	Nonporous membrane mass transfer coefficient	m/s
k _{pm}	Porous membrane mass transfer coefficient	m/s
k _l	Liquid mass transfer coefficient with reaction	m/s
k ^o _l	Liquid mass transfer coefficient with no reaction	m/s
K _{ov}	Overall mass transfer coefficient	m/s
L	Length of the tube	m
l	Thickness	m
M _w	Molecular weight	-
p	Pressure	bar
P	Permeability	Barrers
R	Gas constant	Bar L/K mol

Re	Reynolds number	-
r_p	Pore radius	m
$r_{p,max}$	Maximum pore radius	M
S	Solubility	$m^3(SYP)/m^3bar$
Sc	Schmidt number	-
Sh	Sherwood number	-
T	Temperature	K
V	Volume	m^3
x	Distance	m
Greek characters		
α	Selectivity	-
Υ	Surface tension	N/m
Δ	Finite difference	-
ε	Porosity	-
θ	Contact angle	°
μ	Dynamic viscosity	Pa s
ρ	Density	Kg/m^3
τ	Tortuosity	-
Subscripts		
A	Component A	-
B	Component B	-
B,0	Component B at the bulk	-
f	Feed	-
i	Component i	-
i,i	Component i at the interface	-
i,0	Component I at the bulk	-
p	Permeate	-
Abbreviations		
AMP	2-amino-2-methyl-1-propanol	
DEA	Diethanolamine	
DGA	Diglycolamine	
DIPA	Diisopropanolamine	
MEA	Monoethanol amine	
MDEA	N-methyl diethanolamine	
PDMS	Polydimethylsiloxane	
PE	Polyethylene	
PEI	polyetherimide	
PES	Polyethersulfone	
PET	Polyethylene terephthalate	
PI	Polyimide	
PP	Polypropylene	
PPO	Poly(phenylene oxide)	
PS	Polysulfone	
PTFE	Polytetrafluoroethylene	

PTMSP	Poly(1-trimethylsilyl-1-propyne)
PVDF	Polyvinylidene fluoride
TEA	Triethanoamine

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CHAPTER 1: INTRODUCTION

“Science is the great antidote to the poison of enthusiasm and superstition”.

- Adam Smith.

Carbon dioxide is one of the major contributors to the greenhouse effect. Natural gas can contain significant amounts of CO₂, oscillating between 5-70% (William Echt 2009). The presence of carbon dioxide reduces the heating value of natural gas, and produces, due to its acidic character, corrosion in the pipelines and equipment (Astarita 1983), what makes relevant removing of it from natural gas. Export gas from the platform had to be dehydrated and meet a pipeline specification of 8% CO₂ (William Echt 2009).

The physical and chemical properties of the biogas are similar to those of natural gas. The main constituents of biogas are methane (CH₄), carbon dioxide (CO₂) and trace of hydrogen sulfide (H₂S). The constituents depend on the source's compositions but CO₂ concentration can vary between 24-41% (Rasi, Veijanen et al. 2007). This carbon dioxide needs to be removed from biogas depending on the applications.

The most extended method to remove the CO₂ in the industry is the gas absorption in packed towers, spray towers, venturi scrubbers, bubble columns, etc. Despite of its popularity, this technology has several disadvantages as high energy consumption during desorption, flooding or entrainment (Simons, Nijmeijer et al. 2009).

1.1 Membrane contactors

In the last decades, a new alternative technology, the membrane contactors, have been developed. It may be considered as a combination of a gas absorption technology and membrane technology. This new method offers several advantages over the other technologies. In a membrane contactor the membrane is the interface between the gas and the absorption liquid. This membrane acts like a barrier between the two phases, avoiding mixing them, while the absorption liquid provides the selectivity to the separation.

Membrane contactors have been investigated extensively since the 1980s for a wide range of applications. The main of them are summarized in table 1.

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Table 1. Main membrane contactors applications (Enrico Drioli 2005) (Klaassen, Feron et al. 2005).

Operations	Applications
Control of dissolved gases in liquids	Bubble-free ozonation, bubble-free oxygenation in aqueous and blood streams, etc.
Aroma compounds from aqueous feeds	
Wastewater treatments	VOCs removal, extraction of aromatic compounds, ammonia removal, etc.
Metal ions extraction	Copper, chromium (VI), cobalt, zinc, etc
Liquid-liquid extractions	Separation of phenylacetic acid from mandelic, separation of acetic acid from water, etc.
Pure water production by membrane distillation	Pure water production by membrane distillation
Concentration of agro-food and biological solutions by membrane and osmotic distillation	Concentration of juices and must, recovery of toxins and solute-free water from blood and plasma, etc.
Gaseous streams treatments	Acid gas removal, VOCs removal, SO ₂ and Hg removal, separation of oxygen from air, etc.
Phase transfer catalysis	Catalytic oxidation of benzyl chloride by H ₂ O ₂ , production of S-naproxen, etc
Membrane emulsifiers	Preparation of fine particles, monodispersed oil/water emulsions, etc.
Membrane crystallizers	Production of crystals of salt and proteins.
New applications	Interfaces for mass spectroscopy, removal of salt contained in water droplets dispersed in oil, etc.

But one of the most interesting applications of membrane contactors is CO₂ capture from combustion flue gas, natural gas sweetening and biogas. Particularly, in this case, carbon dioxide diffuses from the gas through the membrane and then is selectively absorbed in the liquid, as is shown in figure 1. Depending on the type of membranes used, the membrane can contribute to the selectivity of the process (Simons, Nijmeijer et al. 2009).

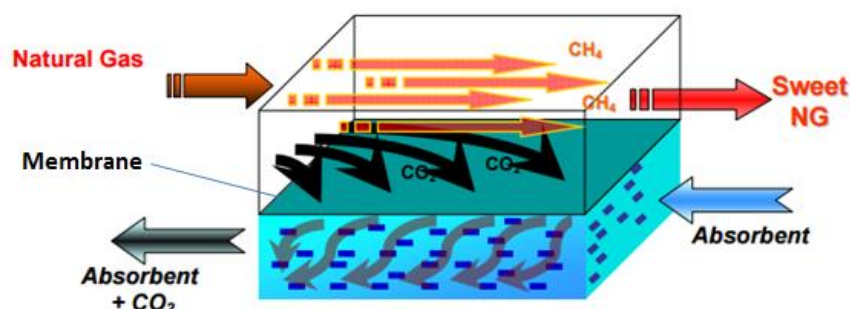


Figure 1. Scheme of membrane contactor in natural gas sweetening (Karen Nessler Seglem 2011).

Table 2 shows how, in the last years, big efforts have been made to investigate CO₂ capture using membrane contactors. A number of different membrane configurations have been studied: flat sheet, spiral wound, rotating annular and hollow fiber. This last one is the configuration which has received most attention and is available for industrial use. This is due to the compact units and high specific surface area (Mansourizadeh and Ismail 2009).

Table 2. Some of the investigation of CO₂ capture with membrane contactors in last years.

Membrane	Configuration	Absorbent	Reference
PP, PTFE	Flat sheet, Hollow fiber	Water, propylene carbonate, n-Formyl morpholine, Glycerl triacetate	(Dindore, Brilman et al. 2004)
PP, PTFE	Hollow fiber	MEA, AMP	(deMontigny, Tontiwachwuthikul et al. 2006)
PP	Capillary	MEA	(Bottino, Capannelli et al. 2008)
PVDF, PTFE	Hollow fiber	MEA	(Rajabzadeh, Yoshimoto et al. 2009)
PP, PPO	Hollow fiber	MEA	(Simons, Nijmeijer et al. 2009)
PVDF	Hollow fiber	Water, NaOH	(Mansourizadeh, Ismail et al. 2010)
PP coated by PTMSP	Hollow fiber	MEA, MDEA, TETA	(Chabanon, Bouallou et al. 2011)
PVDF, PS	Hollow fiber	MDEA-DEA, MDEA-MEA	(Hedayat, Soltanieh et al. 2011)
-	Hollow fiber	Propylene carbonate	(Cai, Hawboldt et al. 2012)
PS	Hollow fiber	Water	(Rahbari-Sisakht, Ismail et al. 2012)
PVDF	Hollow fiber	Water	(Rahbari-Sisakht, Ismail et al. 2012)
PEI	Hollow fiber	MEA	(Zabih A. Tarsa 2015)

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As stated before, membrane contactors have several advantages over others gas separation methods:

1. Membrane contactors are a flexible modular energy efficient device with a high specific surface area and can achieve a very high selectivity and a high driving force even at low concentrations, what results in very compact equipment (Mansourizadeh and Ismail 2009).
2. The contacting area remains constant even at high or low flow rates, avoiding the typical problems of flooding or unloading that packed towers have. Thus, it's easier to achieve a flexible operation (Bottino, Capannelli et al. 2008).
3. Dense membranes are usually not able to achieve a high removal efficiency and a high selectivity simultaneously, while membrane contactors can get it even at very low concentrations without any loss of the main gas (Mansourizadeh and Ismail 2009).
4. Scaling-up the membrane contactors is more straightforward than other technologies. Increased capacity can be achieved by adding more modules. This also permit to operate over a wide range of capacities (Bottino, Capannelli et al. 2008).
5. For acid gas capture, membrane contactors have lower costs than conventional absorbers (Mansourizadeh and Ismail 2009).

In the other hand, membrane contactors have also some disadvantages:

1. The membrane adds another resistance to the mass transfer that doesn't exist in an absorption process. Depending on the type of membrane this resistance could be neglected or not. However, membrane resistance can be highly increased if the liquid wets the membrane pores (Wang, Zhang et al. 2005) what makes the operation economically unviable.
2. Membrane contactors performance can be affected by the operation conditions as pressure or temperature. The pressure of the liquid side should be higher than the gas side in order to avoid the bubble formation on the liquid side what means loss of gas components. But also, a high pressure in the liquid side can lead to membrane wetting. In addition, the temperature range of the membrane contactor is limited by the thermal stability of the membrane (Li and Chen 2005).

Despite the great opportunities and advantages of this technology, some challenges need to be faced. Some of the most important of the are: the development of novel microporous membranes with excellent antiwetting, chemical and thermal resistances, the utilization of new effective absorbents with low cost for regeneration and excellent compatibility to the membrane used and the development of novel membrane modules that can enhance mass transfer in both the gas and liquid phases (Zhang and Wang 2013). All these factors will be studied in this chapter.

1.2 Absorbents in membrane contactors

Membrane contactors combine membrane with absorption technology. Absorption is clasified in physical, where the gas component is physically dissolved in the liquid phase, or chemical, where the gas component reacts with the liquid phase. Each one have advantages and disadvantages, but only chemical absorption can achieve high purities. Furthemor, chemical absorbents have a higher selectivity, absorption rate and capacity (Mansourizadeh and Ismail 2009).

Absorbent used will have a significantly effect in the performance of the process, so the selection of it will be crucial. The following characteristics should be taken in account (Mansourizadeh and Ismail 2009) (Li and Chen 2005):

- Reaction rate: high absorption rate can be achieved using a high reactive solution for the gas component what reduces the size of the membrane contactor.
- Surface tension: membrane pores can be penetrated and cause the membrane wetting if absorbent solutions with low surface tension are used.
- Easiness of regeneration: chemical absorbents usually need to be regenerated, where big amounts of energy is needed. If the absorbent is regenerated easily, the consumption of energy will be lower.
- Compatibility with the membrane materials: the absorbent shouldn't react with the membrane materials in order to keep a good process performance.
- Others characteristics: availability, prize, environment friendly, etc.

Table 3 shows the most common chemical absorbents used for acid gas removal, which are normally classified in aqueous solutions and amines.

Table 3. Chemical absorbents applied for acid gases removal (Mansourizadeh and Ismail 2009).

Chemical absorbents	Type
NaOH	Aqueous solutions
KOH	
K ₂ CO ₃	
Na ₂ CO ₃	
Na ₂ SO ₃	
NaHCO ₃	
NH ₃	
MEA	Amines
DEA	
MDEA	
TEA	
DIPA	
DGA	
AMP	

1.3 Membrane properties

1.3.1 Membrane structure

The effectiveness of the operation is significantly affected by the membrane structure. In gas separation the most common types of membranes used are porous and composite. Normally, a composite membrane consists in a thin layer of a dense, or semi-porous, polymer over a porous membrane as support. The top layer can be also other kind of polymer, as PTMSP, which is a high free volume polymer, halfway between dense and porous polymers. This kind of membrane is illustrated in figure 2.

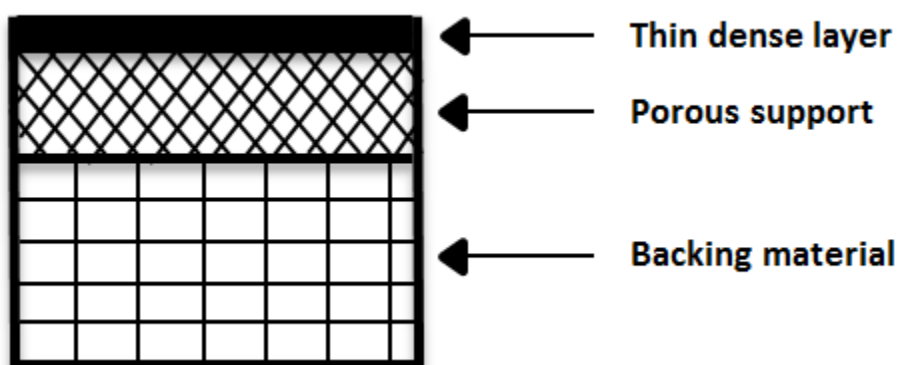


Figure 2. Illustration of a composite membrane structure.

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The most used parameters to compare different membranes are permeability and selectivity. The permeability is an intrinsic characteristic of a membrane to allow the flow through it of a given molecule regardless the pressure applied, the membrane area or the thickness. The selectivity is the ability of a membrane to separate two molecules and is normally given as the ratio between their permeability.

Porous membranes have high permeability but low selectivity, while dense membranes have much less permeability and it depends strongly on the free fractional volume (FFV) of the polymer (free volume/total volume). In general, polymers with higher FFV are more permeable (Mulder 1996).

However, in a membrane contactor the selectivity is not very important due to the absorbent is the main contributor of it in the operation (Mansourizadeh and Ismail 2009). Sometimes, protection against wetting or undesired reaction between absorbent and the membrane material is needed. In these cases composite membranes can be used due to their dense top layer that can serve as a stabilization layer (Li and Chen 2005).

The most common membranes used in gas separation are summarized in table 4.

Table 4. Membrane materials commonly used in gas separation.

Membrane	Type	Reference
PS (polysulfone)	Porous	(Rahbari-Sisakht, Ismail et al. 2012)
PES (Polyethersulfone)		(Bakeri, Ismail et al. 2014)
PE (Polyethylene)		(Falk-Pedersen and Dannström 1997)
PTFE (Polytetrafluoroethylene)		(Falk-Pedersen and Dannström 1997)
PEI (polyetherimide)		(Zabih A. Tarsa 2015)
PP (polypropylene)		(Bottino, Capannelli et al. 2008)
PPO (poly(phenylene oxide))		(Simons, Nijmeijer et al. 2009)
PVDF (polyvinylidene fluoride)		(Wang 2004)
PTMSP (poly(1-trimethylsilyl-1-propyne))	Dense or composite	(De Sitter, Winberg et al. 2006)
PDMS (polydimethylsiloxane)		(Zimmerman, Singh et al. 1997)
PI (polyimide)		(White, Blinka et al. 1995)

1.3.2 Wettability

Membrane wetting occurs when the liquid enters to the pores of the membrane (figure 3b, 3c). This is an undesired event because increases significantly the mass transfer resistance (Wang, Zhang et al. 2005), that can make the operation economically unviable. Thus, the wettability determines the operability of the membrane contactor. Normally, hydrophobic membranes are used to avoid this problem, getting the pores filled by gas (figure 3a).

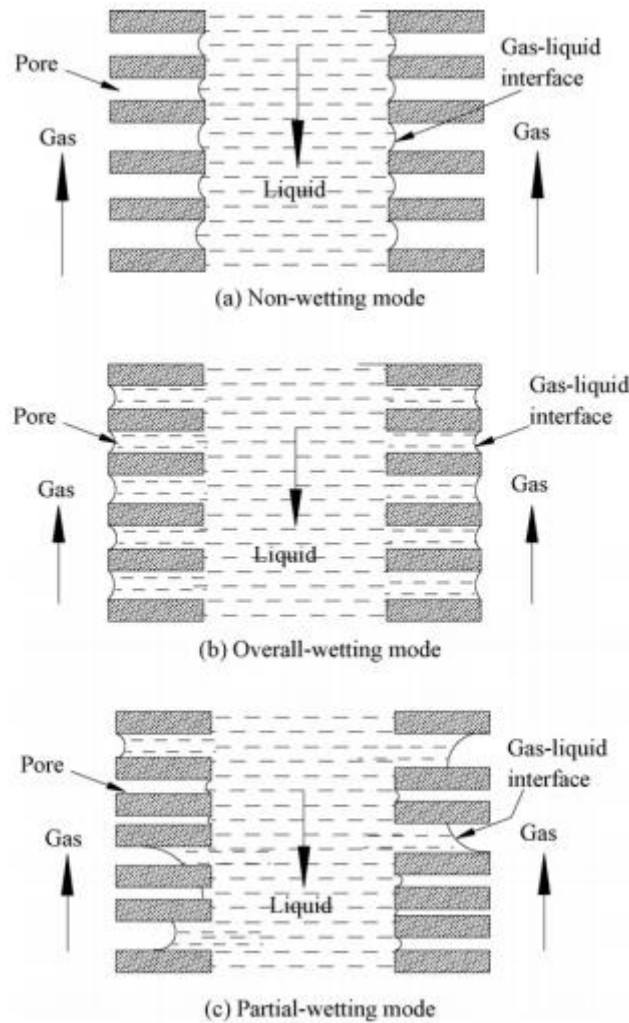


Figure 3. Operation modes in a hydrophobic microporous membrane module and pore wetting patterns gas–liquid interfaces at pores: (a) non-wetting mode, (b) overall-wetting mode, and (c) partial-wetting mode (Lu, Zheng et al. 2008).

The minimum pressure (breakthrough pressure) what makes the liquid enters the pores can be estimated by the Laplace-Young equation (1).

$$\Delta P = \frac{2\gamma \cos\theta}{r_{p,max}} \quad (1)$$

where γ is the surface tension of the liquid, θ the contact angle between the liquid phase and the membrane and $r_{p,max}$ the maximum membrane pore radius.

Wetting problems can be avoided by following some tips (Li and Chen 2005):

- Using hydrophobic membranes. Chemical absorbents used for CO₂ absorption are usually aqueous solution, so the contact angle will increase using hydrophobic membranes, and hence, increasing the liquid pressure range.

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- Membrane surface modification. Hydrophobic modification of a membrane surface can reduce the wettability. This can be achieved by many different techniques (interfacial polymerization, pore filling and more).
- Composite membrane. These kinds of membranes are composed by a dense film and a porous support. The dense film should be hydrophobic to avoid wetting problems, but also should be highly permeable to the targeted gas.
- Selection of denser membranes. The wettability will be lower if denser membranes are selected. However, the mass transfer membrane resistance can increase significantly and, as said before, the operation can be economically unviable.
- Selection of liquids with suitable surface tension.

1.3.3 Chemical stability

The long-term performance of the contactor is greatly affected by the chemical stability of the membrane. Any reaction between the liquid and the membrane material could degrade the matrix and the surface of it. The compatibility of the membrane to the solvent have to be studied in order to avoid this problem (Li and Chen 2005) (Mansourizadeh and Ismail 2009).

Also, membranes with a non-high chemical stability can experience the aging phenomenon. Permeability values can be reduced when a membrane is affected by aging (Starannikova, Khodzhaeva et al. 2004). There are three mechanism of aging of PTMSP:

- Physical aging caused by relaxation accompanied by increases in density and reduction of free volume.
- Chemical aging caused by partial oxidation of the polymer in contact with molecular oxygen from air.
- Absorption aging induced by capture of some non-volatile impurities from environment: they can be components of aerosols, oil from vacuum pump or even plasticizers from O-rings used in permeation cells while measuring the permeability.

One of the most studied solutions to improve polymer stability and to avoid aging is crosslinking. This technique consists on connecting two or more macromolecules to each other with covalent bonds. Crosslinking changes the physical, mechanical and chemical properties of the polymer. Certainly, these changes on the properties can improve stabilization and decrease aging. But, on the other hand, it can decrease permeability values and while uncrosslinked polymers usually dissolve in an appropriate solvent, crosslinked polymers will become insoluble (Mulder 1996).

1.3.4 Thermal stability

The thermal stability of the membrane depends on the glass transition temperature T_g for amorphous polymers. Over this temperature, the properties of the polymers change drastically. The glass transition temperature is mainly determined by the chain flexibility and chain interaction of the polymer structure (Mulder 1996). Thus, the temperature of the process will restrict the membrane material. For the CO_2 off-shore removal from natural gas, since the separation can be carried out at ambient temperatures, membrane with moderate T_g can be considered.

Some polymers are semi-crystalline and consist on an amorphous and a crystalline fraction, where no significant mass transfer takes place. On passing through the glass transition temperature the amorphous glassy state is transformed into the rubbery state but the crystalline phase remains unchanged. So for these kinds of polymers, the glass transition temperature doesn't make a big difference on their properties (depending on the percentage of glass phase), and the loss of their properties happen after overcome the melting temperature T_m . Glass transition temperature is normally measured with the tensile modulus, as shown in figure 4, which is a characteristic parameter for a given polymer and may be defined as the force applied across an area necessary to obtain a given deformation.

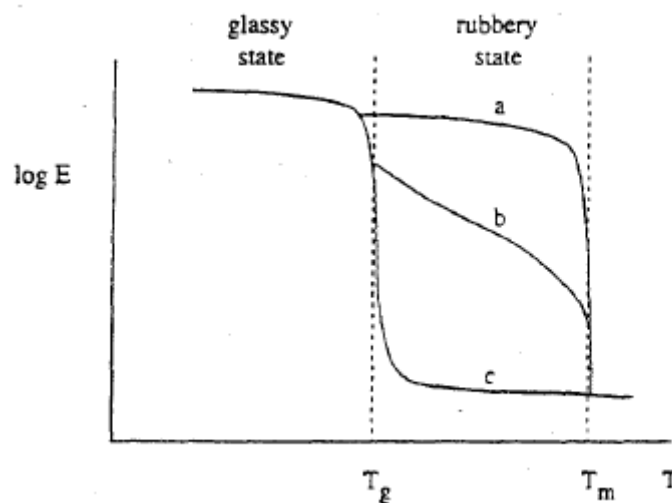


Figure 4. Tensile modulus of a semi-crystalline polymer as a function of the temperature. a) crystalline polymer; b) semi-crystalline polymer; c) amorphous polymer (Mulder 1996).

The glass transition temperatures of the most common membrane materials for gas separation are summarized in table 5.

Table 5. Glass transition temperature of membrane materials (Mulder 1996).

Membrane material	T _g (°C)
PS (polysulfone)	190
PES (Polyethersulfone)	230
PE (Polyethylene)	-120
PTFE (Polytetrafluoroethylene)	126
PEI (polyetherimide)	217
PP (polypropylene)	-15
PVDF (polyvinylidene fluoride)	-40
PTMSP (poly(1-trimethylsilyl-1-propyne))	200
PDMS (polydimethylsiloxane)	-123
PI (polyimide)	300

1.4 Membrane materials

The membrane materials should have a good stability and low wettability. But as the stability of a polymer increases it generally becomes more difficult to process. The two effects, stability and processability, opposes each other. Thus, very stable ladder polymers are not soluble and cannot be processed from the melt as are a number of other thermally stable polymers. In terms of membrane preparation, this means that the polymer must be soluble in a more or less normal solvent in order to apply appropriate preparation techniques.

The most common used membranes have all a relative good chemical and thermal stability and mechanical properties. But not all of them can be easily dissolved during membrane preparation and, at the same time, to have low wettability. Also the cost has to be account since some of them can be very expensive. Table 6 shows the main properties of more often used membrane materials in membrane contactors.

CHAPTER I: INTRODUCTION

Table 6. Main properties of membrane materials (Park, Deshwal et al. 2008), (Rahbari-Sisakht, Ismail et al. 2012), (Ismail and Mansourizadeh 2010), (Khaisri, deMontigny et al. 2009), (White, Blinka et al. 1995), (Bakeri, Ismail et al. 2014), (Zabih A. Tarsa 2015), (Bakeri, Ismail et al. 2010).

Membrane material	Chemical stability	Thermal stability	Mechanical properties	Wettability	Solubility	Cost
PS	High	High	High	Medium	High	-
PES	High	High	High	High	High	Low
PE	-	-	High	Low	-	-
PTFE	High	High	High	Low	Low	High
PEI	High	High	Medium	High	High	-
PP	High	High	High	Medium	Low	Low
PVDF	High	High	High	Medium	High	Low
PTMSP	High	High	High	Low	High	-
PDMS	High	High	High	Low	High	-
PI	High	High	High	Low	High	High

CHAPTER 2: MASS TRANSFER IN MEMBRANE CONTACTOR

“Every natural science contains as much truth as much mathematics contains”.
- Immanuel Kant.

Investigation and studying of the mass transfer is crucial since determines how good the separation will be. Numerous models have been developed to describe mass transfer, and they can be very important since they can describe which parameters affect to the mass transfer, and thus, how to improve it and achieve a better separation.

Mass transfer of a gas component from gas to liquid through a composite membrane contactor occurs in four steps, as illustrated in figure 5:

1. Transfer of gas component from gas bulk to membrane surface.
2. Transfer of gas component through the microporous membrane (PVDF).
3. Transfer of gas component through nonporous membrane (PTMSP).
4. Transfer of gas component from membrane surface to liquid bulk.

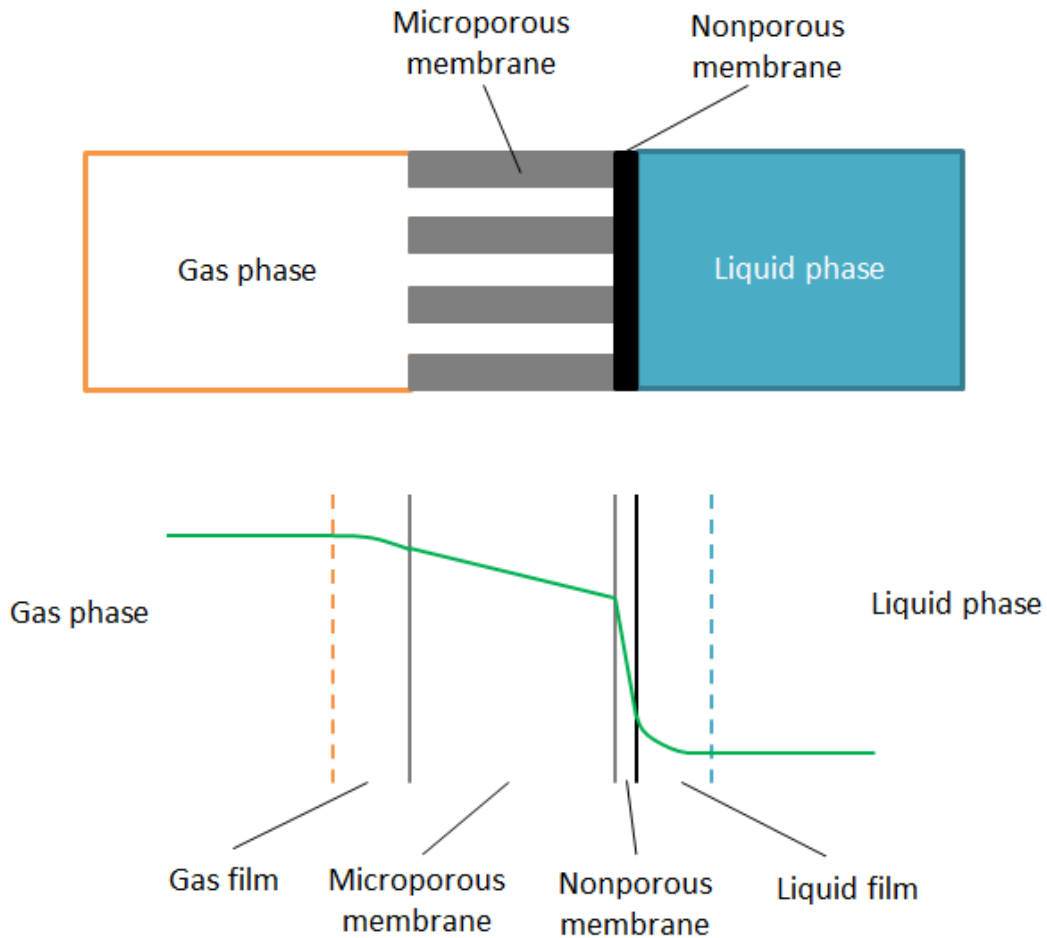


Figure 5. Concentration profile in a composite membrane contactor.

2.1 Mass transfer in gas phase

Molecular diffusion is the principal phenomenon responsible for mass transfer in gas phase. Based on Fick's law the mass transfer through gas film can be calculated by equation (2) (Lewis and Whitman 1924).

$$J_i = k_g \cdot (p_{i,0} - p_{i,i}) \quad (2)$$

where J is flux of component i through gas film, $p_{i,0}$ and $p_{i,i}$ are bulk and interfacial partial pressures of diffusing gas, k_g is mass transfer coefficient for gas film, which depends on diffusivity and film thickness. Gases with low diffusivity show high gas film resistance ($1/k_g$).

2.2 Mass transfer in porous membrane

Some different models have been developed to describe mass transfer in a porous membrane. When the pores are small (20 nm – 0.2 μm) and/or when the pressure of the gas is low, collisions between the gas molecules are less frequent than collisions with the pore wall, as figure 6 shows. This kind of gas transport is called Knudsen and is the most suitable model for asymmetric membranes, like PVDF (Mulder 1996). In this regime the flux is given equation (3).

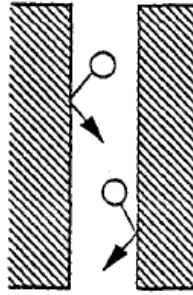


Figure 6. Schematic drawing of Knudsen diffusion (Mulder 1996).

$$J = \frac{\pi \cdot n \cdot r_p^2 \cdot D_k \cdot \Delta p}{R \cdot T \cdot \tau \cdot l} \quad (3)$$

where r_p is the pore radius, Δp the driving force expressed as pressure gradient (partial pressure for mixed gas), τ is the tortuosity which depends on the kind of structure of the membrane, l is the membrane thickness and D_k is the Knudsen diffusion coefficient given by equation (4).

$$D_k = 0.66 \cdot r_p \cdot \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M_w}} \quad (4)$$

where T and M_w are the temperature and molecular weight, respectively.

The separation between different molecules is then inversely proportional to the ratio of the square root of the molecular weights of the gases.

But since the scope of this work is to study a PTMSP-PVDF composite membrane, it's necessary also to go through the transport in nonporous membrane, as PTMSP is.

2.3 Transport in nonporous membrane

The transport of a gas through a nonporous membrane can be described by solution-diffusion mechanism represented by equation (5) (Mulder 1996).

$$P=S \cdot D \tag{5}$$

where S is the solubility, which indicates the amount of gas sorbed by the membrane under equilibrium conditions. And D is the diffusivity, which represents how fast the gas is transported through the membrane and is dependent on the geometry of the fluid molecules. Normally, as the molecular size increases the diffusivity decreases.

For ideal systems the solubility is independent of the concentration, so the sorption isotherm is linear (Figure 7a), expressed with the Henry's law. But for cases in which the solubility depends on the concentration the sorption isotherm is a curve (Figure 7b and Figure 7c).

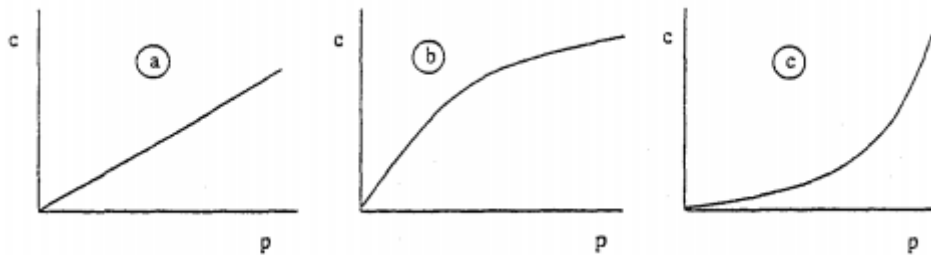


Figure 7. Schematic graphics of sorption isotherm for a) ideal system and b) c) non-ideal system (Mulder 1996).

For glassy polymers, like PTMSP, the dual sorption model can be used, where two sorption mechanisms take place at the same time, Henry's law and Langmuir sorption (Mulder 1996). For this model, the concentration of gas in the polymer "c" is expressed as equation (6).

$$c = c_d + c_h = k_d \cdot p + \frac{c'_h \cdot b \cdot p}{1 + b \cdot p} \tag{6}$$

where c is the total gas concentration, c_d is the gas concentration based on Henry's Law, c_h is the gas concentration based on Langmuir sorption, k_d is the Henry's Law constant, b and c'_h are the hole solubility coefficient and the saturation solubility coefficient of Langmuir, respectively.

Table 7. Dual sorption parameters for CO₂, CH₄ and N₂ (Merkel, Bondar et al. 2000).

Parameters	CO ₂	CH ₄	N ₂
k_d (cm ³ /cm ³ atm)	1.05	0.5	0.08
c'_h (cm ³ /cm ³ polymer)	130	62	74
b (atm ⁻¹)	0.04	0.05	0.014

CHAPTER II: MASS TRANSFER IN MEMBRANE CONTACTOR

In the case of $b \cdot p \ll 1$, what seeing b parameter from table 7 is easily achieved at low pressures, the gas solubility in glassy polymers is proportional to the applied gas pressure as modeled by Henry's law, represented by equation (7).

$$c = S \cdot p \quad (7)$$

where c , S and p is the concentration, solubility and pressure, respectively, of a given component.

The transport through the membrane takes place with a flux based on the Fick's law, represented by equation (8).

$$J = -D \cdot \frac{dc}{dx} \quad (8)$$

where J is the flux of the component, D is the diffusivity and dc/dx is the concentration gradient for a component over the length x , the partial pressure gradient for gases, between feed and the permeate side of the membrane. This gradient is known as the driving force and is the responsible for inducing the flux. Whenever a concentration or partial pressure gradient exist, a proportional flux will be induced.

Integrating equation (8) under steady-state conditions over a membrane with a thickness l , a feed partial pressure p_f and a permeate partial pressure p_p , the flux for a component can be expressed as in equation (9).

$$J = \frac{S \cdot D \cdot (p_f - p_p)}{l} \quad (9)$$

And combining this equation with equation (7) and (5) gives equation (10).

$$J = \frac{P}{l} \cdot (p_f - p_p) = \frac{P}{l} \cdot \Delta p \quad (10)$$

2.4 Mass transfer in liquid phase

Absorption of gas in liquid depends on the diffusion through liquid film and on the rate of reaction between gas and solvent in the case of chemical absorption. If there's no chemical reaction, physical absorption take place and the amount of gas taken up by liquid is estimated by Henry's law. Flux of a gas through liquid can be estimated by equation (11) (Lewis and Whitman 1924).

$$J_i = k_l \cdot (C_{i,i} - C_{i,0}) \quad (11)$$

where $C_{i,i}$ and $C_{i,0}$ are interfacial and bulk concentrations of absorbed gas, and k_l is liquid side mass transfer coefficient.

CHAPTER II: MASS TRANSFER IN MEMBRANE CONTACTOR

In absorption process where chemical reaction occurs, diffusion through liquid film and reaction between solvent and gas molecules takes place both at the same time, so concentration of gas and solvent both changes along liquid film. Due to chemical reaction, mass transfer is improved and liquid side mass transfer coefficient is corrected by a factor called Enhancement factor. This is the ratio of liquid side mass transfer coefficients with reaction, k_l , and without reaction, k_l^0 , as expressed in equation (12). When chemical reaction doesn't occur, Enhancement factor is equal to 1, thus both coefficients are equal.

$$E = \frac{k_l}{k_l^0} \quad (12)$$

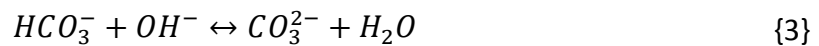
This factor can be calculated using the Hatta number (Ha) and infinite enhancement factor E_∞ . Hatta number describes the relation between the rate of the reaction and the rate of physical mass transfer. For a first order reaction between two reactants, A and B, Hatta number can be calculated with equation (13).

$$Ha = \sqrt{\frac{D_A \cdot k \cdot C_{B,0}}{k_l}} \quad (13)$$

Infinite enhancement factor can be calculated with different equations depending on how fast is reaction compare to physical absorption. For the system of this work, CO₂ as gas absorbed and NaOH as solvent, the reaction is considered fast (Tontiwachwuthikul, Meisen et al. 1992). This is all reaction take place in the liquid film. For this regime, Enhancement factor is expressed as equation (14) shows.

$$E_\infty = Ha \quad (14)$$

The reactions occurring during absorption of CO₂, into sodium hydroxide solution can be expressed by the following equations:



Reaction {1} represents the process of physical dissolution of gaseous CO₂, into the liquid solution, in which the rate is comparatively very high to the rest of reactions, so the equilibrium at the interface can be assumed. Furthermore, the rate of reaction {3} is significantly higher than that of reaction {2}. Hence, reaction {2} governs the overall rate of the process, expressed by the equation (15) (Pohorecki and Moniuk 1988).

$$r = k \cdot C_{OH^-} \cdot C_{CO_2} \quad (15)$$

2.5 Overall mass transfer in membrane contactor

The flux of a gas component “i” can be expressed in terms of an overall mass transfer coefficient as in equation (16).

$$J_i = K_{ov} \cdot \left(\frac{p_{0i}}{H} - C_{0i} \right) \quad (16)$$

where J_i is the flux of a gas component i going through the contactor, k_{ov} is the overall mass transfer coefficient, p_{0i} is partial pressure of i in bulk gas phase, H is Henry’s law constant and C_{0i} is concentration of i in bulk liquid phase.

All the driving forces for transportation through the contactor are incorporated in concentration difference between bulk gas and bulk liquid as an overall driving force. Overall mass transfer coefficient can be calculated as the sum of all the mass transfer coefficients, as showed in equation (17).

$$\frac{1}{K_{ov}} = \frac{H}{k_g} + \frac{H}{k_{pm}} + \frac{H}{k_{npm}} + \frac{1}{k_l} \quad (17)$$

where k_g , k_{pm} , k_{npm} and k_l are the gas film, porous membrane, non-porous membrane and liquid film resistances respectively.

Gas film and liquid film with no reaction coefficient are related with Sherwood number as show equation (18).

$$Sh = \frac{k_g \cdot d_h}{D} = a \cdot Re^b \cdot Sc^c \cdot \left(\frac{d_h}{L} \right)^d \quad (18)$$

where Re is the Reynolds number, Sc the Schmidt number, and a, b, c and d are constants. Notice that the equation appear k_g but it could also be k_l^0 .

$$Re = \frac{\rho \cdot v \cdot d_h}{\mu} \quad (19)$$

$$Sc = \frac{\mu}{\rho \cdot D} \quad (20)$$

In these equations, d_h the hydraulic diameter, μ the dynamic viscosity, v the flow velocity, ρ the density of the fluid, L the length of the tube or channel and D the diffusion coefficient.

CHAPTER II: MASS TRANSFER IN MEMBRANE CONTACTOR

From equation (18) it can be seen that the mass transfer coefficient k_g or k_l^0 is mainly a function of the flow velocity (v), the diffusion coefficient of the solute (D), the viscosity, the density and the module shape and dimensions. Of these parameters, Flow velocity and diffusion coefficient are the most important (Mulder 1996).

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"We must have perseverance and above all confidence in ourselves. We must believe that we are gifted for something and that this thing must be attained".

- Marie Curie.

3.1 Materials

3.1.1 PTMSP (poly(1-trimethylsilyl-1-propyne))

PTMSP was the polymer used as thin layer over the PVDF support, provided by Fluorochem Ltd (figure 8). PTMSP is a polymer which has been investigated since 1983 by the research group of Higashimura and Masuda at Kyoto University in Japan (Masuda, Isobe et al. 1983). PTMSP is a glassy polymer which is distinct from other ones because of the presence of bulky side groups which obstruct the packing of polymer chains getting a high free fractional volume (FFV) and allow extraordinarily high permeability values of sorbed molecules (Rutherford 2001).

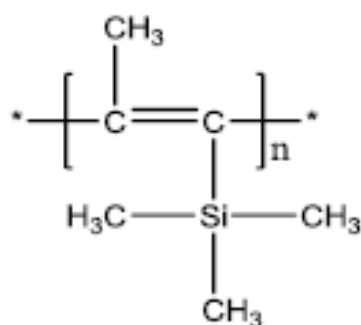


Figure 8. Chemical structure and how it looks PTMSP polymer.

3.1.2 PVDF (polyvinylidene fluoride)

The support of the membrane was PVDF, which is a semicrystalline polymer containing a crystalline phase and an amorphous phase. The crystalline phase provides thermal stability and the amorphous phase flexibility towards membranes. PVDF is stable to the aggression of most of the corrosive chemicals and organic compounds including acids, alkaline, strong oxidants and halogens. This polymer also has a good potential application in membrane-based gas absorption due to its hydrophobicity nature (Ismail 2015).

Membrane support was provided by NADIR® and all the data related is shown in table 8.

Table 8. Support PVDF membrane data.

Support membrane data	
Membrane material	PVDF
Backing material	PET
Nominal pore size [μm]	0,2
Thickness [μm]	180-220

Composite PTMSP-PVDF membrane studied in this work is illustrated in figure 9. It is composed by a thin PTMSP film, PVDF as support and PET as backing material.

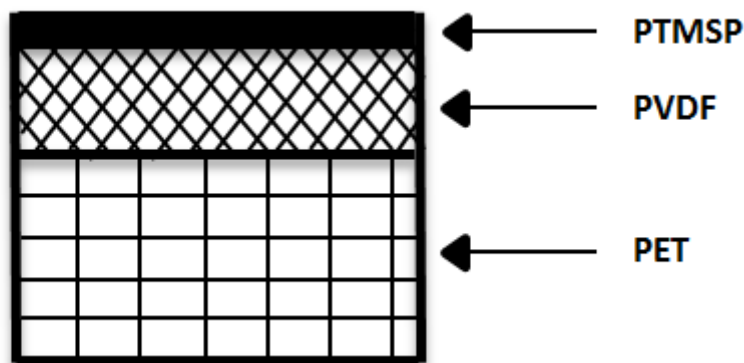


Figure 9. Scheme of the membrane used in this work.

3.1.3 Gases

The gases used in the gas permeability tests were N₂, CH₄ and CO₂, all provided by AGA.

3.1.4 Toluene

Toluene at 99.9% of purity was used as solvent for the PTMSP. It was purchased from SIGMA-ALDRICH.

3.1.5 Sodium hydroxide

Sodium hydroxide, provided by Fluka in pellets form, was used as absorbent in water solution. This aqueous solution has been extensively used in CO₂ capture applications, due to its basic nature, and its kinetics is well known (Pohorecki and Moniuk 1988).

3.1.6 Glues

Two different glues were used:

- Araldite® 2000 PLUS is an adhesive lightweight and form long-term bonds that are resistant to demanding conditions and include a high resistance to shear, peel, compression, moisture and extreme temperature changes. This glue was provided by HUNTSMAN.
- LOCTITE® EA 9483 is a low viscosity and high strength, industrial grade epoxy adhesive. Once mixed, the two-part epoxy cures at room temperature. This glue was purchased from Henkel.

3.2 Membrane preparation

3.2.1 Dense PTMSP membrane

Dense films of pure PTMSP were prepared from solution of 2% of the polymer in toluene. Then, the suspensions were magnetically stirred for 1 day at room temperature. After that, the solutions were filtered with 1.5 µm PTFE filters and coated in a Petri dish. Finally, the solutions were dried for 1 day at ambient conditions and subsequently at vacuum for 1 day more. They were weighed after the drying process to ensure that no toluene was remaining.

3.2.2 Composite PTMSP-PVDF membrane

Sheets of PVDF membrane were cut and cleaned with ethanol to keep the surface out of any dirt. After dry up, a film of 2% PMTSP in toluene solution (already filtered) was applied over a PVDF sheet with a blade, as is shown in figure 10. Then, the membranes were dried at ambient conditions for 1 day and subsequently at vacuum for 1 day more.

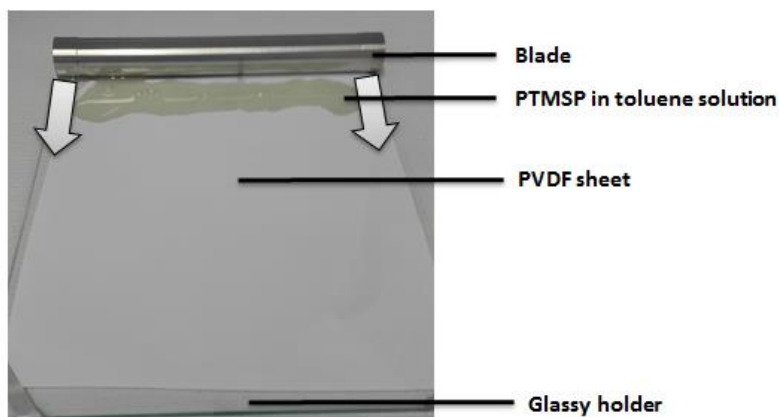


Figure 10. Making of composite PTMSP-PVDF membrane.

3.3 Membrane characterization

Characterization of the membrane materials is crucial for the prediction and the understanding of the membrane performance.

3.3.1 Contact angle measurement

The contact angle θ between membrane and water is a measure of the membrane wettability. It is defined as the angle between the solid and the tangent to the drop at the three phase intersection as indicated in figure 11.

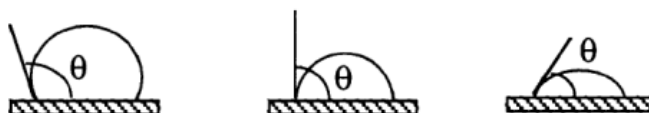


Figure 11. Different contact angles of liquid droplets on a nonporous material (Mulder 1996).

Materials with low affinity to water have a contact angle θ greater than 90° , what means low wettability, whereas with high affinity, the value would be lower than 90° , what means liquid wets the surface (Mulder 1996).

Contact angles were measured by Theta Lite Optical Tensiometer, shown in figure 12, delivered by Biolin Scientific. The software, OneAttension, was used for the Young-Laplace equation to fit the water-drop profile.

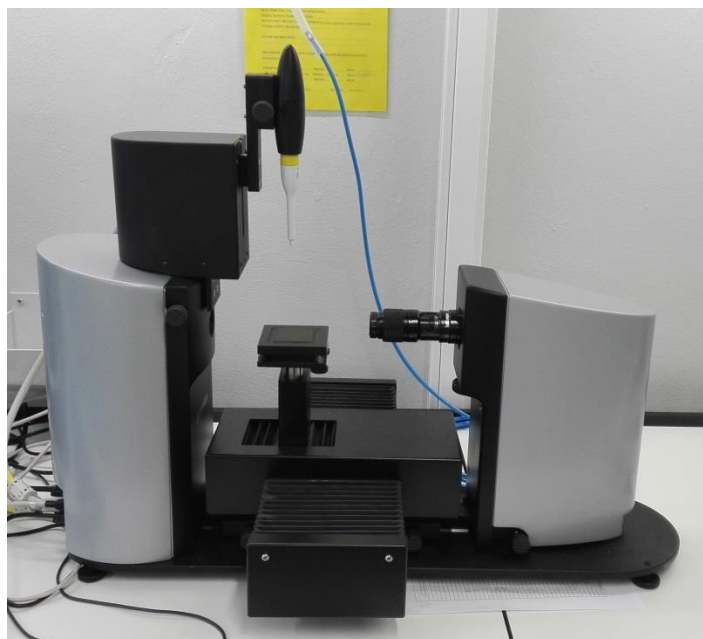


Figure 12. Theta Lite Optical Tensiometer.

The local operation manual for the apparatus was used when doing the contact angle measurements. The software OneAttention was opened and the sessile drop method was selected. A calibration ball was placed on a magnetic holder on the sample stage. The ball was brought into the image on the screen and zoomed appropriately by adjusting the zoom lens. When the calibration ball was in the center and focused, “calibration” was pressed.

Experimental parameters were set, and the calibration ball was replaced by a membrane. Automatic dispenser was used to place a water drop on the membrane surface. When the drop touched the surface the contact angle was measured for 10 seconds.

3.3.2 SEM analysis

Scanning electron microscope Hitachi TM3030Plus (Figure 13) was used to observe the structure of the membrane as well as to measure the thickness of the thin dense layer. SEM images were obtained following the steps described below.



Figure 13, Scanning electron microscope Hitachi TM3030Plus.

First, it was necessary to prepare the sample. A small piece of membrane was cut from the big membrane sheet. It's essential to make a clean-cut; in other case it wouldn't be possible to get a good SEM image due to the overlapping of the two polymers. For that, the small piece of membrane was frozen by introducing in liquid nitrogen. After some minutes, the membrane was taken from the liquid nitrogen and cut by bending it, getting a clean-cut.

The piece of membrane was glued with carbon glue onto the sample holder with the clean-cut facing up as is shown in figure 14.



Figure 14. Sample holder for SEM.

CHAPTER III: EXPERIMENTAL

Before measuring with SEM, the sample needs to be protected against the SEM radiation. So the sample was coated with gold particles using the sputter coater Q150R ES (figure 15) provided by Quorum Technologies.

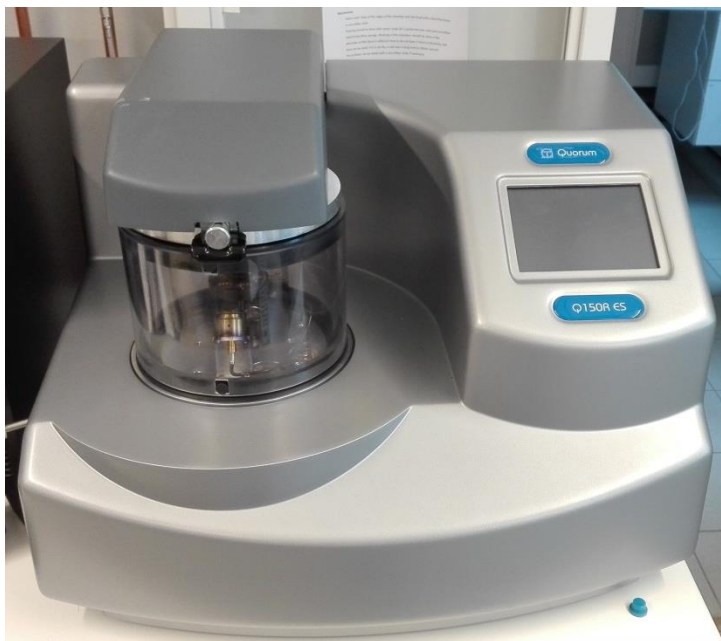


Figure 15. Sputter coater Q150R ES.

3.3.3 Membrane area and thickness

It's essential for calculations of permeability to know the membrane area. But since the boundaries between the membrane and the aluminum tape were glued, this area is unknown, so to find it out, a scanner was used.

The membrane was placed in the scanner and subsequently was scanned. Once the image was obtained, ScionImage software was used to measure the membrane area.

The pure PTMSP membrane thickness was measured by Mitutoyo as shown in figure 16. The thickness of the membrane was measured at different points on the surface and the mean value was used.



Figure 16. Mitutoyo thickness measurements tool.

For the measure of composite PTMSP-PVDF membrane thickness the SEM images were used.

3.4 Membrane gas permeability

Permeability is a crucial parameter since determines how good is a membrane to allow the flow though it of a molecule. So, the higher permeability, the better gas transport, and thus, the better performance of the contactor where the membrane is used.

Permeability of three gases was tested, both in pure PTMSP and PTMSP-PVDF membrane, in the following order: N₂, CH₄ and CO₂, to avoid possible effects on the membrane. N₂ and CH₄ are considered to be non-interacting gases, while CO₂ may show some interaction (Mulder 1996).

Firstly, the membrane was mounted inside the module. For that, the membrane was masked with aluminum tape on both sides leaving a small membrane cross sectional area. Subsequently, the boundary between the aluminum tape and the membrane was glued to prevent gas leakage from feed side to permeate side. The masked membrane was then placed on a metal sinter, which works as a protection for the membrane, on the bottom part of the module. An O-ring, at the upper part of the module, sealed the membrane module when the upper part and the bottom part were assembled. All this process is illustrated in figure 17.



Figure 17. Montage of the membrane in the module.

The module was then connected to the gas permeation system illustrated in figure 18.

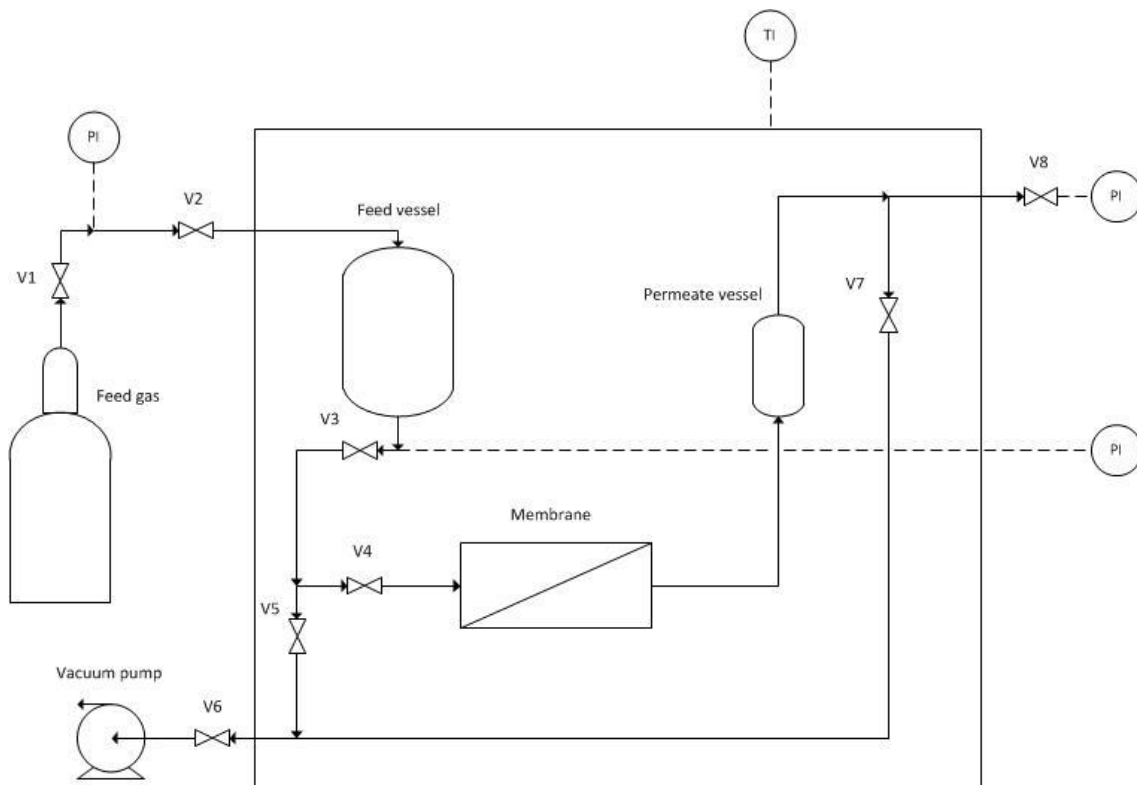


Figure 18. Diagram of the set-up used in membrane permeability test.

Once the module was connected the LabView program file was opened. Before performing the permeability tests the system needs to be evacuated of gas in order to achieve vacuum. So V1, V4, V5 and V7 kept closed, while V2, V3, V6 and V8 were opened. The vacuum pump was turned on then and V5 opened. The feed side pressure sensor showed a decrease of pressure. After that, V7 was slowly opened and the permeate side sensor showed a drop of pressure. And then, V4 was slowly opened. The system was set like this during a night in order to achieve vacuum.

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To ensure that there aren't any leakages in the system, a leak test was performed. So that, V4 and V7 were closed and the pump turned off. The system was left like this for approximately one hour to see if there was an increase in pressure, what it would mean a leakage.

Before start the test, V1 and V2 were opened to fill the feed vessel until the wanted pressure, keeping V4 and V5 closed, and V6, V7 and V8 opened to maintain vacuum in the permeate side. Once the desired pressure in the feed side is reached, V1 and V2 were closed. Finally to perform the test, the LabView was started to logging, V7 was closed, V3 opened, V4 slowly opened and the pump was turned off.

The pressure rise was measured by a MKS Baraton® 0-100mbar pressure transducer. The test took about 10-20 minutes. The permeate pressure transducer was logged in LabView obtaining the evolution of the permeate pressure over the time. With this data, a plot of dp/dt was calculated by linear regression in Microsoft Excel. Calculations and are fully explained in Annex III.

3.5 Membrane contactor measurements

Once permeability was studied, the membrane was tested on a lab-scale flat sheet membrane contactor. The objective of these experiments was to understand which are the main variables affecting the system. This knowledge let to understand how the membrane works and how the system can be improved, manipulating all the variables to optimize the performance during a separation process.

As in the last section, firstly the membrane had to be mounted in the module and it was done in a similar way. The membrane was masked and fixed to the module using aluminum tape and also the boundary between the membrane and the gas phase was glued, using LOCTITE® EA 9483, to prevent any leakage. After this, the module was closed and completely sealed due to the two O-rings, one sealing gas phase, and the other sealing liquid phase, as illustrated in figure 19.

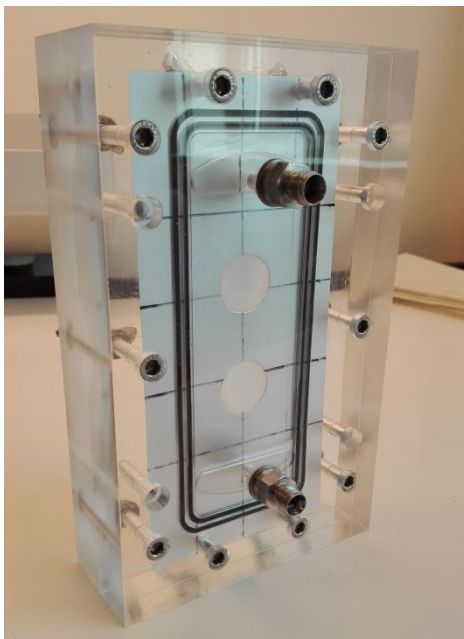


Figure 19. Membrane contactor module.

The set-up showed in figure 20 was used to test the membrane contactor. The system consists on a determined mixture of carbon dioxide and nitrogen stream coming to the membrane contactor. As explained on Chapter 1, certain amount of CO_2 permeates through the membrane to the liquid side. The rest of the gas stream comes out of the contactor to the SIMTRONICS GD10 IR analyzer where the concentration of CO_2 is continuously measured. The liquid is pumped, using Heidolph pump drive 5201, from liquid tank to the membrane contactor, where absorbs some amount of the CO_2 , and exits coming to the wastes tank. All the flows and pressure were controlled using ALICAT RS 385 flow meter and WIKA transmitter s-10 respectively.

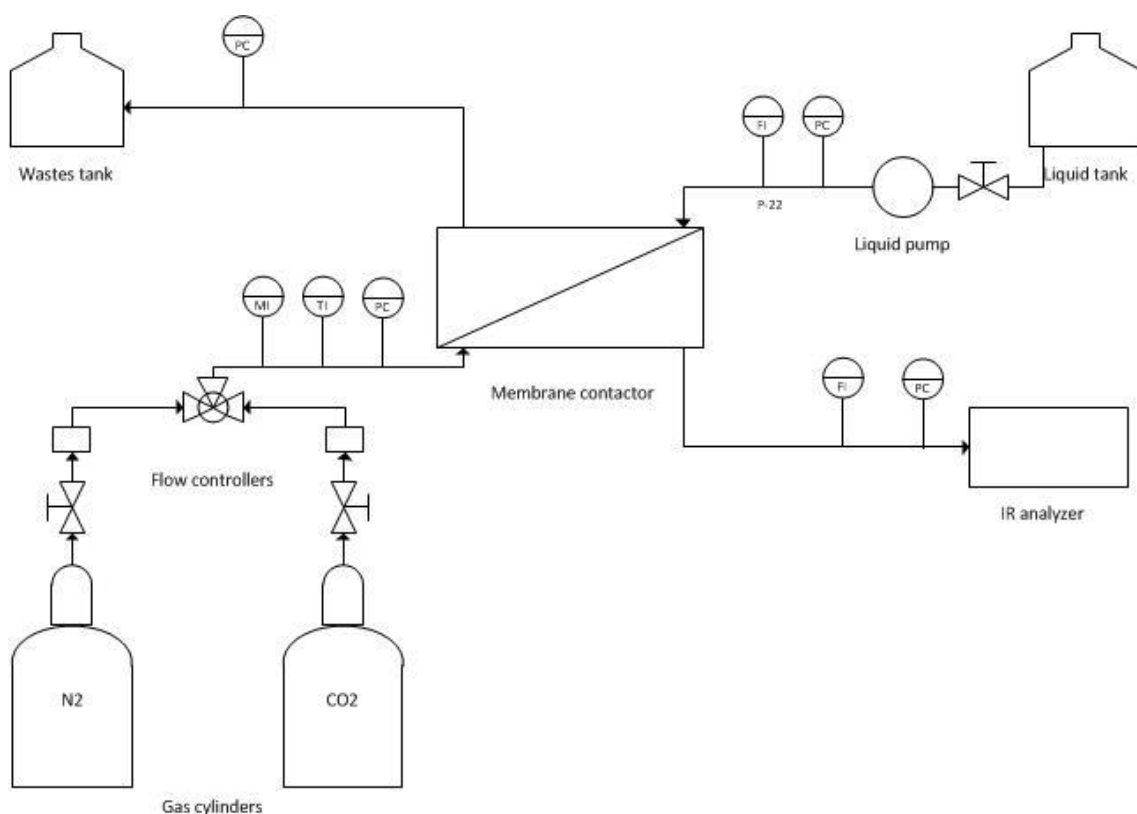


Figure 20. Scheme of membrane contactor set-up.

All the tests were performed at room temperature and setting gas and liquid flow rates as well as gas and liquid pressure. After setting all the variables, the experiment was started to logging, and was stopped after achieving a constant value of CO₂ concentration at the IR analyzer. Feed liquid pH was measured at the beginning of each day and compared to pH of a sample taken from the liquid coming out of the contactor at the end of each test.

Nitrogen was used instead of methane, which is commonly used for lab-scale experiments for safety reasons (Yampolskii 2010). This is because both of them are considered inert gases, characterized by low critical temperature, what makes the permeability not dependent on applied pressure, and they have a similar kinetic diameter (Mulder 1996), as is showed in table 9. Thus, all these similarities make nitrogen a very good substitute of methane to study the CO₂/CH₄ mass transfer avoiding explosion potential.

Table 9. Critical temperature and kinetic diameter of nitrogen and methane (Mulder 1996).

	Nitrogen	Methane
Critical Temperature (K)	126	191
Kinetic diameter (Å)	3.64	3.8

Distilled water and 0.001 M NaOH solution were used as liquid absorbents.

CHAPTER 4: RESULTS AND DISCUSSION

“Science does not give us absolute and final certainty. It only gives us assurance within the limits of our mental abilities and the prevailing state of scientific thought”.
- Ludwig von Mises.

4.1 Membrane characterization results

4.1.1 Contact angle results

Contact angle was measured for unsupported PTMSP membrane and composite PTMSP-PVDF. For the composite one it was measured three times:

- Firstly just after been made which corresponds to the case called PTMSP-PVDF no aging.
- Secondly after 3 month of storage at ambient conditions which corresponds to the case called PTMSP-PVDF storage aging.
- And finally after been used in the contactor, corresponding to the case PTMSP-PVDF contactor aging.

As said before, the contact angle is closely related to the wettability of the material. So the aim of these measurements is to know the how hydrophobic are the membranes (PTMSP and PTMSP-PVDF), and how can hydrophobicity change by the aging effect.

The results are summarized in table 10 and pictures of the measures are collected in Annex I. They show a similar contact angle between supported and unsupported membrane. However, the supported membrane after been stored for 3 months show a lower contact angle. Storage of PTMSP membranes can be affected by chemical aging, caused by oxidation with atmosphere oxygen (Starannikova, Khodzhaeva et al. 2004). This oxidation may reduce the wettability properties of the membrane.

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The difference of contact angle is even higher for the membrane used in contactor with a gap of almost 20°. Thus, exposure to water and NaOH solution during the membrane contactor experiments looks to have a negative effect over the wettability property of the membrane. However, all membranes showed a contact angle higher than 90°, meaning that they are hydrophobic.

Table 10. Summarized contact angle results. PTMSP corresponds to unsupported PTMSP membrane. PTMSP-PVDF corresponds to composite PTMSP-PVDF just after been made. PTMSP-PVDF storage aging corresponds to the same membrane after 3 months of storage. PTMSP-PVDF contactor aging corresponds to the same membrane after been used in contactor.

Membrane	Contact angle (°)
PTMSP	111
PTMSP-PVDF	112
PTMSP-PVDF storage aging	104
PTMSP-PVDF contactor aging	94

4.1.2 SEM analysis results

The images got in SEM, presented in figure 21, show the three different parts of the membrane. On the top of the membrane (left side of both images), a very thin layer is located, corresponding to the PTMSP layer. And, as can be seen, it is the densest layer of the entire membrane, showing no pores for these magnifications. Right under PTMSP layer, a porous section is located, corresponding to the PVDF support. As can be seen, this layer is much thicker than the PTMSP one. And, finally, under the PVDF there is a fibrous section, corresponding to the PET, as backing material.

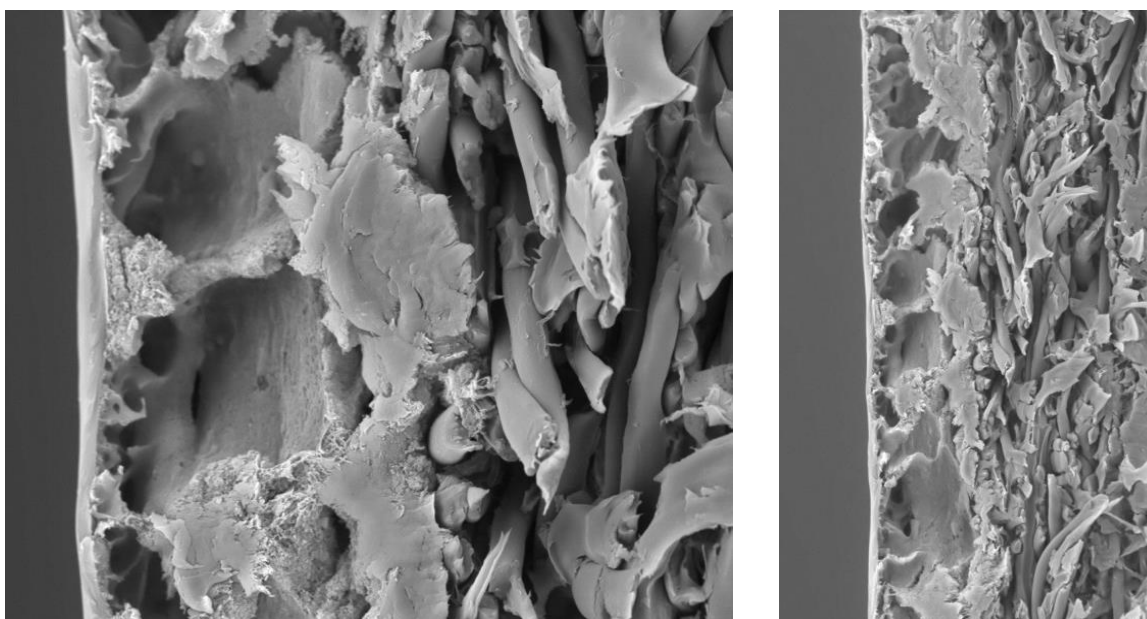


Figure 21. PTMSP-PVDF SEM images. Magnification of the images is x1000 for the left one and x300 for the right one.

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SEM images were also used to measure the thickness of the PTMSP layer of the composite membranes. Once the images were focused, the measurements tool was used and the thickness was measured in different points of the membrane, taking an average for the rest of the calculations. Images of these measurements are shown in Annex II

4.1.3 Membrane gas permeability results

All gas permeability results are summarized in table 14, table 15, table 16, table 17 and table 18 in Annex IV. Very low permeability values have been obtained during the tests, so, some modifications were made to try to understand the problems and make the membrane work.

Firstly, membrane 2.1 was tested, using Araldite® 2000 PLUS adhesive for the montage and a rotatory pump to reach vacuum. After getting such bad results (table 15), and consulting literature, rotatory pump was replaced by a diaphragm one, as oil from rotatory pump might affect the membrane, and membrane 2.2 was tested. Very low permeability values, although a little higher, were obtained again. Finally, membrane 2.3 was tested, using LOCTITE® EA 9483 as adhesive for the montage, instead of Araldite® 2000 PLUS, and high permeability values were obtained. Notice that the three pieces of membranes belong to the same sheet, so there isn't any difference on structure or composition between them. It was also tested a membrane (membrane 3) after been used in the contactor, to see what effect it may cause the exposure and time in the contactor over the permeability. And finally, an unsupported PTMSP membrane was tested to compare it with the supported PTMSP-PVDF one. Table 11 summarizes the membranes tested in chronologic order.

Table 11. Membranes tested on permeability experiments in chronologic order.

Membrane	Vacuum pump type	Montage adhesive
PTMSP-PVDF 2.1	Rotatory pump	Araldite® 2000 PLUS
PTMSP-PVDF 2.2	Diaphragm pump	Araldite® 2000 PLUS
PTMSP-PVDF 2.3	Diaphragm pump	LOCTITE® EA 9483
PTMSP-PVDF 3 (after been used in the contactor)	Diaphragm pump	LOCTITE® EA 9483
PTMSP	Diaphragm pump	LOCTITE® EA 9483

4.1.3.1 PTMSP permeability results

Although this membrane was the last one tested, it is presented the first one in order to compare the permeability values with the rest of membranes. Theoretically, the permeability of the unsupported PTMSP membrane and the PTMSP-PVDF should be similar since the PVDF is a porous membrane which allows the gases go through it very easily. Thus, the resistance to the mass transfer of PVDF support is negligible compare to the resistance of the PTMSP membrane.

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All the PTMSP permeability results are collected in table 14. Permeability was measured for all gases once a day, for 3 days, considering the first day as the day after setting the membrane in the module and setting vacuum for a night. Figure 22 and figure 23 shows the evolution of the permeability and selectivity respectively, for the three gases for the days measured.

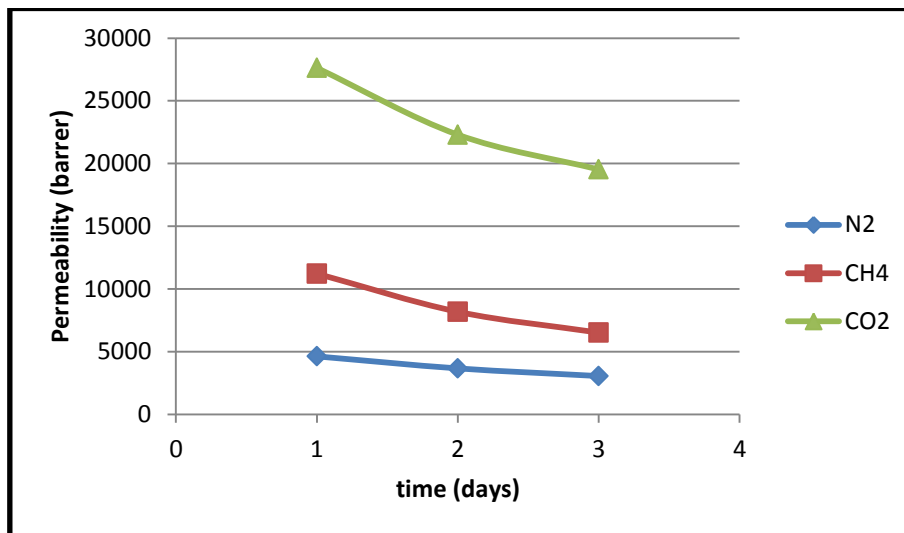


Figure 22. Evolution of N₂, CH₄ and CO₂ permeability.

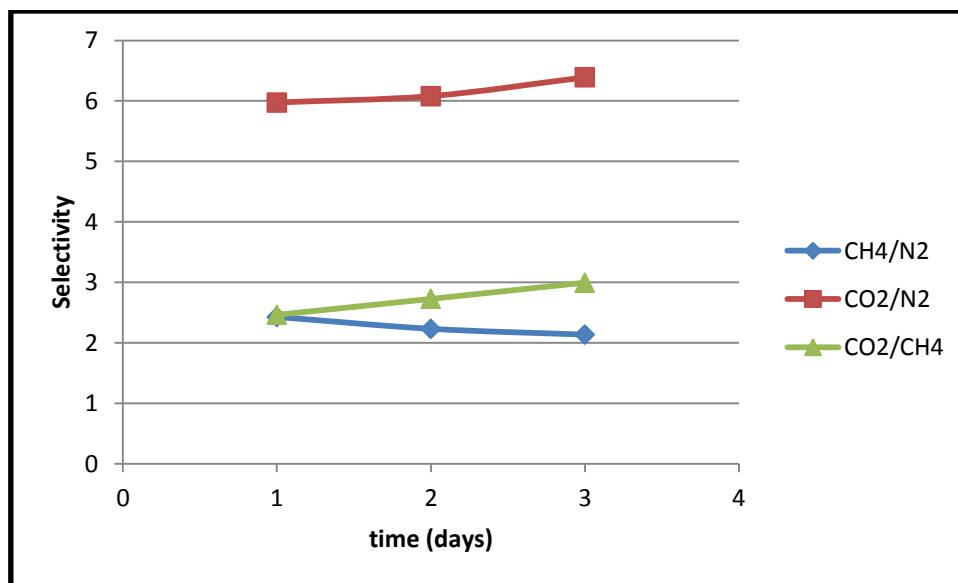


Figure 23. Evolution of N₂, CH₄ and CO₂ selectivity.

As can be seen, the permeability drops quickly from one day to other for each of the gases, while selectivity of carbon dioxide increases slightly. This may be caused by the aging of the membrane, what will be discussed later, once the results for the PTMSP-PVDF have been presented. However, despite this aging phenomenon, the first day permeability values, which they must not have suffered too much aging, agree with the range found in literature, as table 12 shows. The pressure didn't make any difference in the permeability values of any of the gases.

CO ₂ Permeability (barrers)	CO ₂ /CH ₄ Selectivity	Reference
27600	2.7	This study
18000	4.3	(Takada, Matsuya et al. 1985)
28000	2.2	(Ichiraku, Stern et al. 1987)
32000	-	(Morisato, Shen et al. 1996)
37000	2.0	(Robeson 1999)
29000	2.1	(Nagai, Masuda et al. 2001)
13620	3.1	(Gomes, Nunes et al. 2005)
7040	4.1	

Table 12. CO₂ permeability and CO₂/CH₄ selectivity of pure PTMSP membrane in literature and in this study.

4.1.3.2 PTMSP-PVDF permeability results

Figure 24 and figure 25 show the permeability of N₂ and CO₂ respectively at different pressures for the 2.1, 2.2 and 2.3 membranes tested. As shown, the pressure doesn't look to have any effect in the permeability, being practically constant for 2, 4 and 5 bar, as happened with unsupported membrane.

Much more important is the difference between the permeability values of the three membranes. There is a small variation on the permeability between the membranes 2.1 and 2.2, and a big variation for membrane 2.3. These variations and very low values on the permeability of the membrane may be due to the well-documented phenomenon of fast aging of this polymer during storage and/or exploitation (Starannikova, Khodzhaeva et al. 2004).

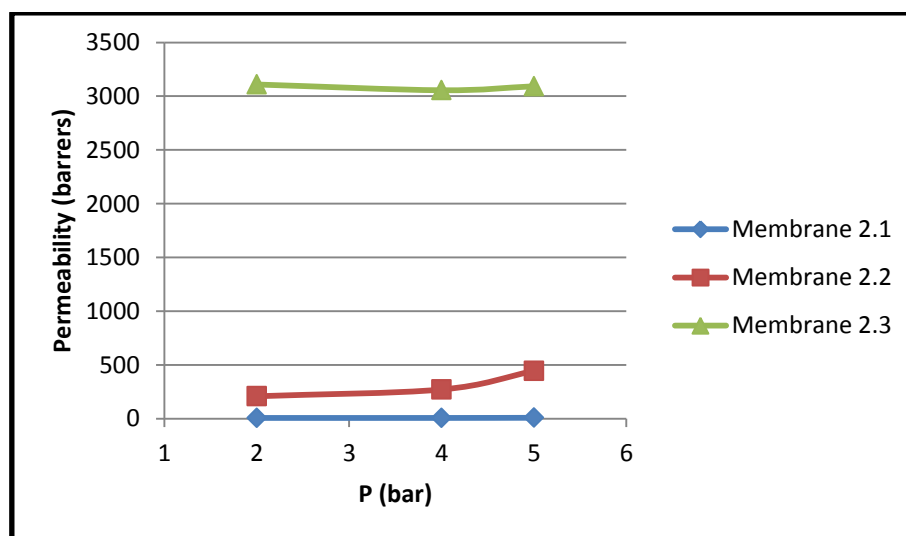


Figure 24. Comparison of N₂ permeability of the three membrane 2.1, 2.2, 2.3 (see table 11) and effect of the pressure.

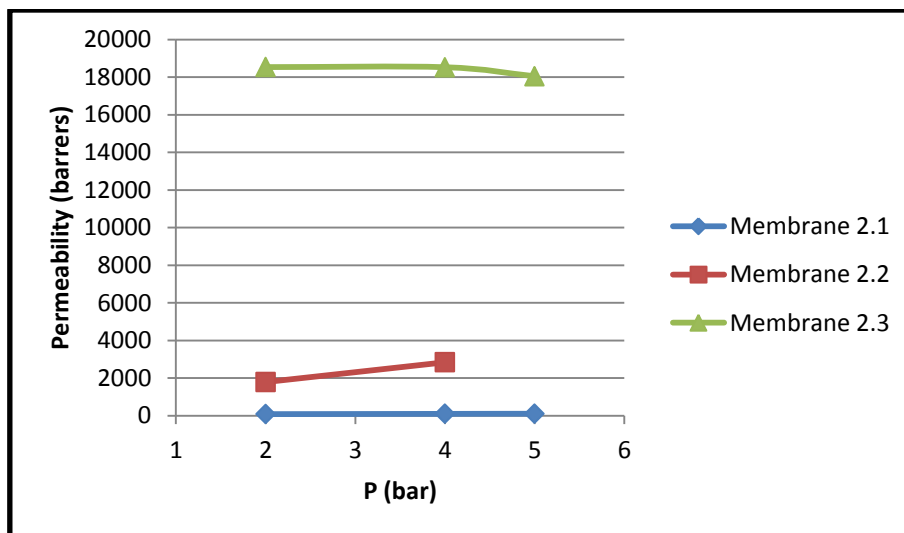


Figure 25. Comparison of CO₂ permeability of three membranes (see Table 11. Membranes tested on permeability experiments in chronologic order. and effect of the pressure

As stated in Chapter 1, oil from pump may cause aging on membranes and that's probably the reason for the difference of permeability between membrane 2.1 and membrane 2.2. Other authors have experienced and studied this effect (Nagai and Nakagawa 1995) (Nagai, Mori et al. 1997). However, the results show that the big difference on the membrane permeability is caused by the glue used on the montage. Membrane 2.3, glued with LOCTITE® EA 9483 showed approximately ten times more permeability than membrane 2.2, glued with Araldite® 2000 PLUS, and the effect is as huge for nitrogen as for carbon dioxide.

Glue effect may be caused by some chemicals it may have or some chemical interactions between the glue and the membrane. It is not the scope of this work to study why Araldite® 2000 PLUS affect this membrane like that, but the results show this glue have a devastating effect on PTMSP membranes.

Permeability was measured 3 different days during an interval of 5 days: the first day (referring first day as the day after a night setting vacuum), the second one and the fifth one. The results of these measurements are reflected on figure 26 and figure 27.

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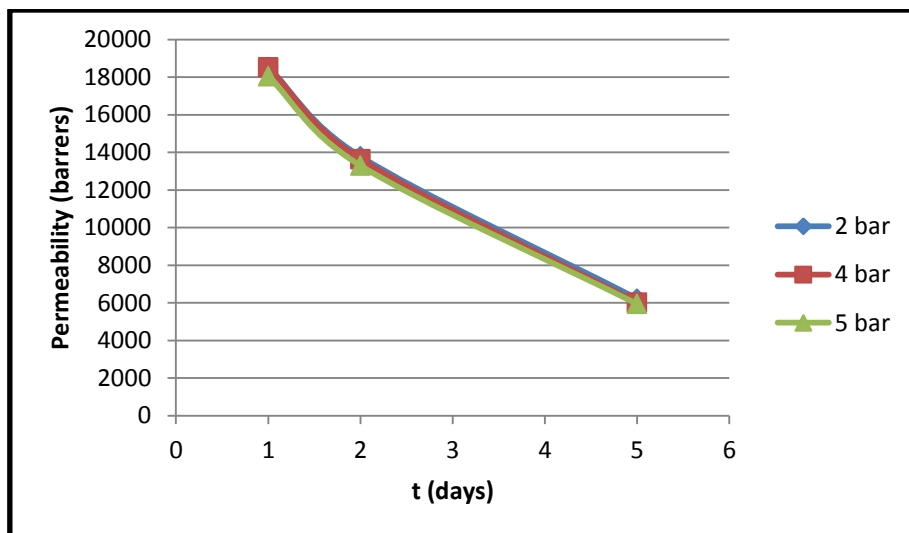


Figure 26. Membrane 2.3 CO₂ permeability over time.

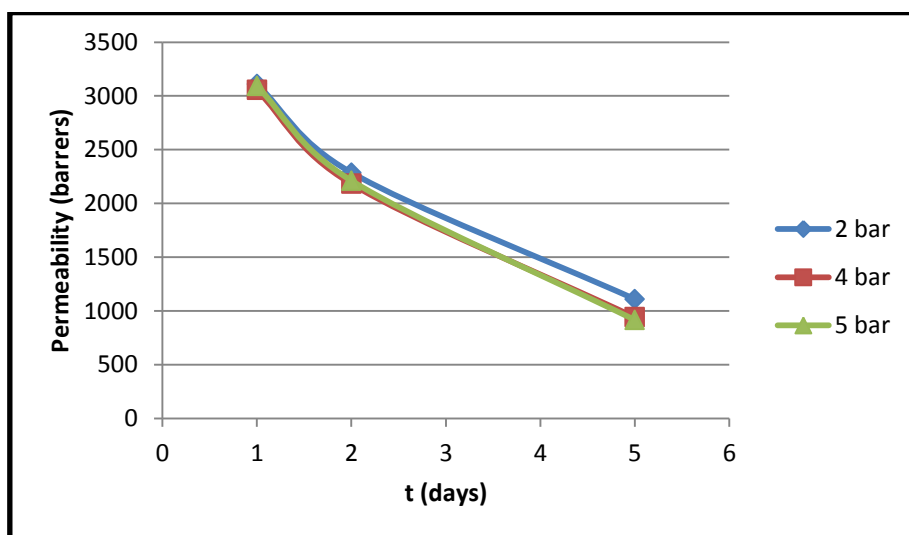


Figure 27. Membrane 2.3 N₂ permeability over time.

As can be seen, permeability values both for CO₂ and N₂ are reduced over time. They show a greater depletion of the permeability in the first day, and after that, a softer reduction, as happened with unsupported PTMSP membrane. This may be caused, again, by the fast aging of this polymer.

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Comparing aging of PTMSP with PTMSP-PVDF membranes, as shown in figure 28, it can be seen that the aging is even faster on the supported one. This may be due to the membrane thickness dependency of the aging. Unsupported PTMSP membrane had a thickness of about 22 μm while the supported one presented a thickness of about 6 μm . This cannot be ignored since the physical aging of PTMSP membrane is directly related with the membrane thickness (Dorkenoo and Pfromm 2000). Membranes with a higher thickness will suffer much less aging than thinner ones. This is probably the reason why the supported membrane shows a lower initial permeability than the unsupported one. The aging is so fast that during the vacuum time, before the first measure, the permeability drops greatly.

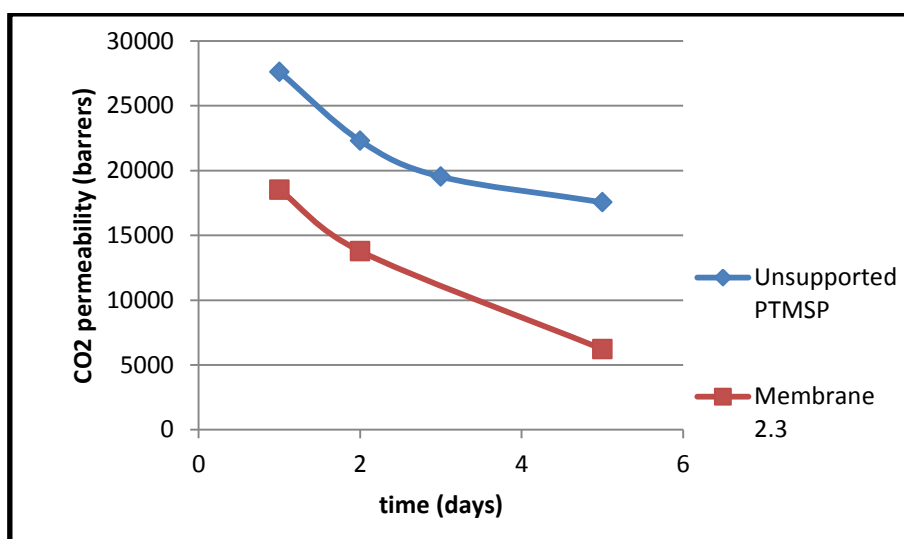


Figure 28. Comparison between aging effect over unsupported PTMSP and composite PTMSP-PVDF membrane.

It has been shown that the glue and the pump have an effect over the membrane, accelerating greatly the aging these last figures show that a very fast aging keep taking place even when using a diaphragm pump and LOCTITE® EA 9483 as glue.

One of the possible promoters of this fast aging is the glue. Despite LOCTITE® EA 9483 has much lower harmful effect over the membrane than Araldite® 2000 PLUS, as can be seen comparing results of membrane 2.2 and 2.3, it is unknown if LOCTITE® EA 9483 actually has some effect over the membrane, increasing the aging. This is hard to know but this possibility should be taken in account.

O-rings can also affect to the membrane properties by releasing non-volatile impurities, accelerating the decreasing of the permeability over time (Starannikova, Khodzhaeva et al. 2004). In addition, the simple exposure of the membrane to vacuum over time reduces the permeability by the relaxation of the unrelaxed volume what causes a tighter chain packing (Shao, Samseth et al. 2009) (Nagai and Nakagawa 1995) (Nagai, Mori et al. 1997) (Dorkenoo and Pfromm 2000). Even more, storage of the membrane at atmosphere condition may cause chemical aging by oxidation (Starannikova, Khodzhaeva et al. 2004). All these factors are responsible, in varying degrees, of the fast aging of the membranes.

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Crosslinking is an available solution to improve the resistance to aging of PTMSP. Some authors have investigated about it, obtaining nice results, improving greatly the resistance to aging (Shao, Samseth et al. 2009) (Tomaso 2013).

Permeability of PTMSP-PVDF membrane after being used in the contactor was also studied. Figure 29 compares the permeability of the membrane 2.3 during 5 days, with the permeability of the membrane 3 measured after the exposure to liquid during 5 days in the contactor.

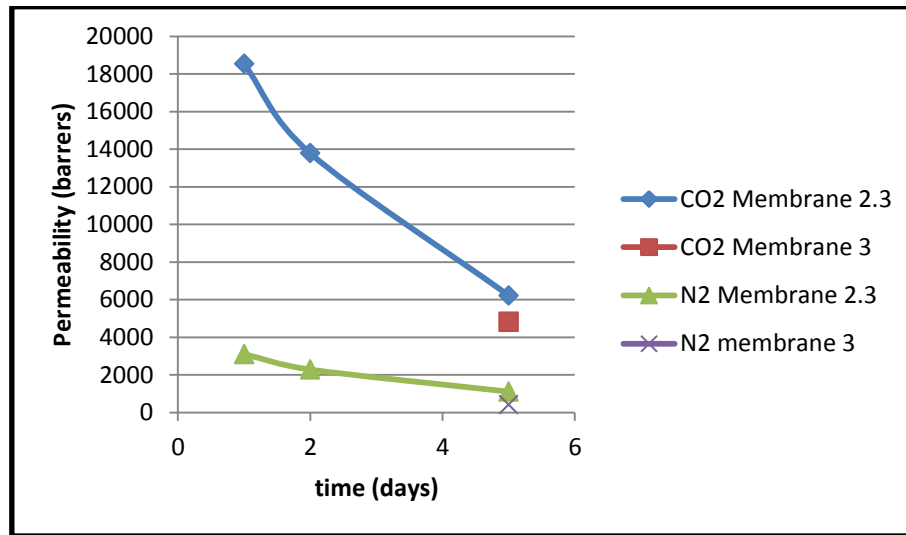


Figure 29. Comparison between aging of membrane 2.3 and membrane 3.

As can be seen, in both cases the permeability is reduced by the effect of aging and the case in which the membrane was exposed to liquid the reduction is bigger. However, it doesn't show a significantly greater aging.

4.2 Membrane contactor measurements results

In order to understand the mass transfer through the contactor, the effect of the inlet concentration of CO₂, gas flow rate, liquid flow rate, liquid and gas pressure were studied. All experiments were run at room temperature and with the same membrane.

Table 13 shows the experiments matrix. For each one of the experiments, the flux of CO₂ and the removal efficiency of CO₂ were calculated as they are the two most important parameters. The flux indicates how much carbon dioxide goes from gas phase to liquid phase per area of membrane. Thus, a higher flux of CO₂ indicates a better mass transfer. But also is very important the removal of CO₂, defined as the amount of carbon dioxide that goes from gas phase to liquid phase, respect the amount of CO₂ going into the system. The ways to calculate these two parameters are explained in detail in annex V and all the results obtained in the membrane contactor are collected in annex VI.

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Notice that to get absolute values of flux and CO₂ removal are not the scope of this work since the contactor doesn't have an optimized design and the CO₂ molecules can just bypass the zones of the contactor with membrane area. Despite that, it is highly interesting to see the effect of the different variables, obtaining relative results that can be very useful to understand the mass transfer in the contactor for this membrane.

Table 13. Membrane contactor experiments matrix

Inlet CO ₂ (%)	Gas flow rate (l/min)	Liquid flow rate (ml/min)	Liquid	Gas pressure (bar)
Inlet CO₂ concentration effect 1st day				
30	0.03	10	Water	1
50	0.03	10	Water	1
70	0.03	10	Water	1
Inlet CO₂ concentration effect 2nd day				
30	0.03	10	Water	1
50	0.03	10	Water	1
70	0.03	10	Water	1
Gas flow rate effect				
50	0.02	10	Water	1
50	0.05	10	Water	1
Gas pressure effect				
30	0.03	10	Water	1.5
50	0.03	10	Water	1.5
70	0.03	10	Water	1.5
30	0.03	10	Water	2
50	0.03	10	Water	2
70	0.03	10	Water	2
Solution effect				
30	0.03	10	Solution	1
50	0.03	10	Solution	1
70	0.03	10	Solution	1
50	0.03	10	Solution	1.5
50	0.03	10	Solution	2
Liquid flow rate effect				
50	0.03	20	Solution	1
50	0.03	20	Solution	1.5
50	0.03	20	Solution	2

Before starting to see the effect of the variables, the following event needs to be explained. The first day, the three first experiments were carried out with distilled water, keeping constant the gas (0.03 l/min) and liquid flow rate (10 ml/min), and the pressure in the gas phase (1 bar), and varying the inlet concentration of CO₂ to 30, 50 and 70%. The next day (day 2), the same experiments were carried out, but this time, the results of flux obtained were lower, the half approximately as showed in figure 30.

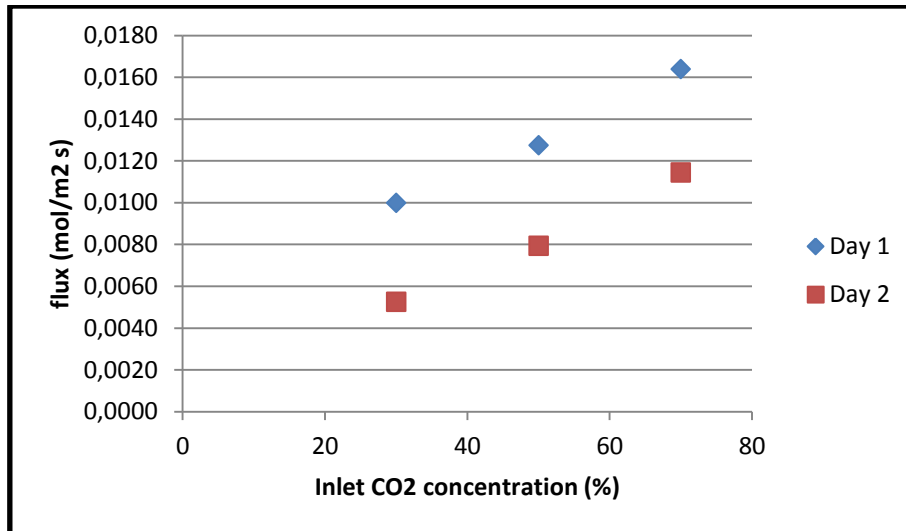


Figure 30. Difference between day 1 and day 2 CO₂ flux.

This event could be due to aging of membrane, which can reduce the permeability of the membrane quickly, as was explained previously. However, after day 2, the results for same conditions were stable. To ensure that this was not a measurement mistake, a new membrane was set into the module, after the rest of the experiments were carried out, to see if this event happened again.

So, a new membrane was set, and the outlet CO₂ concentration was measured during almost a day, keeping all the parameters constant as in the previous experiments and setting the inlet CO₂ concentration at 50%. Notice that the outlet CO₂ concentration is directly related to the flux since, the more flux, the less outlet CO₂ concentration, as reflected in equation (23). As shown in figure 31, the performance of the contactor improves continuously in the first hours, and remains in a very good performance for some hours more, what can correspond to the results of flux of the first day in figure 30 that are quit higher than the ones of day 2. After that, the performance of the contactor starts to worse, and after several hours, the system stabilizes, what can correspond to the results of day 2 in figure 30. Thus, this result makes sense with the ones of the other membrane.

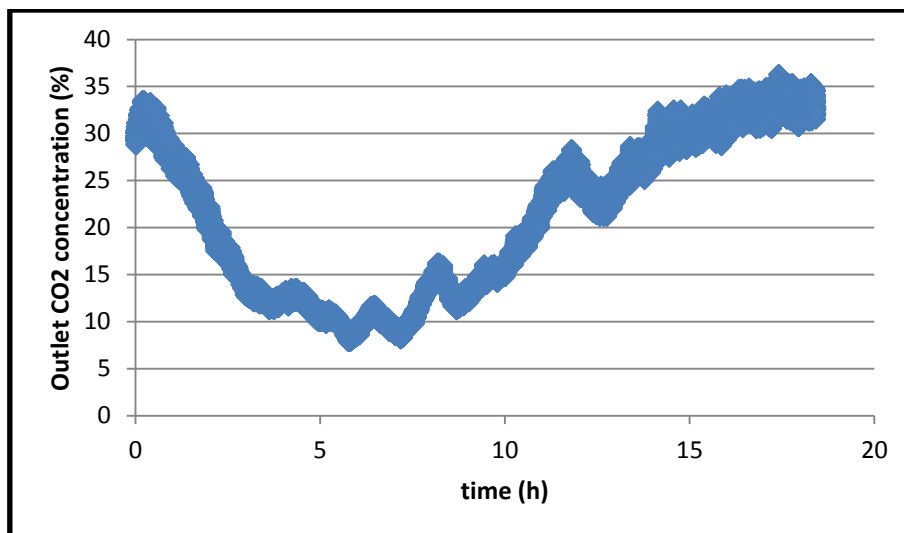


Figure 31. Evolution of outlet CO₂ concentration over time.

However, it couldn't be found a consistent explanation for this behavior. The improvement of the performance at the beginning could be due to a slow stabilization of the system that is tending to an outlet CO₂ concentration. This only would be possible if the characterization time (defined as gas flow rate divided by the gas phase volume of the system) for the experiments were very high, like about 5 hours. Nevertheless, the characterization time for the rest of experiments was about 20-30 minutes, discarding that the system behavior is due to high characterization times and so, high stabilization times. Thus, this behavior is more likely due to the membrane.

4.2.1 Gas flow rate effect

For these experiments, the inlet concentration of CO₂ was set to 50%, the liquid flow rate to 10 ml/min, the gas pressure to 1 bar and distilled water was used as absorbent. The gas flow rate was varied to 0.02, 0.03 and 0.05 l/min, obtaining the results showed in figure 32 and figure 33.

Figure 32 shows an increase of the flux as the gas flow rate is higher. This is logical since as the gas flow rate increases, the amount of CO₂ entering the system it also increases, so more amount of CO₂ will go through the membrane. But it also shows that as the gas flow rate is higher, the effect over the flux is lower. This can be due to different factors. One is that as the gas flow rate increases, the velocity of the gas increases, so the CO₂ molecules can bypass easier the membrane area. Another factor is that as the velocity of the gas increases, less time of contact has the CO₂ molecules with the membrane area. And also, another factor is that as the velocity of the gas is higher, the gas phase film resistance is lower, making the rest of the resistances more important. All these three factors can be an explanation to understand why an increment in the gas flow rate doesn't produce a proportional increment in the flux.

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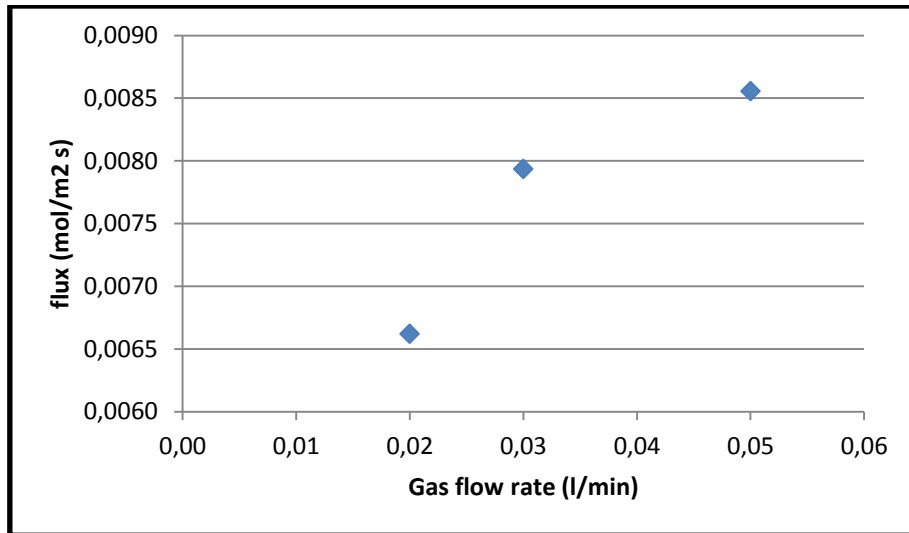


Figure 32. Effect of gas flow rate over CO₂ flux.

Figure 33 shows how the removal of CO₂ is lower as the gas flow rate is increases. Thus, although the flux increase as the gas flow rate is higher, the removal of CO₂ decreases because, as said before, rising gas velocity reduces contact time between CO₂ molecules and the membrane surface. This is in agreement with other mass transfer studies in membrane contactors (Chabanon, Bouallou et al. 2011) (Bottino, Capannelli et al. 2008).

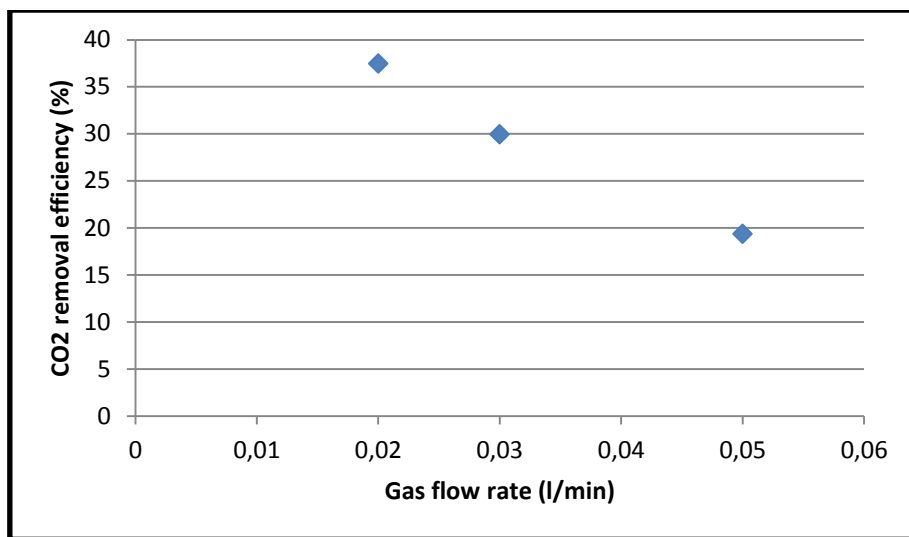


Figure 33. Effect of gas flow rate over CO₂ removal efficiency.

4.2.2 Inlet CO₂ concentration effect using water and NaOH solution

The effect of the inlet CO₂ concentration is showed in figure 34 and figure 35. They were carried keeping constant the gas (0.03 l/min) and liquid flow rate (10 ml/min), and the pressure in the gas phase (1 bar) and setting the inlet concentration of CO₂ to 30, 50 and 70%. Both absorbents, distilled water and NaOH solution, were tested. As can be seen, the flux increases as the inlet concentration of CO₂ is higher. This is logical since an increasing of the inlet CO₂ concentration means an increasing of the driving force, improving the mass transfer.

When using NaOH solution, the results are slightly higher than using water but show a good improvement at high CO₂ concentration. So using NaOH doesn't seem to be very important when the inlet flow of CO₂ in the gas phase is not very high (30 and 50% cases), but makes a difference when the inlet CO₂ flow is higher (70% case). That big difference between using water and using NaOH solution is due to the improvement of the mass transfer in the liquid side. As explained in Chapter 3, NaOH solution improves the liquid mass transfer by reacting with the CO₂ molecules. Thus, it seems that the liquid film resistance is not very important at low CO₂ flows but it plays an important role as the CO₂ flow is higher.

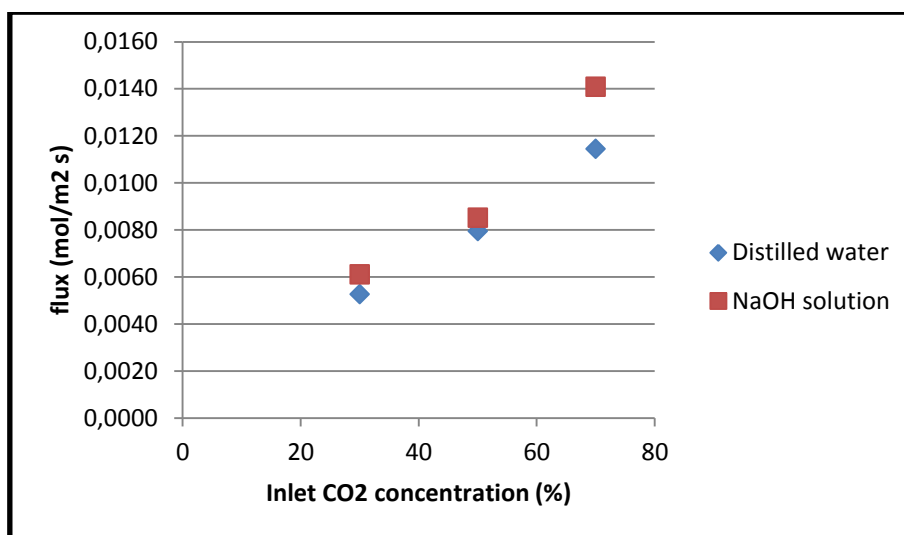


Figure 34. Inlet CO₂ volumetric concentration effect over CO₂ flux.

In figure 35 can be seen that using NaOH solution always enhances the CO₂ removal efficiency, respect the distilled water cases, due to the improvement of the liquid mass transfer. However, the CO₂ removal doesn't seem to be very affected by the inlet CO₂ concentration, getting for the three experiments very similar values. This is probably because when the inlet concentration of CO₂ is higher, at the same time that the driving force is increased, the probability that the molecules bypass the membrane also increases.

Similar behavior has been found in literature (Yan, Fang et al. 2007) in which a higher concentration of CO₂ in the feed improves the flux but doesn't make almost any effect over the removal efficiency.

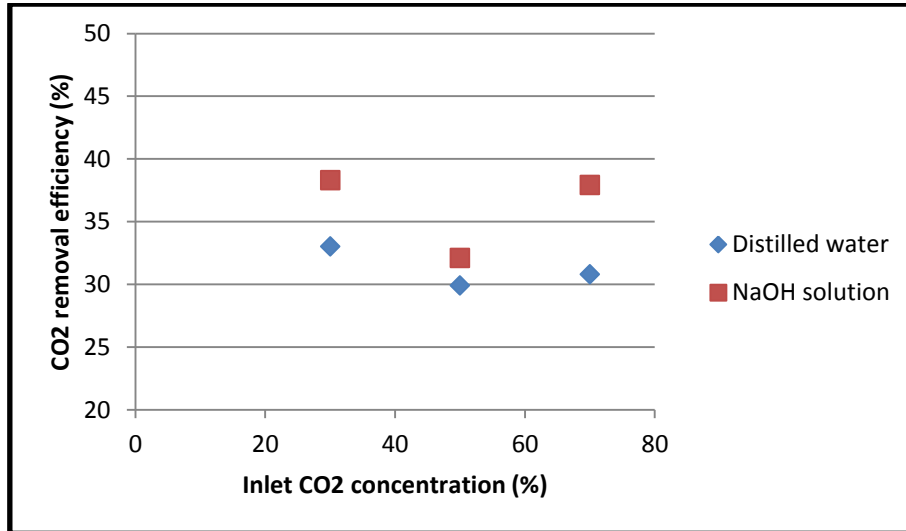


Figure 35. Inlet CO₂ volumetric concentration effect over CO₂ removal efficiency.

It also can be seen that the removal efficiency has a curvy behavior showing a minimum (for the three tests) for the 50% inlet concentration test. It is not clear the reason of this behavior but it could be due to two opposite effects of increasing the inlet CO₂ concentration. As the inlet concentration is higher, the driving force increases, but at the same time, the amount of CO₂ bypassing the membrane also increases. So these two effects can make to appear a minimum for the removal efficiency.

4.2.3 Solution effect at different pressures

To see the effect of solution at different pressures, the inlet CO₂ concentration was set to 50%, liquid flow rate to 10 ml/min, gas flow rate to 0.03 l/min and the pressure. Under these conditions, distilled water and NaOH solution were tested at a gas pressure of 1, 1.5 and 2 bar. Figure 36 and figure 37 show the effect of using solution at different gas pressure over the flux and the removal of CO₂.

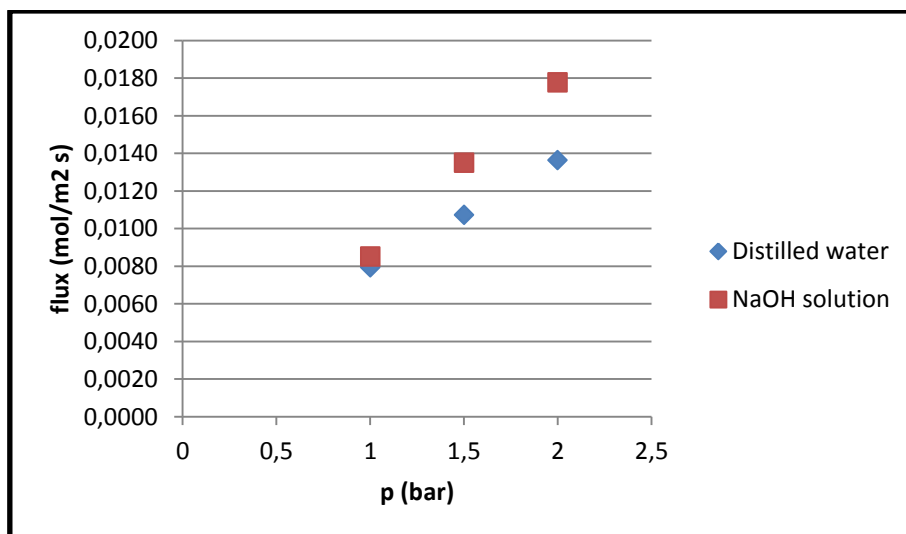


Figure 36. Solution effect at different pressures over CO₂ flux.

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An improvement in the flux as well as in efficiency removal is appreciated as the pressure is higher due to the increase of the driving force. Both the flux and the CO₂ removal are enhanced when using NaOH solution, agreeing with literature (Mansourizadeh, Ismail et al. 2010), and the effect is greater as the pressure increases. As said before, NaOH solution enhances the liquid mass transfer. Seeing the two figures, it can be said that, as the pressure increases, the liquid film resistance is more important, thus, an improvement in the liquid mass transfer makes a bigger difference.

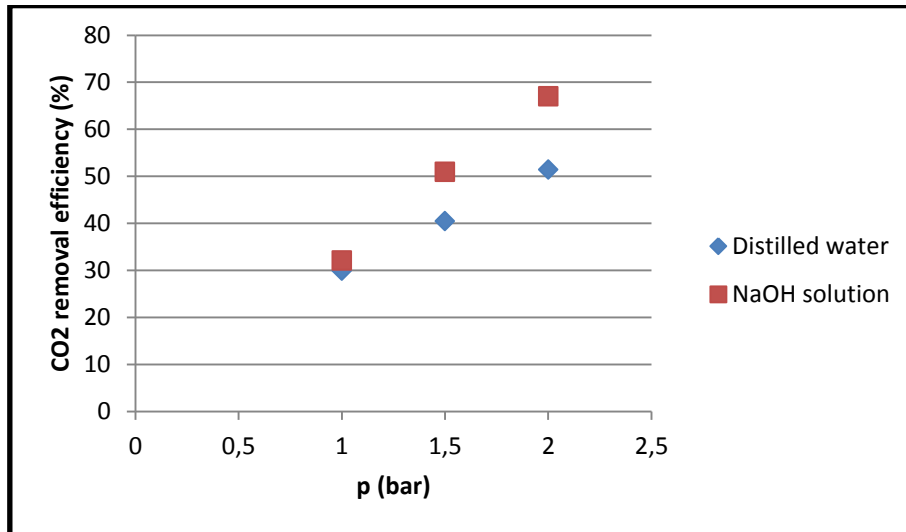


Figure 37. . Solution effect at different pressures over CO₂ removal efficiency.

4.2.4 Gas pressure effect at different inlet CO₂ concentration

For these experiments, gas flow rate was set to 0.03, liquid flow rate to 10 ml/min and distilled water was used as absorbent. For each Inlet CO₂ concentration, 30, 50 and 70%, gas pressure of 1, 1.5 and 2 bar was set.

Figure 38 and figure 39 show the effect of gas pressure over the flux and the CO₂ removal efficiency for different inlet CO₂ concentration using distilled water as absorbent. As is showed, as the pressure increases the flux enhances greatly as the driving force, the partial pressure of CO₂ in gas phase is higher, improving the mass transfer, agreeing with literature (Nguyen, Lasseguette et al. 2011). It is also possible to see that the effect of the pressure is greater for lower inlet CO₂ concentrations. This is because at higher CO₂ concentration levels, the gas phase resistance is not so important, and the rest of the resistances take importance, and so the effect of increasing the pressure is not so great.

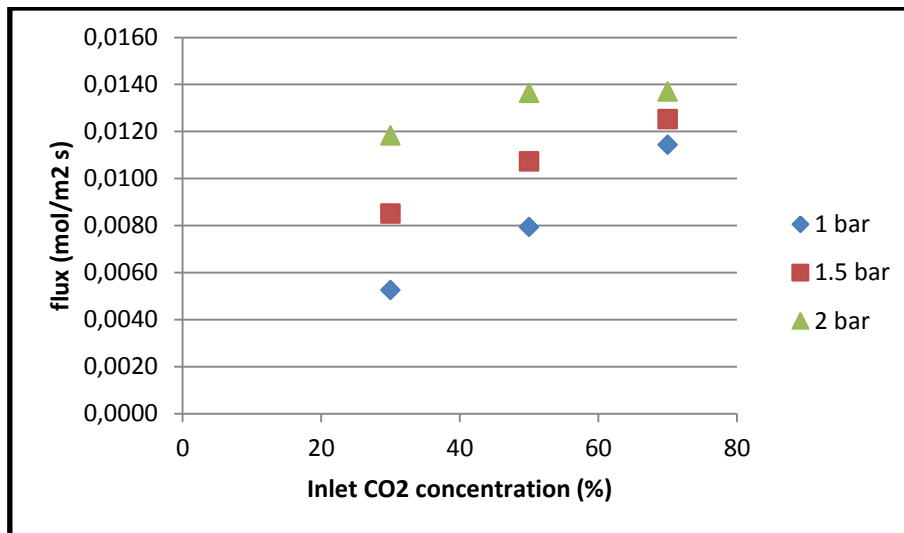


Figure 38. Pressure effect over CO₂ flux using distilled water.

Figure 39 shows that at low inlet concentration of CO₂, the effect of the gas pressure enhances greatly the removal efficiency of CO₂ since, as showed in figure 38, the flux increases highly. But as the inlet CO₂ concentration is higher, the improvement on the removal of CO₂ decreases, coinciding with the low improvement of the flux of figure 38. For instance at 2 bars and 30% of inlet CO₂ concentration the system achieves a high removal, but if the concentration increases to 50%, the removal of CO₂ decreases due to the flux is slightly improved, but the amount of CO₂ entering the system is much higher, so the amount of CO₂ that the membrane can permeate in comparison to the amount of CO₂ entering the system has been decreased.

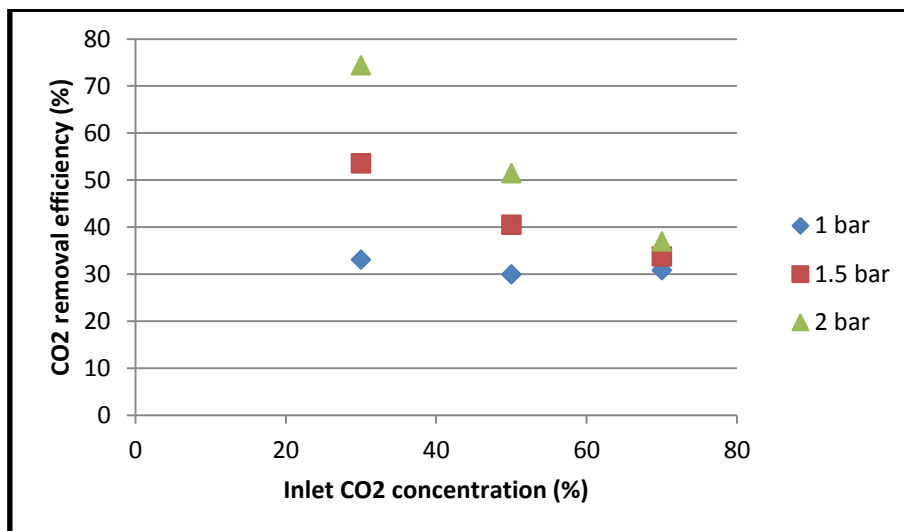


Figure 39. Pressure effect over CO₂ removal efficiency using distilled water.

4.2.5 Liquid flow rate effect using NaOH solution

Figure 40 and figure 41 show the effect of liquid flow rate over the flux and the CO₂ removal efficiency for different pressure using NaOH as absorbent. These experiments were carried out keeping constant the gas flow rate to 0.03 l/min, liquid flow rate to 10 ml/min and inlet concentration of CO₂ to 50% while increasing the liquid flow rate to 20 ml/min was set for each gas pressure (1, 1.5 and 2 bar).

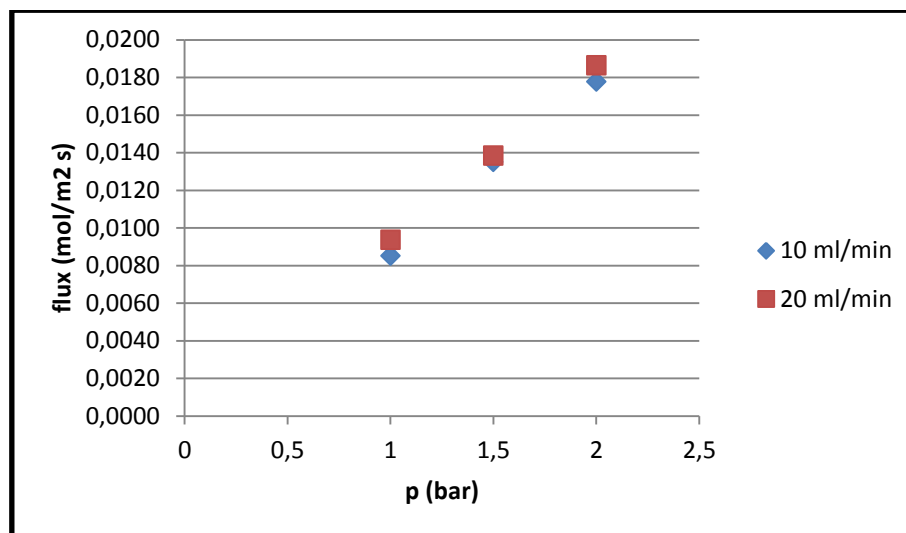


Figure 40. Liquid flow rate effect over CO₂ flux at different pressures.

As can be seen, increasing liquid flow rate improves slightly the flux and the CO₂ removal efficiency, but the effect is almost negligible. The idea of increasing the liquid flow is to improve the liquid mass transfer. If a high flow of CO₂ is coming from the gas phase to liquid phase, the OH⁻ ions can be consumed, and in that case, an increasing on the liquid flow rate could improve the mass transfer by a faster refreshing of OH⁻ ions. However, these experiments don't look to be that case, so the effect is very low.

Other of the effects of increasing the liquid flow rate is the decreasing of the thickness of the liquid film. For this case it looks that the increasing of the liquid flow rate is not enough to see any effect. To see if the liquid flow rate has some effect over the flux, a bigger increase should be tried, but the equipment didn't allow perform experiments with liquid flow rate much higher than 20 ml/min.

In agreement with this results, in literature (deMontigny, Tontiwachwuthikul et al. 2006) was found that the liquid flow rate doesn't have a significantly effect in the performance of a PTFE membrane contactor. However, in this same study, the performance of a PP membrane contactor was improved by increasing the liquid flow rate. Also other studies show an enhancement of the flux and the removal efficiency as the liquid flow rate increases (Mansourizadeh, Ismail et al. 2010). Thus, it can be said that the importance of liquid flow rate depends on the membrane and conditions of the experiments.

CHAPTER IV: RESULTS AND DISCUSSION

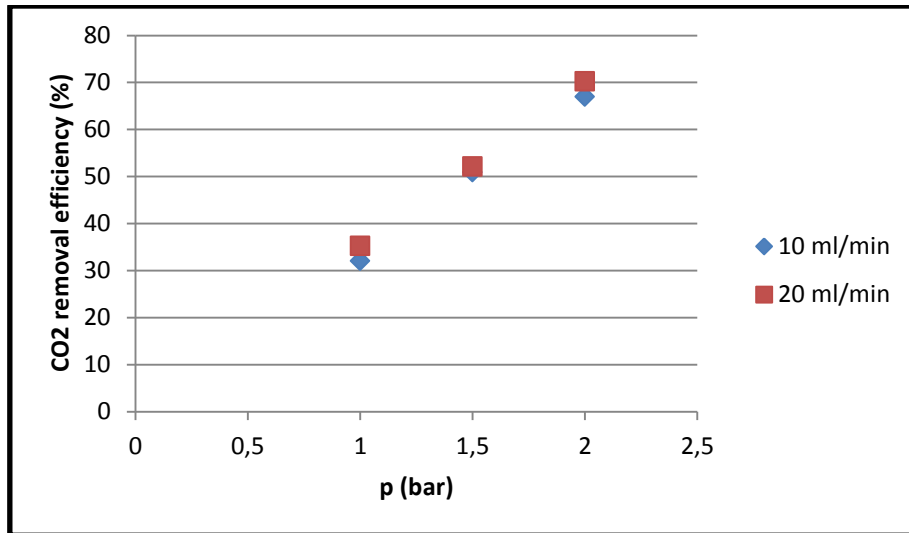


Figure 41. Liquid flow rate effect over CO₂ removal efficiency at different pressures.

CHAPTER 5: CONCLUSIONS AND FUTURE RECOMMENDATIONS

“The scientific man does not aim at an immediate result. He does not expect that his advanced ideas will be readily taken up... His duty is to lay the foundation for those who are to come, and point the way”.

- Nikola Tesla.

5.1 Conclusions

PTMSP supported and unsupported has been proved to be suitable membranes for CO₂ capturing, showing a very high CO₂ permeability and a good CO₂/CH₄ selectivity. And the permeability has been shown as pressure-independent for both of them. But, on the other hand, they experience a very fast aging, being permeability reduced drastically over time. This aging may be caused for multiple factor: oil from pumps, non-volatile components from glue and O-rings, exposure to vacuum and storage at ambient conditions. During this study, oil from pump was avoided using a diaphragm pump, and glue effect was minimized, as far as possible, using LOCTITE® EA 9483 adhesive. However, the rest of the factors couldn't be avoided. Unsupported PTMSP membrane show a better resistance to aging than supported one because the resistance to physical aging is higher as the membrane is thicker, and unsupported membrane presented 5 times higher thickness than supported ones. However, this problem can be solved by crosslinking. Other studies showed a great improvement on the aging resistance of crosslinking PTMSP membranes.

Experiments in membrane contactor showed also aging during the first day of performing, and that's the reason why CO₂ flux drops from day 1 to day 2. However, after that, the results were stable from one day to other. This was checked performing a one-day-test with a new membrane piece. This test showed how the system improves its performing in the first hours, but then, it starts to perform worse until it stabilizes.

Several variables were tested in the membrane contactor in order to understand the mass transfer process. After performing all the experiments, the following conclusions were derived:

CHAPTER V: CONCLUSIONS AND FUTURE RECOMMENDATIONS

- As the gas flow rate is higher, the CO₂ flux increases because more CO₂ is entering to the system so more amount of carbon dioxide will be able to go through the membrane. However, as the gas flow rate is higher, the CO₂ removal efficiency decreases due to the velocity of the gas increases, so the contact time between the membrane and the carbon dioxide is lower.
- Increasing the inlet concentration of CO₂ makes the flux of CO₂ through the membrane higher because the driving force is higher. Nevertheless, the effect of the inlet concentration of carbon dioxide is practically negligible over the removal efficiency.
- The gas pressure has a positive effect both over the flux and the removal efficiency since increases the driving force.
- The effect of the pressure is greater for lower inlet CO₂ concentrations. This is because at higher CO₂ concentration levels, the gas phase resistance is not so important, and the rest of the resistances take importance, and so, the effect of increasing the pressure is not so great.
- Using NaOH solution instead of distilled water increases both the flux and the removal efficiency since reduces the liquid film resistance. Moreover, the effect is greater as the pressure in the gas side is higher because in those cases, the liquid film resistance plays a more important role.
- Liquid flow rate doesn't show to have practically any effect in this range of conditions.

5.2 Future recommendations

The stability of the membrane was a problem during the whole project. That's why I would recommend using crosslinking PTMSP membranes for further works. Crosslinking of PTMSP membranes has already been investigated with very good results.

Some variables couldn't be tested in the membrane contactor. It would be interesting to study the temperature effect as well as the effect of different absorbents or the effect of traces of gases found the gas natural and biogas streams.

The membrane has demonstrated it has a great potential so it would be very interesting to try this material in a better module type. Flat sheet membrane contactor helps to understand the mass transfer but it's a very low optimizing design and can be greatly improved by other module types like hollow fiber modules.

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ANNEX I: CONTACT ANGLE MEASURES PICTURES

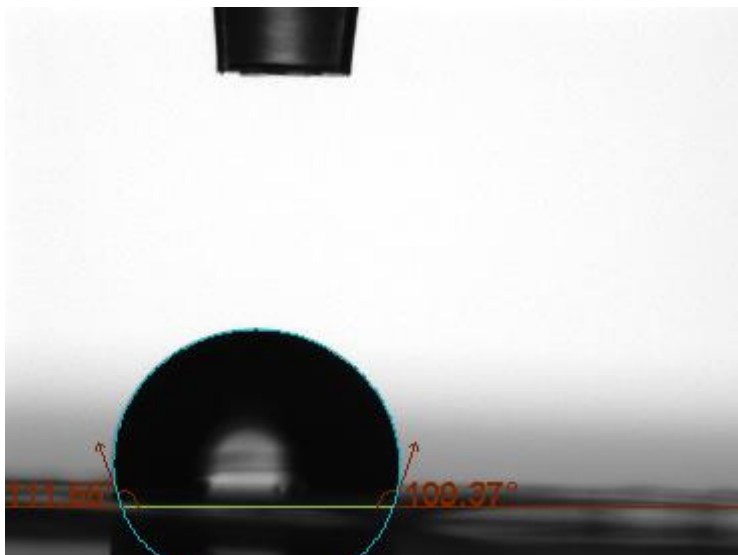


Figure 42. Contact angle of PTMSP corresponding to unsupported PTMSP membrane.

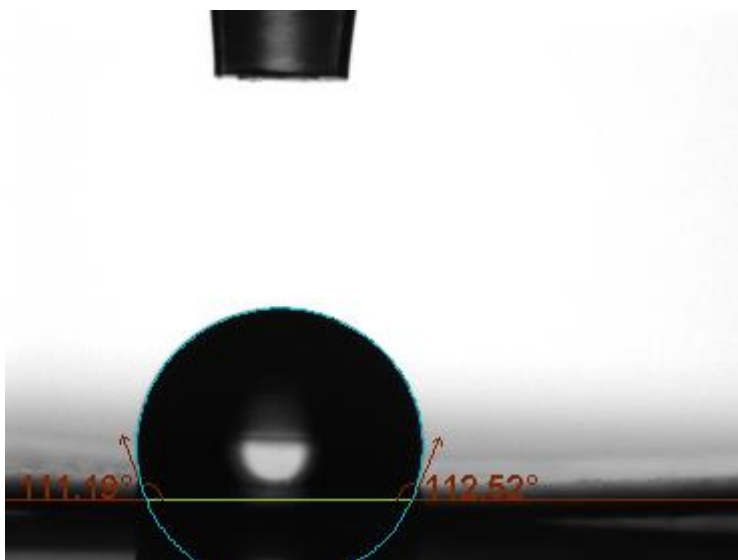


Figure 43. Contact angle of PTMSP-PVDF corresponding to the supported membrane just after been made.

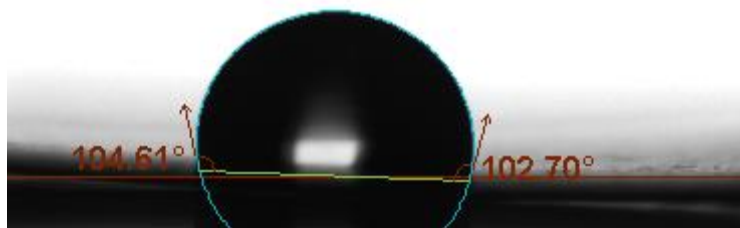


Figure 44. Contact angle of PTMSP-PVDF storage aging corresponding to the supported membrane after 3 months of storage.

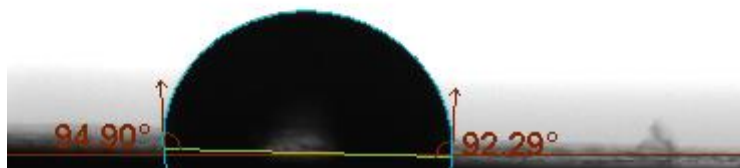


Figure 45. Contact angle of PTMSP-PVDF contactor aging corresponds to the supported membrane after been used in contactor

ANNEX II: SEM IMAGES FOR THICKNESS MEASUREMENTS

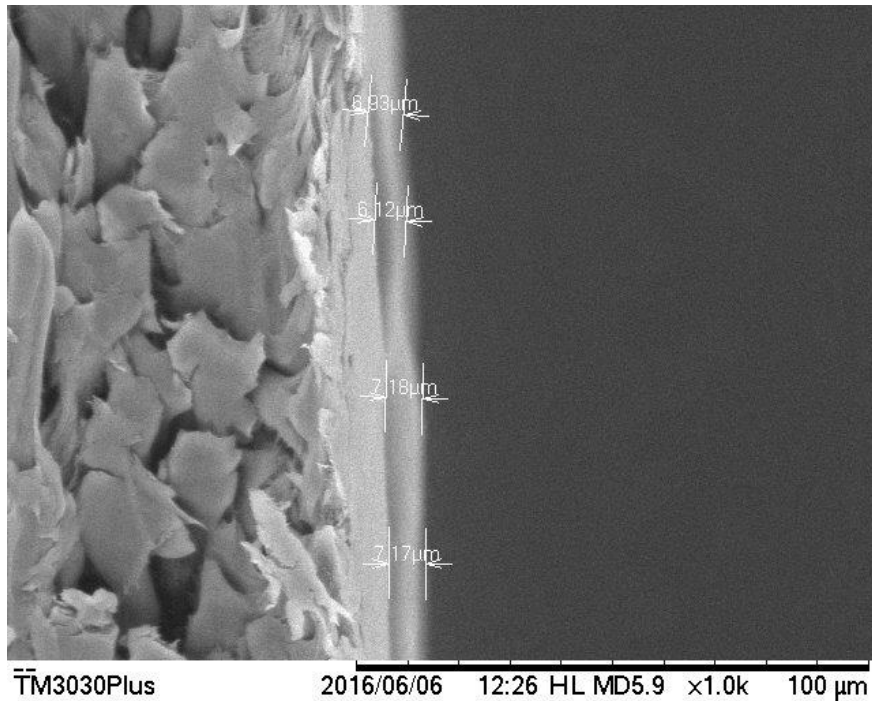


Figure 46. Membrane thickness for membrane 2.1, 2.2 and 2.3 PTMSP-PVDF.

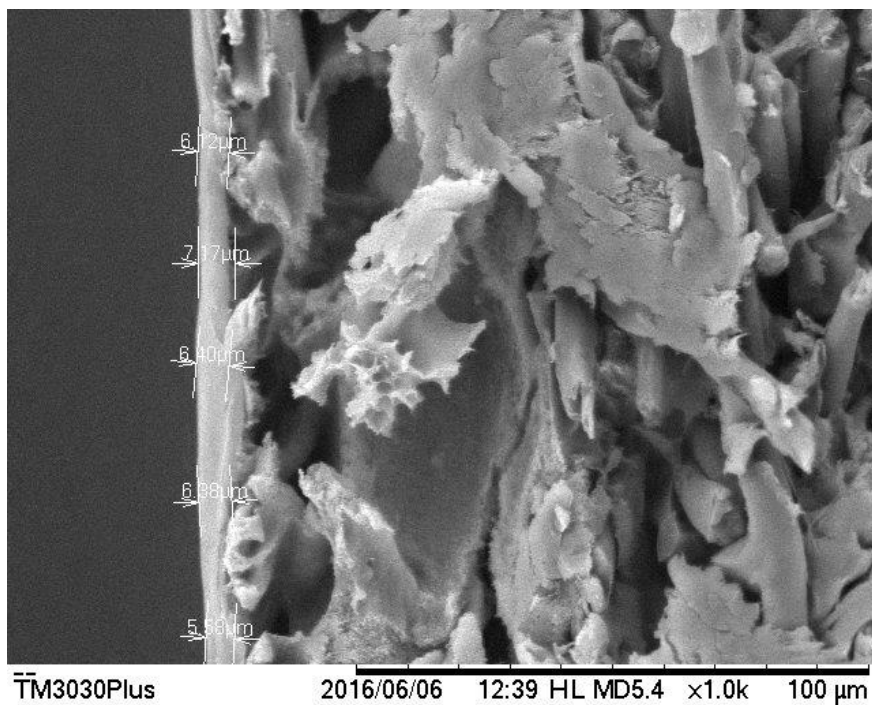


Figure 47. Membrane thickness for membrane 3 PTMSP-PVDF.

ANNEX II: PERMEABILITY AND SELECTIVITY CALCULATIONS

Permeability was calculated using the equation (21):

$$P = \frac{l \cdot V \cdot T_0}{A \cdot T \cdot p_0 \cdot (p_f - p_p)} \cdot \frac{dp}{dt} \quad (21)$$

where P is the gas permeability (1 Barrer = $27.4 \cdot 10^{-10} \text{ m}^3(\text{STP}) \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$), l is the film thickness (μm), A is the membrane area (cm^2), V is the volume in the chamber (cm^3), $T_0 = 273.15 \text{ K}$ is the standard temperature, T is the gas temperature (K), $p_0 = 1.0133 \text{ bar}$ is the standard pressure, p_f and p_p are the feed and permeate pressure (mbar) respectively, and dp/dt is the steady state pressure change (mbar/s).

The feed pressure was set at 2, 4 and 5 bars, the volume in the chamber was previously measured, and the dp/dt was logged and fit using Microsoft Excel. The area and thickness of the membrane were measured as explained in Chapter 2. Thus, all parameters are known to calculate permeability.

Selectivities were calculated using equation (22):

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (22)$$

ANNEX III: PERMEABILITY AND SELECTIVITY RESULTS SUMARIZED

Table 14. Unsupported PTMSP membrane permeability results.

PTMSP membrane							
Days	P(bar)	Permeability (barrers)			Selectivity		
		N ₂	CH ₄	CO ₂	CH ₄ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄
1	2	4620	11200	27600	2.4	6.0	2.5
	4	4600	11100	26900	2.4	5.9	2.4
	5	4600	1100	26300	2.4	5.7	2.4
2	2	3700	8200	22300	2.2	6.1	2.7
3	2	3000	6500	19500	2.1	6.4	3.0

Table 15. Membrane 2.1 permeability results.

Membrane 2.1						
P(bar)	Permeability (barrers)			Selectivity		
	N ₂	CH ₄	CO ₂	CH ₄ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄
2	7	7	85	1.0	12.1	7.1
4	7	11	100	1.5	9.3	7.1
5	8	9	107	1.0	12.5	8.6

Table 16. Membrane 2.2 permeability results.

Membrane 2.2			
P(bar)	Permeability (barrers)		Selectivity
	N ₂	CO ₂	CO ₂ /N ₂
2	209	1789	8.6
4	271	2841	10.5
5	444	-	-

Table 17. Membrane 2.3 permeability results.

Membrane 2.3							
Days	P(bar)	Permeability (barrers)			Selectivity		
		N ₂	CH ₄	CO ₂	CH ₄ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄
1	2	3100	-	18500	-	6.0	-
	4	3050	-	18500	-	6.1	-
	5	3090	-	18000	-	5.8	-
2	2	2290	-	13800	-	6.0	-
	4	2180	-	13600	-	6.3	-
	5	2210	-	13300	-	6.0	-
5	2	1110	1710	6230	1.5	5.6	3.6
	4	940	1650	6020	1.8	6.4	3.6
	5	916	1670	5940	1.8	6.5	3.6

Table 18. Membrane 3 permeability results.

Membrane 3 (tested after been used in contactor)						
P(bar)	Permeability (barrers)			Selectivity		
	N ₂	CH ₄	CO ₂	CH ₄ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄
2	406	869	4816	2.1	11.8	5.5

ANNEX IV: MEMBRANE CONTACTOR CALCULATIONS

Two parameters were calculated: CO₂ flux and CO₂ removal efficiency. The flux is defined as the CO₂ flow rate that comes from gas phase to liquid phase per area of membrane and it was calculated with equation (22):

$$F_{CO_2} = \frac{\dot{m}_{CO_2in} - \dot{m}_{CO_2out}}{A} = \frac{(\dot{m}_{Gin} \cdot x_{CO_2in}) - (\dot{m}_{Gout} \cdot x_{CO_2out})}{A} \quad (23)$$

where \dot{m}_{Gin} and \dot{m}_{Gout} are the gas flow rates of gas in the inlet and outlet respectively, and x_{CO_2in} and x_{CO_2out} are the volumetric concentration of CO₂ in the inlet and outlet respectively. The inlet gas flow rates and CO₂ concentrations are set while the outlet ones are measured in each experiment. The area of the membrane is measured after all experiments as explained in Chapter 3.

CO₂ removal efficiency was calculated using equation (23):

$$\eta_{CO_2} = \frac{(\dot{m}_{Gin} \cdot x_{CO_2in}) - (\dot{m}_{Gout} \cdot x_{CO_2out})}{\dot{m}_{Gin} \cdot x_{CO_2in}} \quad (24)$$

ANNEX V: MEMBRANE CONTACTOR RESULTS

Inlet CO ₂ concentration	Gas flow rate (l/min)	Liquid flow rate (ml/min)	Absorbent	Gas pressure (bar)	CO ₂ flux (mol/m ² s)	CO ₂ removal (%)
30	0.03	10	Water	1	0.0100	62.75
50	0.03	10	Water	1	0.0128	48.07
70	0.03	10	Water	1	0.0164	44.13
30	0.03	10	Water	1	0.0053	33.03
50	0.03	10	Water	1	0.0079	29.91
70	0.03	10	Water	1	0.0114	30.80
50	0.02	10	Water	1	0.0106	39.79
50	0.05	10	Water	1	0.0136	51.23
30	0.03	10	Water	1.5	0.0085	53.53
50	0.03	10	Water	1.5	0.0107	40.44
70	0.03	10	Water	1.5	0.0125	33.73
30	0.03	10	Water	2	0.0118	74.32
50	0.03	10	Water	2	0.0136	51.43
70	0.03	10	Water	2	0.0137	36.90
30	0.03	10	Solution	1	0.0061	38.31
50	0.03	10	Solution	1	0.0085	32.10
70	0.03	10	Solution	1	0.0141	37.93
50	0.03	10	Solution	1.5	0.0135	50.91
50	0.03	10	Solution	2	0.0178	66.99
50	0.03	20	Solution	1	0.0094	35.28
50	0.03	20	Solution	1.5	0.0138	52.15
50	0.03	20	Solution	2	0.0186	70.28

Table 19. Membrane contactor results.

RISK ASSESSMENT

ID	9108	Status	Date
Risk Area	Risikovurdering: Helse, miljø og sikkerhet (HMS)	Created	09.06.2016
Created by	Jaime Garrido López	Assessment started	09.06.2016
Responsible	Jaime Garrido López	Actions decided	
		Closed	

EEART, Master student, 2016, Jaime Lopez

Valid from-to date:

2/1/2016 - 14/13/2016

Location:

3 - Gløshaugen / 314 - Kjemi 4 / 1020 - 2. etasje

Goal / purpose

Identify all the possible risk of the activity in the laboratory and avoid/reduce/eliminate them.

Background

The laboratory activity consists on preparation of membranes, permeability tests and experimental study of membrane contactor.

Description and limitations

Membranes need to be prepared using PTMSP polymer into toluene solution. Permeability test are carried out with N₂, CO₂ and CH₄ in the set-up of room 218. Experimental study of membrane contactor is carried out in FellesLab, using nitrogen and carbon dioxide as gases, and water and NaOH solution as absorbents.

Prerequisites, assumptions and simplifications

Personal protective equipment, well equipped laboratories.

Attachments

[Ingen registreringer]

References

[Ingen registreringer]

Summary, result and final evaluation

The summary presents an overview of hazards and incidents, in addition to risk result for each consequence area.

Hazard: Preparing solution of PTMSP in toluene

Incident: Inhalation

Consequence area:

Helse

Risk before actions:



Risiko after actions:



Incident: Spillage

Consequence area:

Helse

Risk before actions:



Risiko after actions:



Hazard: Performing N2 permeability tests

Incident: Leakage

Consequence area:

Helse

Risk before actions:



Risiko after actions:



Hazard: Performing CO2 permeability tests

Incident: Leakage

Consequence area:

Helse

Risk before actions:



Risiko after actions:



Hazard: Performing CH4 permeability tests

Incident: Leakage

Consequence area:

Helse

Risk before actions:



Risiko after actions:



Ytre miljø

Risk before actions:



Risiko after actions:



Incident: Explosion

Consequence area:

Helse

Risk before actions:



Risiko after actions:



Materielle verdier

Risk before actions:



Risiko after actions:



Incident: Fire

Consequence area:

Helse

Risk before actions:



Risiko after actions:



Materielle verdier

Risk before actions:



Risiko after actions:



Hazard: Performing membrane contactor experiments

Incident: Leakage of CO₂ or N₂

Consequence area:

Helse

Risk before actions:



Risiko after actions:



Incident: Spillage of water or 0.001M NaOH solution

Consequence area:

Helse

Risk before actions:



Risiko after actions:



Hazard: Preparing NaOH solution

Incident: Spillage of NaOH solution

Consequence area:

Helse

Risk before actions:



Risiko after actions:



Final evaluation

Units this risk assessment spans

- Institutt for kjemisk prossteknologi

Participants

May-Britt Hägg
Arne Lindbråthen
Maria Teresa Guzman Gutierrez

Readers

[Ingen registreringer]

Others involved/stakeholders

[Ingen registreringer]

The following accept criteria have been decided for the risk area Risikovurdering:
Helse, miljø og sikkerhet (HMS):

Helse



Materielle verdier



Omdømme



Ytre miljø



Overview of existing relevant measures which have been taken into account for this risk assessment

The table below presents existing measures which have been taken into account when assessing the likelihood and consequence of relevant incidents.

Hazard	Incident	Measures taken into account
Preparing solution of PTMSP in toluene	Inhalation	Extractor hood
	Spillage	Personal protective equipment
Performing N ₂ permeability tests	Leakage	Ventilation
Performing CO ₂ permeability tests	Leakage	Ventilation
Performing CH ₄ permeability tests	Leakage	Methane alarm
	Leakage	Ventilation
	Explosion	Methane alarm
	Explosion	Ventilation
	Fire	Fire alarm
	Fire	Methane alarm
	Fire	Ventilation
Performing membrane contactor experiments	Leakage of CO ₂ or N ₂	Ventilation
	Spillage of water or 0.001M NaOH solution	Personal protective equipment
Preparing NaOH solution	Spillage of NaOH solution	Personal protective equipment

Existing relevant measures with descriptions:

Personal protective equipment

Goggles, lab coat, gloves, fire extinguisher.

Fire alarm

Fire detectors in all the rooms where has been worked.

Methane alarm

Methane detectors in all the rooms where has been worked with methane.

Extractor hood

[Ingen registreringer]

Ventilation

All rooms are perfectly ventilated.

Risk analysis with evaluation of likelihood and consequence

This part of the report presents detailed documentation of hazards, incidents and causes which have been evaluated. A summary of hazards and associated incidents is listed at the beginning.

The following hazards and incidents has been evaluated in this risk assessment:

- **Preparing solution of PTMSP in toluene**
 - Inhalation
 - Spillage
- **Performing N₂ permeability tests**
 - Leakage
- **Performing CO₂ permeability tests**
 - Leakage
- **Performing CH₄ permeability tests**
 - Leakage
 - Explosion
 - Fire
- **Performing membrane contactor experiments**
 - Leakage of CO₂ or N₂

- Spillage of water or 0.001M NaOH solution
- **Preparing NaOH solution**
 - Spillage of NaOH solution

Overview of risk mitigating actions which have been decided, with description:

Preparing solution of PTMSP in toluene (hazard)

Preparation of the membranes requires using toluene as solution.

Preparing solution of PTMSP in toluene/Inhalation (incident)

Toluene tends to produce high amounts of vapour that can be easily inhaled.

Overall assessed likelihood of the incident: Unlikely (1)

Comment to likelihood assessment:

Keeping under a extractor hood when using toluene.

Assessment of risk for the consequence area: Helse

Assessed likelihood (common for incident): Unlikely (1)

Assessed consequence: Very large (4)



Comment to consequence assessment:

Exposure to high vapour concentrations may produce central nervous system depression with headache, nausea, giddiness, unconsciousness and death

Preparing solution of PTMSP in toluene/Spillage (incident)

Spillage of toluene over the skin or eyes while preparing the membrane.

Overall assessed likelihood of the incident: Unlikely (1)

Comment to likelihood assessment:

Using appropriate gloves for toluene and goggles.

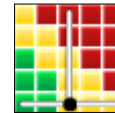
Assessment of risk for the consequence area: Helse

Assessed likelihood (common for incident): Unlikely (1)

Assessed consequence: Large (3)

Comment to consequence assessment:

Liquid toluene degreases the skin and may cause cracking.



Performing N2 permeability tests (hazard)

Performing N2 permeability tests/Leakage (incident)

Leakage of nitrogen to the environment.

Overall assessed likelihood of the incident: Less likely (2)

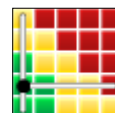
Comment to likelihood assessment:

[Ingen registreringer]

Assessment of risk for the consequence area: Helse

Assessed likelihood (common for incident): Less likely (2)

Assessed consequence: Small (1)



Comment to consequence assessment:

Nitrogen has no effect over the human health, and the rooms keep a good ventilation

Performing CO2 permeability tests (hazard)

Performing CO2 permeability tests/Leakage (incident)

Leakage of CO2 from the system to the environment.

Overall assessed likelihood of the incident: Less likely (2)

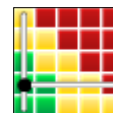
Comment to likelihood assessment:

[Ingen registreringer]

Assessment of risk for the consequence area: Helse

Assessed likelihood (common for incident): Less likely (2)

Assessed consequence: Small (1)



Comment to consequence assessment:

CO2 doesn't have any consequence over human health and the rooms are well ventilated.

Performing CH4 permeability tests (hazard)

Performing CH4 permeability tests/Leakage (incident)

Leakage of CH4 from the system to the environment.

Overall assessed likelihood of the incident: Less likely (2)

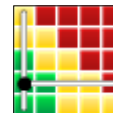
Comment to likelihood assessment:

[Ingen registreringer]

Assessment of risk for the consequence area: Helse

Assessed likelihood (common for incident): Less likely (2)

Assessed consequence: Small (1)



Comment to consequence assessment:

Methane doesn't have any effect over human health and all the rooms are well ventilated.

Performing CH4 permeability tests/Explosion (incident)

In certain concentrations with air, methane can be explosive.

Overall assessed likelihood of the incident: Unlikely (1)

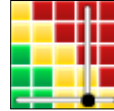
Comment to likelihood assessment:

Very unlikely since the rooms are well ventilated and there are methane alarms that are activated before getting close to the explosive concentration.

Assessment of risk for the consequence area: Helse

Assessed likelihood (common for incident): Unlikely (1)

Assessed consequence: Very large (4)



Comment to consequence assessment:

An explosion can make big physical damage to a person.

Performing CH4 permeability tests/Fire (incident)

Methane is a flammable gas.

Overall assessed likelihood of the incident: Unlikely (1)

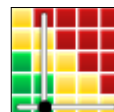
Comment to likelihood assessment:

Very unlikely since the rooms are well ventilated and there are methane alarms that are activated before getting close to the flammability concentration.

Assessment of risk for the consequence area: Helse

Assessed likelihood (common for incident): Unlikely (1)

Assessed consequence: Medium (2)



Comment to consequence assessment:

Fire can be dangerous since produce burns over human but there are fire alarms and extintors in all rooms, so the consequences are minimal.

Performing membrane contactor experiments (hazard)

In these experiments, nitrogen and carbon dioxide are used as gases and distilled water and 0.001M NaOH solution as absorbents.

Performing membrane contactor experiments/Leakage of CO₂ or N₂ (incident)

Overall assessed likelihood of the incident: Less likely (2)

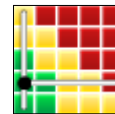
Comment to likelihood assessment:

[Ingen registreringer]

Assessment of risk for the consequence area: Helse

Assessed likelihood (common for incident): Less likely (2)

Assessed consequence: Small (1)



Comment to consequence assessment:

Nitrogen and carbon dioxide have no effect over human health.

Performing membrane contactor experiments/Spillage of water or 0.001M NaOH solution (incident)

Spillage of water or 0.001 NaOH solution into eyes caused by break of tubing.

Overall assessed likelihood of the incident: Less likely (2)

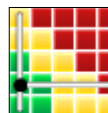
Comment to likelihood assessment:

[Ingen registreringer]

Assessment of risk for the consequence area: Helse

Assessed likelihood (common for incident): Less likely (2)

Assessed consequence: Small (1)



Comment to consequence assessment:

Water has no effect over human health. NaOH solution starts to have effect over human health over 0.05M and in these experiments only 0.001M was used.

Preparing NaOH solution (hazard)

Preparing NaOH solution/Spillage of NaOH solution (incident)

Spillage over the skin or eyes

Overall assessed likelihood of the incident: Likely (3)

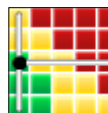
Comment to likelihood assessment:

[Ingen registreringer]

Assessment of risk for the consequence area: Helse

Assessed likelihood (common for incident): Likely (3)

Assessed consequence: Small (1)



Comment to consequence assessment:

NaOH solution only causes irritation in skin or eyes.

Overview of risk mitigating action which have been decided:

Below is an overview of risk mitigating actions, which is intended to contribute towards minimizing the likelihood and/or consequence of incidents:

Overview of risk mitigating actions which have been decided, with description:

