Atmospheric CO$_2$ capture for the artificial photosynthetic system

Adrianna Nogalska[1,*], *Adrianna* Zukowska[2], and *Ricard* Garcia-Valls[1]

[1]Universitat Rovira i Virgili, Av. dels Països Catalans 26, 43007 Tarragona, Spain
[2]Uniwersytet im. Adama Mickiewicza, Chemistry Faculty, ul. Umultowska 89B, 61-614 Poznań, Poland

Abstract. The scope of these studies is to evaluate the ambient CO$_2$ capture abilities of the membrane contactor system in the same conditions as leaves works during photosynthesis, such as ambient temperature, pressure and low CO$_2$ concentration, where the only driving force is the concentration gradient. The polysulfone membrane was made by phase inversion process and characterized by ESEM micrographs which were used to determine the thickness, asymmetry and pore size. Besides, the porosity of the membrane was measured from the membrane and polysulfone density correlation and hydrophobicity was analyzed by contact angle measurements. Moreover, the compatibility of the membrane and absorbent solution was evaluated, in order to exclude wetting issues. The prepared membranes were introduced in a cross flow module and used as contactor between the CO$_2$ and the potassium hydroxide solution, as absorbing media. The influence of the membrane thickness, absorbent stirring rate and absorption time, on CO$_2$ capture were evaluated. The results show that the efficiency of our CO$_2$ capture system is similar to stomatal carbon dioxide assimilation rate.

1 Introduction

Growth of carbon dioxide concentration in Earth's atmosphere is one of the main issues troubling the modern world. Since the Industrial Revolution started, global average level of CO$_2$ concentration rose from 280 ppm to 404 ppm (May, 2016) and it is the highest recorded in last 650,000 years [1]. Fossil fuel combustion emission, which is the main cause of the carbon dioxide atmospheric growth, is increasing year by year [2]. These factors are forcing us to invent new technologies and develop ones already existing to reduce global warming effects. The best inspiration for scientists is always nature. Our planet was taking care of the balance of CO$_2$ since billions of years by, among others, photosynthesis.

The approach of the present work is to capture CO$_2$ from atmosphere, such as photosynthetic organisms do. The system works as a leaf, where CO$_2$ is captured directly from the air through the membrane pores and is passed to the next compartments to be finally converted to methanol or hydrocarbons and used as fuel in fuel cells.

---

[*] Corresponding author: adrianna.nogalska@urv.cat

The first step, which is CO_2 fixation, determines the speed of the entire process. CO_2 assimilation rate in stomata reaches between 15–40 µmol/m^2*s [3–6]. Stomata are small adjustable pores situated on the leaf surface. The central role of stomata is regulating gas exchange between the inside of the leaf and the external environment, e.g. during photosynthesis it allows CO_2 to diffuse into the leaf. The system designed for carbon dioxide capture process mimics stomata function. It consists on a porous polysulfone membrane contactor which uses a basic solution to absorb carbon dioxide in form of carbonate or bicarbonate. As CO_3^{2-} and HCO_3^{-} will be further converted to methanol by electro reduction, there is no need for a recovery of the absorbent. The membrane contactor is permeable for the gas and provides high contact surface area. Recently they started to be used for carbon dioxide capture as a hybrid of membrane separator and chemical absorption.

In the membrane contactors, the porous membrane separates gas and liquid phase and the absorption process is driven by pressure or concentration gradient. Mass transfer process includes following steps: convective-diffusive transport of solute from the bulk gas to the membrane surface, transfer through the membrane pores to the liquid membrane surface and a convective-diffusive transfer of a solute to the bulk liquid followed by the physical or chemical absorption. The overall mass transfer coefficient consists of individual resistances. The resistances are: the gaseous phase boundary layer ($1/k_G$), the membrane ($1/k_m$) and the liquid phase boundary layer ($1/k_L$). The overall process is well-known as a "resistance in series" model and overall mass transfer resistance ($1/K_o$) can be obtained by adding the individual resistances [7].

$$\frac{1}{K_0} = \frac{1}{k_G} + \frac{1}{k_m} + \frac{1}{k_l}$$

(1)

A precise knowledge of mass transfer coefficient is essential for simulation, industrial design and use of membrane contactors. Simplified equation for its theoretical value is:

$$k_m = \frac{D * \varepsilon}{\tau * z}$$

(2)

In this equation D stands for effective diffusion coefficient of CO_2, ε is the membrane porosity, z is membrane thickness and τ is a tortuosity coefficient. It is essential to know that this is simplified equation and deviations from reality are highly possible to appear [8].

A great amount of polymers have been studied as materials for membranes in CO_2 capture studies including e.g. polyacetylenes [9], polyaniline [10], poly(ethylene oxide) [11], polyolefin [12], polypropylene [13] and others [14]. Polysufone, chosen in the study, is a thermally and chemically stable polymer, easy to handle. Besides, its use in membrane preparation process results in production of membranes with specific morphology, which is easy to control by changing production conditions [15].

Previous studies on polysulfone membrane contactors for ambient CO_2 capture were performed in the system equipped with peristaltic pump in order to decrease the absorbent mass transfer resistance by increase of the liquid flow rate. In the current studies experiments ware carry out in static conditions, where the liquid flow is zero, to evaluate the impact of the pump. Membranes with the same morphology with different thickness, macrovoids size and the hydrophobicity were used in the research. Besides the influence of the membrane characteristics, absorbent liquid resistance and absorption time were analysed.

2 Materials and methods

2.1 Materials

Polysulfone (SIGMA-ALDRICH) in form of pellets was used for membrane preparation with NMP $\geq$ 99,0% (SIGMA-ALDRICH). Potassium Hydroxide (85%, pellets) (SIGMA-ALDRICH) were used as absorption liquid for CO_2.

2.2 Flat sheet membranes preparation

Polysulfone membranes were made via phase inversion method. The preparation conditions are summarized in Table 1. Polymeric solution used for the fabrication consisted of 20% wt. polysulfone dissolved in 1-Methyl-2-pyrrolidone during 48 h stirring. Resulting solution was cast on a glass support by using a casting knife of particular thickness and immediately immersed into water, where membranes precipitate. Prepared flat sheet membranes were dried at ambient conditions. As the only changed factor in the process is thickness, further membranes names are associated with the size of the casting knife used in the preparation, as fallows: membrane 250, membrane 200 and membrane 100.

Table 1. Membrane preparation process details.

Process	Immersion precipitation
Polymeric solution	20% Polysulfone in NMP
Coagulation bath	Distilled water
Casting knife [μm]	250, 200, 100
Support	Glass

2.3 Environmental scanning Electron Microscopy (ESEM) and morphology analysis

The morphology of fabricated membranes was investigated with Environmental Scanning Electron Microscopy (FEI Quanta 600). Membranes were fractured in liquid nitrogen and fixed to the support suitable for the cross-section analysis. The ESEM micrographs were recorded with 350 magnification.

Obtained micrographs were analyzed with Ifme [16] and ImageJ software, where membrane asymmetry, mean pore size, microvoid size and thickness is calculated based on the cross section structure of the membrane. Moreover, the overall porosity was determined by using densities of the membrane and the polymer, according to the equation:

$$\varepsilon = \left(1 - \frac{\rho_m}{\rho_p}\right)100\%$$

(3)

where ρ_m corresponds to the membrane density and ρ_p to the polysulfone density (1.24 g/cm^3).

As membrane wetting is an unwanted phenomena in gas-liquid membrane contactor operations, membrane hydrophobicity and its affinity for the absorbent solution needs to be evaluated. Therefore, membrane swelling and contact angle measurements of both, water and absorbent solution were done.

Membrane (2 cm^2) was immersed into the water and absorbent solution for 24 h and swelling was calculated based on the membrane weight before (w_1) and after immersion (w_2) by the following equation:

$$Swelling = \frac{(w_2 - w_1)}{w_1} 100\%$$ (4)

Hydrophobicity was analyzed by contact angle measurements (Dataphysics OCA 15EC). A 3 µL droplet of milli-q water or potassium hydroxide solution was placed on the bottom surface of the membrane. The measurements were performed only on the bottom surface of the membranes, because it is in contact with the solvent during operation. A contact angle was calculated from a digital image by SCA software included in the apparatus.

2.3 CO$_2$ absorption studies

Experiments were performed to determine the influence of speed of solution stirring, the membrane thickness and time of exposition of membrane contactor on the CO$_2$ absorption rate from ambient air. Firstly, membranes of different thickness were examined and placed in a module with capacity of 100 ml. The absorbent was KOH aqueous solution in the concentration of 0.64 M. It was stirred with different RPM ranging in 0-1000. The time of experiment was fixed to be 1 hour. Bottom side of the membrane was in contact with the absorbent solution while top was exposed to the air (Figure 1.) with a contact area of 19 cm^2. Samples were collected and analysed for CO$_2$ content by using CO$_2$ ion-selective electrode (Thermo Scientific connected with Thermo Scientific Orion Dual Star pH/ISE Benchtop meter). The absorption flux was calculated based on the following equation:

$$J_{CO2} = \frac{n_{CO2}}{t * A}$$ (5)

where n_{CO2} is CO$_2$ moles in the absorbent solution of 100 ml [µmol] obtained from the measurements, t is the time of experiment [s] and A is the area of the flat sheet membrane [m^2].
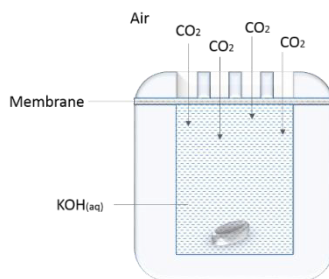

Fig. 1. Module scheme.

Next, membrane with the best absorption properties and the most effective rpm – absorption relation was used to analyse the absorption in function of time. For that purpose, nmp 200 membrane was placed into the system and experiments were conducted without stirring in range of time: 15, 30, 45, 60, 120 min. Collected samples were analysed the same way as previously.

3 Results and discussion

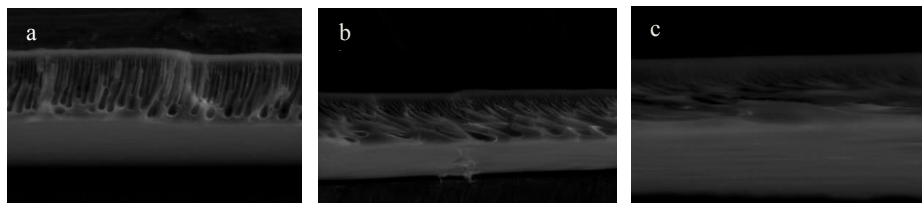## 3.1 Morphology analysis

Fig. 2. ESEM micrographs of the membranes cross seccion: a) 250, b) 200, c) 100.

Resulting membranes have fingerlike macrovoids in porous media. Membranes chracteristics obtained from the analysis of ESEM micrographs are listed in Table 2. It shows that membranes vary in thickness and have increasing macrovoids size respectively to the thickness. The porosity and asymmetry do not change significantly.

Table 2. Membranes characteristics.

Membrane	Thickness [μm]	Assymetry [%]	Mean pore size [μm]	Mean macrovoids size [μm²]	Porosity [%]
100	44.84 [± 1.4]	15	16.89 [± 2.4]	40 [± 26]	66.73
200	88.09 [± 2.4]	14	17.63 [± 1.6]	400 [± 271]	72.53
250	124.19 [± 2.6]	15	11.99 [± 0.3]	610 [± 228]	73.70

3.2 Swelling and contact angle results

The pores wetting is an undesirable phenomena in gas – liquid membrane contactor operations. For that reason we need to exclude the blocking influence of the absorbent solution on the pores. The analysis was done with use of absorbent solution and water as reference. Swelling (Table 3.) and contact angle of the water and KOH solution (Table 4.) were measured.

Table 3. Swelling test measurements results.

Adsorbed liquid	Membrane	Swelling [%]
Water	100	10.96 [±0.55]
	200	55.09 [±2.75]
	250	38.58 [±1.92]
KOH	100	1.21 [±0.06]
	200	n. d.
	250	n. d.

Swelling test results shows that membranes are capable to absorb water but no absorbent solution what is in agreement with contact angle measurements.

Table 4. Water and KOH solution contact angle measurements.

Contact angle liquid	Membrane	Contact angle [°]
Water	100	66.52 [±2.72]
	200	81.85 [±0.82]
	250	67.82 [±1.37]
KOH	100	71.02 [±7.03]
	200	86.72 [±4.74]
	250	75.58 [±5.09]

Despite the prepared membranes are hydrophilic, water contact angle is lower than the one corresponding to absorbent solution. This occurs due to difference in liquid surface tension, thus the interaction with the membrane surface. The tests demonstrate that absorbent solution is adequate for working with polysulfone membranes. The membrane life time is expected to be long as far as, in the tests performed, the polymer does not seems to be affected by the solutions. It might be due to that membrane wetting is very low and, on the other hand, the fouling does not occur in these liquid membrane contactors operations.

3.3 CO_2 absorption results

3.3.1 Influence of the membrane thickness and stirring rate on the contactor absorption capacity
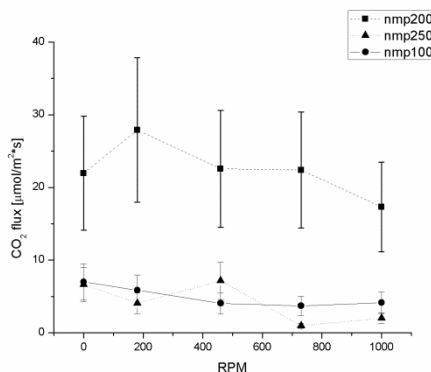

Fig. 3. CO_2 absorption in a function of RPM by different membranes.

It was expected that increasing the mixing of absorbent solution would have a positive influence on the absorption rate, as the fluctuation of the absorbent below the membrane could increase the amount of unreacted potassium hydroxide molecules in the contact with the surface. Nevertheless, studies show that the impact of the mixing is negative or not significant. It looks like the influence of the solutions mass transfer resistance during the static operation of the module is low as the solution remains in the same container. A previously studied case, where the absorbent solution was in a separated flask, and it was circulated through the contactor by the use of pump, revealed the positive influence of the absorbent fluctuations on the absorption rate.

The mass transfer resistance in the membrane can be studied by using of different thickness and hence macrovoids size, as the obtained membranes possess similar internal morphology. The CO_2 passage rate through the membrane phase depends on the distance (membrane thickness), free space (macrovoids size) and the material interaction with absorbent solution. From the study we can conclude that the membrane 200 shows the best results in absorption capacity over the rest of studied membranes. This membrane shows the highest hydrophobicity and macrovoids big enough to the CO_2 pass. Even though the macrovoids are large and open, the distance between air and absorbent is too big when we consider membrane 250. The case of membrane 100 is the opposite, the distance is short but there is not enough free space for CO_2 to pass.

3.3.2 Change of absorption in time

The best conditions from previous experiment were chosen to study the membrane contactor system abilities to absorb CO_2 in passage of time. The experiments were performed with the membrane 200 and without used stirring, as its impact is negligible. In the plot (Figure 4) the change in CO_2 content in the final absorbent solution and its flux through the contactor are displayed together in order to understand the functioning of the system.

The absorbed CO_2 amount is rising within the studied range of time. The system would keep increasing the CO_2 content until the saturation state. The CO_2 flux is decreasing in time and the plateau was achieved after one hour of experiment. The results were expected and seem logic, because according to the equation (5), for the flux, moles are divided by time and area.
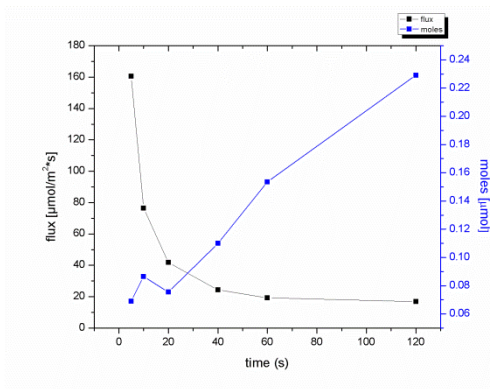

Fig. 4. CO_2 absorption flux and CO_2 content change as a function of time.

3.3.3. Natural stomata vs artificial stomata

As the system is designed based on the natural leaf structure, thus the obtained results will be compare to the natural stomatal CO_2 assimilation rate. For the reference we choose the grape vine leaf assimilation rate value which is 20 μmol/m^2·s, as reported by J. Martínez-Lüscher et al. [3]. The range obtained by us is depending on the experimental conditions ranging in 6–160 μmol/m^2·s. Nevertheless, in the studies of the influence of time presented above, we see the system achieved stabilization with membrane 200 after 1 h of experiment reaching the value of 20 μmol/m^2·s, which should be used as the reference. Results show that the CO_2 assimilation rate in natural stomata is the same range as in our artificial system.

4 Conclusions

Porous polysulfone membranes with different thickness were fabricated and characterized with the purpose to use them as contactors in ambient carbon dioxide capture studies. Compatibility of the membranes and absorbent solutions was evaluated by swelling tests and contact angle measurements. According to the results, we can conclude that polysulfone membranes are compatible to be used with potassium hydroxide solution. Furthermore, the influence of membrane thickness, absorbent solution mixing rate and experimental time on the system absorption capacity were investigated. From the study we can conclude that the membrane nmp 200 shows visible superiority in absorption capacity over the rest of studied membranes, due to the best thickness / macrovoids size ratio and the best hydrophobic properties. Nevertheless, the results showed that the impact of the absorbent solution mixing is not significant. It looks like the influence of the solutions mass transfer resistance during the static operation of the module is low as the solution remains in the same container. As expected, the absorbed CO_2 amount was rising within the studied range of time. The comparison between natural and the artificial stomata revels that the CO_2 assimilation is within the same range. Thus, the designed stomata mimicking unit can be used further in artificial photosynthetic systems.

References

1. J.G. Canadell, C. Le Quere, M.R. Raupach, C.B. Field, E.T. Buitenhuis, P. Ciais, T.J. Conway, N.P. Gillett, R.A. Houghton, G. Marland, Proc. Natl. Acad. Sci. U.S.A. **104**, 18866–18870 (2007)
2. A.P. Ballantyne, C.B. Alden, J.B. Miller, P.P. Tans, J.W.C. White, Nat. Geosci. **2**, 831–836, (2009).
3. J. Martínez-Lüscher, F. Moralez, M. Sanchez-Diaz, S. Delrot, J. Aguirreolea, E. Gomès, I. Pascual, Plant Sci. **236**, 168–176 (2015)
4. W. Tezara, V.J. Mitchell, S.D. Driscoll, D.W. Lawlor, Nature **401**, 914–917 (1999)
5. P. Teszlaka, M. Kocsis, K. Gaal, M.P. Nikfardjam, Sci. Hor. **159**, 41–51 (2013)
6. K. Radglou, Ann. Sci. For. **53**, 268–278 (1996)
7. V.Y. Dindore, D.W.F. Brilman, F.H. Geuzebroek, G.F. Versteeg, Sep. Purif. Technol. **40**, 133–145 (2004)

8. H.F. Svendsen, E. Favre, J. Membrane Sci. **407–408**, 1–7 (2012)

9. S.A. Stern, J. Membrane Sci. **94**, 1–65 (1994)

10. K.H.G. Illing, R.J. Wakeman, A. Jungbauer, J. Membrane Sci. **184**, 69–78 (2001)

11. B.D. Freeman, H. Lin, J. Membrane Sci. **239**, 105–117 (2004)

12. P.H.M. Feron, A.E. Jensen, Sep. Purif. Technol. **27**, 231–242 (2002)

13. A. Witek-Krowiak, A. Dawiec, S. Modelski, D. Podstawczyk, Int. J. Chem. Eng. Appl. **3** (2012)

14. Z.X. Hongqun Yang, M. Fan, R. Gupta, R.B. Slimane, A.E. Bland, I. Wright, J. Environmen. Sci. **20**, 14–27 (2008)

15. C. Torras, *Obtenció de membranes polimèriques selectives* (in *Chemical Engineering Dep.* 2005, Universitat Rovira i Virgili, Tarragona)

16. C. Torras, R. Garcia-Valls, J. Membrane Sci. **233**, 119–127 (2004)