HYBRID SOLVENT ([EMIM][AC]+WATER) TO IMPROVE THE CO₂ CAPTURE EFFICIENCY IN A PVDF HOLLOW FIBER CONTACTOR

L. Gomez-Coma*, A. Garea, A. Irabien

¹ Universidad de Cantabria, Chemical and Biomolecular Engineering Department, E.T.S. de Ingenieros Industriales y Telecomunicación, Universidad de Cantabria, Avda Los Castros s/n 39005 Santander, Spain

*Corresponding author: Tel: +34 942 206777, Fax: +34 942 201591

email: gomezcomal@unican.es

Abstract

Reduce carbon dioxide emissions and therefore global warming is one of the great aims of the XXIth century. Post-combustion processes based on ionic liquids and membrane contactors have emerged as a new attractive alternative to traditionally systems in recent years. This route is ideally suitable for conventional power stations and energy conversion systems. In this work, a non-dispersive absorption in a Polyvinylidene fluoride (PVDF) hollow fiber membrane contactor was used as CO₂ capture system. The ionic liquid (IL) object of study has been the 1-ethyl-3-methylimidazolium acetate [emim][Ac]. This IL has been chosen due to its chemical reaction with CO₂.

Different amounts of distilled water were added into [emim]Ac] in order to solve the problems associated with the viscosity of the ionic liquid. The presence of water may also facilitate binding of CO₂. The purpose of this combined sorbent containing water and an ionic liquid comprising a carboxylate moiety such as acetate, was to achieve competitive efficiencies with traditional processes based on power stations and alkanolamines. Using 30% (vol) water a CO₂ capture efficiency of 72.5% and an overall mass transfer coefficient (K_{overall}) of $9.34 \cdot 10^{-5}$ m s⁻¹ was accomplished. Simulation results of sensitivity analysis pointed out that only two hollow fiber membrane contactors (total length 0.6m)

or a K_{overall} of $1.70 \cdot 10^{-4}$ m s⁻¹ were required in order to reach an efficiency of 90%. The addition of water to the ionic liquid leads to use a hybrid solvent in an intensified process.

Keywords: Carbon dioxide capture, ionic liquids (ILs), membrane contactors, PVDF, water, hybrid solvents.

1. Introduction

The removal of acid gases like carbon dioxide is nowadays an essential part of various industrial processes. Excessive emission of CO₂ brings about the most dramatic increase in global atmospheric temperature, which has drawn more and more attention [1]. Since 2010, atmospheric CO₂ concentration has been kept at a high level, over 390 ppm, which has become an urgent environmental issue [2]. In this sense the fifth Intergovernmental Panel on Climate Change (IPCC) report said that the global CO₂ emission must be cut by 50–80% in 2050 to avoid the serious damage climate change could cause by the rise of CO₂ concentration in the atmosphere [3].

One step toward reducing CO₂ emissions is to capture the CO₂ generated during combustion and to store it in a suitable place. Carbon capture and sequestration (CCS) technology is of particular importance in reducing the anthropogenic CO₂ emissions [4]. CCS has the potential to reduce future world emissions from energy generation by 20% and carbon dioxide valorization is under development [5]. CO₂ is the primary greenhouse gas that emitted through human activities such as composition of fossil fuels for energy, transportation and industrial processes [6]. Around 30% of CO₂ emissions come from fossil fuel power plants and since coal is the lowest cost fuel to produce electric power in comparison with oil and gas and the predictions indicate that fossil fuels will be the dominant energy source in the coming decades, and the amount of energy demand will

increase further by 53% by 2030 [7-8]. The capture is the most expensive step of the capture storage chain [9]. Despite this, it is gaining attention among researchers and policymakers as a short-midterm solution to contain carbon emissions from existing or yet to be built fossil fuelled power plant [10]. Three main methods have received an increasing amount of attention during the past decades, related to the greenhouse effect: pre-combustion, post-combustion and oxy-combustion [11].

This work is focused on the post-combustion capture, which can be considered a technical and economic challenge in itself due to the low concentration and pressure of CO₂ in the gas stream and the lack of recovered compound value [12]. In a typical post-combustion capture process, the treated flue gas is passed through a chemical absorption column where the solvent takes up the carbon dioxide. The CO₂-rich solvent is regenerated by heating in the stripper unit. The CO₂ is then compressed. The most commonly used industrial solvents are divided into physical and chemical solvents. On the one hand, physical solvents depend on the physical solubility of the acid gas in the solvent. On the other hand, chemical solvents involve a chemical reaction between the absorbent and the dissolved acid gas [13].

The main disadvantage in typical capture process is the low concentration of CO_2 in power-plant flue gas, around 15%, means that a large volume of gas has to be handled, which results in large equipment sizes and high capital costs. Traditional solvents such as monoethanolamine (MEA), have been used for CO_2 capture, achieving an outlet stream with a very low CO_2 concentration [14]. However, the cost of aqueous alkanolamines based absorption/desorption processes is high because of more heat duty requirements for the absorbent regeneration [15]. Previous works predict that an amine system used to capture around 90% of the carbon dioxide in flue gas require about 30% of the total power produced by the plant and result in a CO_2 capture cost of \$40–100/ton CO_2 [16]. A study of technical performance and costs estimation are determinant to select optimal operating conditions [16]. Research on some emerging capture technologies such as membranes, ionic liquids and metal organic frameworks (MOFs) is in progress with the aim of reducing capture energy consumption and capital investment [17]. The estimation of capture costs should take into account some restrictions, such as the DOE's goal in 2025 of \$40/tonne CO₂. Recent works are focused their efforts in developing materials, techniques and technologies to achieve a carbon capture and sequestration where in the cost of electricity will not be increased by more than 35% in the levelized cost of energy [18-19]. To achieve this goal is very difficult, because flue gas is hot, dilute in CO₂ content, near atmospheric pressure, high in volume, and often contaminated with other impurities such as O₂, SO_x, NO_x, and ash [19].

Ionic liquids (ILs), have been proposed as an alternative to the volatile, corrosive, and degradation sensitive conventional solvents [20]. ILs are salts with a melting point lower that 373K with a negligible vapor pressure, environmentally benign with high CO₂ solubility and recyclable [21, 22].

Previous works suggested that the CO₂ absorption rate and capacity of ILs are not as high as those of conventional amine solvents. However, these works pointed that the practical application of ILs as efficient CO₂ solvents may be feasible by either the use of high pressure in the scrubbing columns to enhance the absorption capacity or mixing with water to decrease the viscosity and increase the absorption rate [23]. In particular, previous works pointed out the mixtures of acetate based ILs with water can be considered as promising absorbents for carbon dioxide capture [24]. Moreover, recent developments are also related to the mixing of ILs with water, amines, or other organic compounds to improve the CO₂ separation [25]. A promising alternative to common amine processes is the chemisorption of carbon dioxide in ILs which containing a carboxylic anion [26]. Choose an ionic liquid with low volatility, degradability and corrosivity, high reaction rates with CO₂ and high loading capacity is of vital importance [27]. In spite of the attractive tunable properties of ionic liquids, their high viscosities and relatively high cost are two big challenges for ILs to be applicable on the industrial scale. Therefore, in order to integrate ILs into existing industrial processes, the combination of ILs with one or more non-IL components may be interesting to produce an optimal, IL-based hybrid solution amenable for use within an existing process such as carbon dioxide capture. This approach may be more efficient than to design/synthesize new IL for desired properties.

The ionic liquid 1-ethyl-3-methylimidazolium acetate, [emim][Ac], has been used in this work due to its high CO₂ solubility, commercial availability and relative low cost and chemical absorption [14, 20, 23, 28-31]. In order to solve the problems associated with high viscosity in ionic liquids, different quantities of water were added into the ionic liquid [emim][Ac].

Carbon capture with membranes technology is being demonstrated as a technical economically viable due to its compaction and its capacity to be modulated [19]. Merkel et al., (2010) pointed that substituting the traditional towers by membranes which combined with the power usage, results in a decreased in capture cost until about \$23/ton [16]. Lee et al, (2015) described a post-combustion CO₂ capture plant located at the Boryeong power station (South Korea) that could treat 200 tonCO₂/day (10MWe equivalent) [32].

Hollow fiber gas-liquid membrane contactors provide the alternative to conventional gas absorption systems for CO₂ capture from gas streams. This type of contactors offers numerous advantages in comparison with absorption towers; the lack of flooding, channeling or foaming, a stable system which is not sensible to small changes, good mechanical strength, high surface area per unit volume and independent control of gas and liquid flow rates [26, 33, 34]. In addition, hollow fiber membrane contactors are less sensitive to fouling since there is no convection flow through the membrane pores [35]. Moreover, due to the compact nature of the membrane device, these type of absorbers have less energy-consuming, less voluminous, and hence, are more economical. In addition, the modularity of membrane modules makes the design simple and easy to be scaled up linearly and the interfacial area is known and constant [36-37]. Using membrane contactors provides the operating cost savings of 38-42%, and capital cost savings of 35-40% can be achieved [38].

Polymeric membranes appear, currently, to be the most advanced option for membranebased post-combustion carbon capture in terms of CO₂/N₂ permselectivity [39]. The Polyvinylidene fluoride (PVDF), is a hydrophobic polymer soluble in common solvents, has been widely used for resistance, which are important parameters for CO₂ absorption/stripping applications. PVDF also possess low values of surface energy [40, 41].

Taking into account the potential of PVDF polymers, the present study of self-made PVDF fibers was performed in a hollow fiber membrane contactor using as absorbent different proportions of the ionic liquid [emim][Ac] and distilled water. CO₂ capture in terms of efficiency and overall mass transfer coefficient was evaluated. The water effect on the CO₂ capture efficiency was quantified in order to determine the best solvent composition when the [emim][Ac] ionic liquid was used. The intensification factor (I) was also evaluated to compare hollow fiber membrane contactors with the traditional processes. Moreover, a simulation task was realized to estimate the mass transfer as well as operational effects required to achieve a 90% CO₂ recovery.

2. Experimental set up

For the carbon dioxide capture, a Polyvinylidene fluoride (PVDF) improved with the ionic liquid 1-ethyl-3-methylimidazolium acetate [emim][Ac] hollow fiber membrane contactor was home-made by phase inversion. The complete description of the fiber manufacturing method is explained in previous works [14, 42, 43]. The absorption membrane contactor was manufactured by gluing hollow fiber in a PVC shell [14]. The main characteristics of the membrane contactor are given in Table 1.

The [emim][Ac] (≥90%) ionic liquid was supplied by Sigma Aldrich (Spain). Despite its relatively low purity, solubility rates were measured and compared with literature data, similar values were obtained [44, 45].

The experimental setup is shown in Figure 1. The feed gas mixture stream contains 85 vol.% N₂ and 15 vol.% CO₂. Carbon dioxide 99.7±0.01 vol.% and pure nitrogen 99.999±0.001 vol.% were supplied by Air Liquide (Spain). The flow gas (20 mL min⁻¹) was adjusted using a Brook instrument MFC 5850, Emerson Process Management Spain and flowed through the inside of the hollow fibers. The absorbent flowed counter-currently through the shell side. A digital gear pump (Cole Parmer Instrument Company, Hucoa-Erloss S.A, Spain) was used in order to control the liquid line (50 mL min⁻¹). The experiments were carried out at 303K. To obtain isothermal conditions, a convection oven was used in the experimental setup (Memmert UNE 200), as shown in Figure 1. Each experiment was replicated three times, and the average value was calculated.

The outlet CO₂ concentration was continuously monitored using a gas analyzer (Emerson Process) based on non-dispersive infrared (NDIR) spectroscopy [30].

The base-case was with the [emim][Ac] IL as solvent. In order to evaluate the water influence in the process and achieve a high efficiency, different amounts of water were

added in a range between 10-40% quantified by volume into the absorption liquid. The viscosity of the solvent with different contents of water was measured by a rotational viscometer (Smart Series, Fungilab Spain) and the obtained data are shown in Figure 2.

3. Results and discussion

3.1 Carbon dioxide capture

The experiments were carried out with PVDF-[emim][Ac] fibers in order to evaluate the process efficiency with different amounts of water in the absorbent liquid. The presence of water in ionic liquid affects the physicochemical properties of the liquid mixture, i.e., lowering the viscosity of the mixture, and advantage for industrial applications [24]. The gas phase was composed by 15% CO₂ and 85% N₂, typical in many industrial process [46]. The liquid stream was fed through the shell side, while the gas flowed in counter-current through the lumen side. The CO₂ capture efficiency in each experiment was calculated as shown in Equation 1:

$$Efficiency (\%) = \left(1 - \frac{C_{CO_2,out}}{C_{CO_2,in}}\right) 100$$
 (Eq. 1)

where $CO_{2,in}$ is the initial carbon dioxide composition (0.15) and $CO_{2,out}$ is the output value analyzer.

Table 2 shows the results obtained based on the CO₂ capture efficiency ranged between 20.5% in the case of the [emim][Ac] ionic liquid and a maximum value of 72.5 % when 30% of water was added to [emim][Ac]. All the experiments were performed with a gas flow of 20 mL min⁻¹ and 303K. The results indicate that water content in the ILs significantly influenced the efficiency of the process. The effect of water in [emim][Ac] ionic liquid on the efficiency acts mainly on the viscosity of the ionic liquid. This behavior

can be explained by the molecular interactions that water promotes in the ionic liquid [47]. It is also suggested that the carboxylate moity (such as acetate) interacts with water to form a weak reversible bond with CO₂ [48].

This work leads to quantify the effect of water that is important for the proper design of the CO_2 capture unit: estimating the membrane area required to achieve a determined target of CO_2 capture efficiency.

From the obtained results, some remarks are pointed out: (i) the efficiency increases significantly with a higher water content until a maximum of 30% (vol) (ii) the efficiency increases because of the solvent viscosity decreases, and more important (iii) the values obtained with a 30% water content (vol) were really competitive with traditional alkanolamine solvents such as monoethanolamine (MEA) [49].

In addition, with a water volume around 30% in the [emim][Ac], the mass transfer was benefited for the process. The overall mass transfer coefficient, $K_{overall}$ expressed in m s⁻¹ was calculated as in previous works according to the equation 2 [14, 30, 50].

$$N_{CO_2,g} = \frac{Q_g}{A} \left(C_{CO_2,in} - C_{CO_2,out} \right) = K_{overall} \frac{\Delta y lm P_T}{RT}$$
(Eq.2)

being Q_g the gas flow rate (m³ s⁻¹), A the membrane area (m²), P_T the total pressure in the gas phase and Δ ylm the logarithmic mean of the driving force based on gas phase molar fractions [30].

Figure 3 represents the different values of $K_{overall}$, with the highest value of 9.3 10^{-5} m s⁻¹ that corresponds to the 30% water content (vol) in the solvent.

The overall mass transfer coefficients were also transformed according to equation 3. The resulting constant, K_r (s⁻¹), may be useful for comparison to different hollow fiber modules [34].

$$Kr(s^{-1}) = K_{overall}(m s^{-1}) \frac{Fiber area(m^2)}{\text{Shell volume}(m^3)}$$
(Eq. 3)

Table 3 compares the Kr values obtained with different amounts of water and previous data reported in the literature. All values were performed in the temperature range 300±3K. Different type of hollow fiber membrane contactors were compared. Polypropylene (PP) and polysulfone (Ps) hollow fiber membrane contactors possessed the same effective inner membrane area (0.18 m²). Moreover, the results with [emim][Ac] ionic liquid were related with 1-ethyl-3-methylimidazolium ethylsulfate [emim][EtSO4] presents physical absorption and low viscosity [30].

Results with [emim][Ac] ionic liquid and water are rather higher than the other values. Only the value of Kr using PP membrane contactor and [emim][Ac] ionic liquid, 13.7 s⁻¹ is slightly higher. This could be attributed to the fact that the relation between fiber area/shell volume is raised.

3.5. Simulation task to estimate mass transfer and operational effects.

The aim of the numerical analysis was to evaluate the set of conditions as membrane mass transfer coefficient and membrane length, which assure an intensification effect for a membrane contactor compared to a packed column.

A non-wetted operating mode was assumed for the modelling of the PVDF hollow fiber membrane contactor. According to previous works the CO₂ was transferred to the liquid phase by diffusion through the pores filled with gas [51, 52]. The radial position r=0shows the center of the fiber and the axial distance of z=0 is referred to the initial position of the gas in the fiber. The dimensionless differential mass balance on CO₂ (eq. 4) was based on the following assumptions according to previous works [50, 51, 52]; (1) the absorption liquid has negligible concentration of the soluble gas, (2) the process is in steady state and isothermal conditions, (3) there is not an axial diffusion, (4) an ideal gas behavior, (5) constant both fiber and shell side pressures and finally (6) the velocity is fully developed in a laminar flow.

$$\frac{Gz}{2}[1-\bar{r}^2]\frac{\partial\bar{C}_{CO_2}}{\partial\bar{z}} = \frac{1}{\bar{r}}\frac{\partial}{\partial\bar{r}}\left(\bar{r}\frac{\partial\bar{C}_{CO_2}}{\partial\bar{r}}\right) \tag{Eq.4}$$

where the dimensionless variables were:

$$\bar{r} = \frac{r}{R} \tag{Eq. 5a}$$

$$\bar{z} = \frac{z}{L} \tag{Eq. 5b}$$

$$\bar{C}_{CO_2} = \frac{C_{CO_2}}{C_{CO_2,inlet}} \tag{Eq. 5c}$$

The following boundary conditions were used were:

$$\bar{r} = 0 \rightarrow \frac{\partial \bar{C}_{CO_2}}{\partial \bar{r}} = 0$$
 (Eq.6a)

$$\bar{r} = 1 \rightarrow \frac{\partial \bar{C}_{CO_2}}{\partial \bar{r}} = -\frac{Sh}{2} \bar{C}_{CO_2}$$
(Eq.6b)

$$\bar{z} = 0 \rightarrow \bar{C}_{CO_2} = 1 \tag{Eq. 6c}$$

and the dimensionless numbers:

$$Gz = \frac{u_m \, di^2}{D \, L} \tag{Eq. 7a}$$

$$Sh = \frac{K \, di}{D} \tag{Eq. 7b}$$

Finally, the CO₂ outlet concentration was calculated as a dimensionless mixing cup:

$$\bar{C}_{CO_2=L} = 4 \int_0^1 \bar{C}_{CO_2} \left[1 - \bar{r}^2\right] \bar{r} \, d\bar{r} \qquad (Eq.8)$$

The software Aspen Custom Modeler (Aspen Technology Inc.) was used to solve the set of equations.

Figure 4 shows the modelling profile in function of the carbon dioxide outlet concentration and the CO₂ capture efficiency along the module length. As seen in the Figure 4, the experimental and results from simulation were totally in concordance. Table 4 resumes the values of the relative error (simulation respect to experimental). Moreover, the modelling results have been compared with other modules: polysulfone and polypropylene.

Two sensitivity analysis were carried out in order to estimate the effect of two variables: the mass transfer and the module length, on the CO₂ capture efficiency of the membrane process:

(i) The overall mass transfer coefficient, K_{overall}, was varied as shown in Figure 5. Using a K_{overall} higher than $1.70 \cdot 10^{-4}$ m s⁻¹, the efficiencies obtained were upper than the target capture efficiency, 90% CO₂ capture (Figure 5a).

(ii) The fiber length was varied, (Figure 6), to estimate the number of hollow fiber membrane contactors in series necessary to achieve at least a 90% efficiency. Figure 6 shows the influence of the fiber length. Using the ionic liquid without water, ten hollow fiber in series (3 m total length) were necessary to reach the target capture efficiency, while when adding 30% (vol) water to the ionic liquid, only two membrane contactors (0.60m) were required.

The Figure 5b also shows the intensification factor (I). This factor was calculated as the volumetric absorption capacity of the membrane contactor divided by the average volumetric absorption capacity of a packed column. The reference value of a classical packed column was estimated for 1 mol $CO_2 \text{ m}^{-3}\text{s}^{-1}$ using a 30 wt.% MEA solution [53].

The intensification factor reached values from 1.05 (0% vol. water) to 3.75 (30% vol. water) for an operating temperature of 303 K.

The hollow fiber membrane contactors can be coupled in parallel and in series depending on the gas flow and the efficiency required. This fact allows to this membrane technology to compete with traditional systems capture using amines and absorption towers. The addition of water to the ionic liquid leads to use a hybrid solvent in an intensified process. Further work is focused to estimate the implications in the capture costs.

Finally, a study as a function of the dimensionless Sherwood and Graetz numbers was realized. On one hand, Figure 7a shows an analysis in terms of the Sherwood number using a fixed Graetz number ($8.02 \cdot 10^{-3}$). For Sherwood number values greater than $4.7 \cdot 10^{-3}$, efficiencies higher than 90% were achieved. On the other hand, for a constant, dimensionless Sherwood number, the Graetz number was varied (Fig. 7b). Graetz values smaller than $4.5 \cdot 10^{-3}$ and $7.89 \cdot 10^{-3}$ allowed for high efficiencies over 90% CO₂ capture, using 30% and 0% water respectively.

4. Conclusions

The influence of water on a Polyvinylidene fluoride (PVDF) immobilized with [emim][Ac] ionic liquid hollow fiber membrane contactor was investigated in a nondispersive absorption plant for carbon dioxide capture. The flue gas was composed by 15% CO₂ and 85% N₂. The ionic liquid 1-ethyl-3-methylimidazolium acetate [emim][Ac] was used as reference solvent. This ionic liquid was chosen due to its high CO₂ solubility. Different quantities of water were added in order to study the water influence in the process. The hybrid solvent based on a combination of 30% water and 70% [emim][Ac] expressed by volume as absorbent, provided a CO_2 capture efficiency of 72.5%, significantly higher than the reference solvent.

The overall mass transfer coefficient was also evaluated. A value of $9.34 \cdot 10^{-5}$ m s⁻¹ was reached for the hybrid solvent. The K_{overall} was transformed by the term (fiber area/shell volume) and values are rather higher than the other values reported in literature for different module contactors. The content of water in the absorbent could significantly affect the mass transfer of membrane contactor because of the change in viscosity and the molecular interactions that water promotes in the ionic liquid.

From the sensitivity analysis some conclusions were obtained: (i) K_{overall} values upper than $1.70 \cdot 10^{-4}$ m s⁻¹ allow CO₂ capture efficiencies higher than 90%, (ii) using only two hollow fiber membrane contactors in series (0.6 m total length) were required in order to achieve the target CO₂ capture efficiency, that provide competitive results comparing with traditional absorption towers, given an significant intensification factor, up to 4, related to the absorption with MEA solution.

Acknowledgements

This research has been funded by the Spanish Ministry Economy and Competitiveness (Project CTQ2013-48280-C3-1-R).

References

[1] Sheng, Y.; Wang, H.; Liu, J.; Zhang Y. Enhanced Performance of a Novel Polyvinyl Amine/Chitosan/Graphene Oxide Mixed Matrix Membrane for CO₂ Capture. *ACS Sustainable Chem. Eng.* **2015**, 3, 1819–1829.

[2] Sun, L.B.; Kang, Y.H.; Shi, Y.Q.; Jiang, Y.; Liu, X.Q. Highly Selective Capture of the Greenhouse Gas CO₂ in Polymers. *ACS Sustainable Chem. Eng.* **2015**, 3, 3077–3085.

[3] Fang, M.; Ma, Q.; Wang, Z.; Xiang, Q.; Jiang, W.; Xia, Z. A novel method to recover ammonia loss in ammonia-based CO₂ capture system: ammonia regeneration by vacuum membrane distillation. *Greenhouse. Gas. Sci. Technol.* **2015**, 5, 1-11.

[4] S. Zulfiqar, M.I. Sarwar, J. Ind. Eng. Chem. 2015, 21, 1373–1378.

[5] Fernández-Barquín, A.; Casado-Coterillo, C.; Palomino, M.; Valencia, S.; Irabien, A. LTA/Poly(1-trimethylsilyl-1-propyne) Mixed-Matrix Membranes for High-Temperature CO₂/N₂ Separation. *Chem. Eng. Technol.* **2015**, 38(4), 658-666.

[6] Y. Abdollahi, N.A. Sairi, M.K. Aroua, H.R.F. Masoumi, H. Jahangirian, Y. Alias, J. Ind. Eng. Chem. 2015, 25, 168–175.

[7] Luis, P.; Van Gerven, T.; Van Der Bruggen, B. Recent developments in membranebased technologies for CO₂ capture. *Prog. Energ. Combust.* **2012**, 38, 419-448.

[8] J. Wang, L. Huang, Q. Zheng, Y. Qiao, Q. Wang, J. Ind. Eng. Chem. 2016, 36, 255–262.

[9] Chabanon, E.; Bouallou, C.; Remigy, J.C.; Lasseuguette, E.; Medina, Y.; Favre, E.; Nguyen, P.T.; Roizard, D. Study of an innovative gas-liquid contactor for CO₂ absorption. *Energy Procedia*. **2011**, 4, 1769–1776.

[10] Canepa, R.; Wang, M. Techno-economic analysis of a CO₂ capture plant integrated with a commercial scale combined cycle gas turbine (CCGT) power plant. *Appl. Therm. Eng.* **2015**, 74, 10-19.

[11] Kanniche, M.; Gros-Bonnivard, R.; Jaud, P.; Valle-Marcos, J.; Amann, J.;Bouallou, C. Pre-combustion, post-combustion and oxy-combustion in thermal power plant for CO₂ capture. *Appl. Therm. Eng.* **2010**, 30, 53-62.

[12] Luis, P.; Van der Bruggen, B. The role of membranes in post-combustion CO₂ capture. *Greenhouse. Gas. Sci. Technol.* **2013**, 3, 1-20.

[13] Singh, B.; Strømman, A.H.; Hertwich, E.G. Comparative life cycle environmental assessment of CCS technologies. *Int. J. Greenh. Gas. Control.* **2011**, 5, 911–921.

[14] Gomez-Coma, L.; Garea, A.; Rouch, J.C.; Savart, T.; Lahitte, J.F.; Remigy, J.C.; Irabien, A. Membrane modules for CO₂ capture based on PVDF hollow fibers with ionic liquids immobilized. *J. Membr. Sci.* **2016**, 498, 218-226.

[15] Chen, J.; Wang, F. Cost reduction of CO₂ capture processes using reinforcement learning based iterative design: A pilot-scale absorption–stripping system. *Sep. Purif. Technol.* **2014**, 122, 149–158.

[16] Merkel, C.; Lin, H.; Wei, X.; Baker, T.R. Power plant post-combustion carbon dioxide capture: An opportunity for membranes. *J. Membr. Sci.* **2010**, 359, 126–139.

[17] Zhang, X.; Singh, B.; He, X.; Gundersen, T.; Deng, L.; Zhang, S. Post-combustion carbon capture technologies: Energetic analysisand life cycle assessment. *Int. J. Greenh. Gas. Control.* **2014**, 27, 289–298.

[18] Mulukutla, T.; Obuskovic, G.; Sirkar, K.K. Novel scrubbing system for postcombustion CO₂ capture and recovery: Experimental studies. *J. Membr. Sci.* **2014**, 471 16–26.

[19] Li, S.; Rocha, D.J.; Zhou, S.J.; Meyer, H.S.; Bikson, B.; Ding, Y. Post-combustion CO₂ capture using super-hydrophobic, polyetherether ketone, hollow fiber membrane contactors. *J. Membr. Sci.* **2013**, 430, 79–86.

[20] Ramdin, M.; De Loos, T.W.; Vlugt, T.J.H. State-of-the-art of CO₂ capture with ionic liquids. *Ind. Eng. Chem. Res.* **2012**, 51, 8149-8177.

[21] Farahipour, R.; Karunanithi, T. Life Cycle Environmental Implications of CO₂ Capture and Sequestration with Ionic Liquid 1-Butyl-3-methylimidazolium. *ACS Sustainable Chem. Eng.* **2014**, 2, 2495–2500

[22] Ashley, M.; Magiera, C.; Ramidi, P.; Blackburn, G.; Scott, T.G.; Gupta, R.; Wilson, K.; Ghosh, A.; Biswas, A. Nanomaterials and processes for carbon capture and conversion into useful by-products for a sustainable energy future. *Greenhouse. Gas. Sci. Technol.* **2012**, 2, 419-444.

[23] Papatryfon, X.L.; Heliopoulos, N.S.; Molchan, I.S.; Zubeir, L.F.; Bezemer, N.D.; Arfanis, M.K.; Kontos, A.G.; Likodimos, V.; Iliev, B.; Romanos, G.E.; Falaras, P.; Stamatakis, K.; Beltsios, K.G.; Kroon, M.C.; Thompson, G.E.; Klöckner, J.; Schubert, T.J.S. CO₂ capture efficiency, corrosion properties, and ecotoxicity evaluation of amine solutions involving newly synthesized ionic liquids. *Ind. Eng. Chem. Res.* **2014**, 53(30), 12083-12102.

[24] Stevanovic, S.; Podgoršek, A.; Pádua, A.A.H.; Costa Gomes M.F. Effect of water on the carbon dioxide absorption by 1-alkyl-3- methylimidazolium acetate ionic liquids. *J. Phys. Chem. B.* **2012**, 116(49), 14416-14425.

[25] Dai, Z.; Noble, R.D.; Gin, D.L.; Zhang, X.; Deng, L. Combination of ionic liquids with membrane technology: A new approach for CO₂ separation *J. Membr. Sci.* **2016**, 497, 1-20.

[26] Hoff, K.A.; Svendsen, H.F. Membrane contactors for CO₂ absorption. *Chem. Eng. Sci.* **2014**, 116, 331-341.

[27] Pinto, D.D.D.; Knuutila, H.; Fytianos, G.; Haugen, G.; Mejdell, T.; Svendsen, H.F. CO₂ post combustion capture with a phase change solvent. Pilot plant campaign, *Int. J. Greenh. Gas. Control.* **2014**, 31, 153–164.

[28] Gurau, G.; Rodríguez, H.; Kelley, S.P.; Janiczek, P.; Kalb, R..; Rogers, R.D. Demonstration of chemisorption of carbon dioxide in 1,3-dialkylimidazolium acetate ionic liquids, *Angewa. Chem. Int. Ed.* **2011**, 50, 12024-12026.

[29] Blath, J.; Deubler, N.; Hirth, T.; Schiestel, T. Chemisorption of carbon dioxide in imidazolium based ionic liquids with carboxylic anions. *Chem. Eng. J.* **2012**, 181-182, 152-158.

[30] Gomez-Coma, L.; Garea, A.; Irabien, A. Non-dispersive absorption of CO₂ in [emim][EtSO₄] and [emim][Ac]: Temperature influence. *Sep. Purif. Technol.* **2014**, 132, 120–125.

[31] Shiflett, M.B.; Yokozeki, A. Phase behavior of carbon dioxide in ionic liquids: [emim][acetate], [emim][trifluoroacetate], and [emim][acetate] + [emim][trifluoroacetate] mixtures. J. Chem. Eng. Data. 2009, 54, 108-114.

[32] Lee, J.H.; Kwak, N.S.; Lee, I.Y.; Jang, K.R.; Lee, D.W.; Jang, S.G.; Kim, B.K.; Shim, J.G. Performance and economic analysis of commercial-scale coal-fired power plant with post-combustion CO₂ capture. *Korean. J. Chem. Eng.* **2015**, 32(5), 800-807.

[33] Hernández, S.; Lei, S.; Rong, W.; Ormsbee, L.; Bhattacharyya D. Functionalization of Flat Sheet and Hollow Fiber Microfiltration Membranes for Water Applications. *ACS Sustainable Chem. Eng.* **2016**, 4, 907–918.

[34] Albo, J.; Irabien, A. Non-dispersive absorption of CO₂ in parallel and cross-flow membrane modules using EMISE. *J. Chem. Technol.* Biot. **2012**, 87, 1502-1507.

[35] An, L.; Yu, X.; Yang, J.; Tu, S.T.; Yan, J. CO₂ capture using a superhydrophobic ceramic membrane contactor. *Energy Procedia*. **2015**, 75, 2287–2292.

[36] Li, J.L.; Chen, B.H. Review of CO₂ absorption using chemical solvents in hollow fiber membrane contactors. *Sep. Purif. Technol.* **2005**, 41, 109–122.

[37] de Souza-Moraes, L.; Araujo-Kronemberger, F.A.; Conceiçao-Ferraz, H.; Claudio-Habert, A. Liquid–liquid extraction of succinic acid using a hollow fiber membrane contactor. *J. Ind. Eng. Chem.* **2015**, 21, 206–211.

[38] Hoff, K.A.; Juliussen, O.; Falk-Pedersen, O.; Svendsen, H.F. Modeling and Experimental Study of Carbon Dioxide Absorption in Aqueous Alkanolamine Solutions Using a Membrane Contactor. *Ind. Eng. Chem. Res.* **2004**, 43, 4908-4921.

[39] Fernández-Barquín, A.; Casado-Coterillo, C.; Palomino, M.; Valencia, S.; Irabien, A. Permselectivity improvement in membranes for CO₂/N₂ separation. *Sep. Purif. Technol.* **2016**, 157, 102-111.

[40] Mansourizadeh, A. Experimental study of CO₂ absorption/stripping via PVDF hollow fiber membrane contactor. *Chem. Eng. Res. Des.* **2012**, 90, 555–562.

[41] Mansourizadeh, A.; Ismail, A.F. Influence of membrane morphology on characteristics of porous hydrophobic PVDF hollow fiber contactors for CO₂ stripping from water. *Desalination*. **2012**, 287, 220–227.

[42] Savart, T. Conception et réalisation de fibres creuses industrielles d'ultrafiltration en poly (fluorure de vinylidène) (PVDF) contenant des copolymères à blocs, *PhD thesis*. Université Toulouse 3. Paul Sabatier. **2013**.

[43] Lorain, O.; Espenan, J.M.; Remigy, J.C.; Lahitte, J.F.; Rouch, J.C.; Savart, T.; Gerard, P.; Magnet, S. Copolymer having amphiphilic blocks, and use thereof for manufacturing polymer filtration membranes. **2014**, WO2014/139977 (A1).

[44]Santos, E.; Albo, J.; Irabien, A. Acetate based Supported Ionic Liquid Membranes (SILMs) for CO₂ separation: Influence of the temperature. *J. Membr. Sci.* **2014**, 452, 277–283.

[45] Albo, J.; Santos, E.; Neves, L.A.; Simeonov, S.P.; Afonso, C.A.M.; Crespo, J.G.; Irabien, A. Separation performance of CO₂ through Supported Magnetic Ionic Liquid Membranes (SMILMs). *Sep. Purif. Technol.* **2012**, 97, 26–33.

[46] Kundu, S.K.; Bhaumik, A. Novel Nitrogen and Sulfur Rich Hyper-Cross-Linked Microporous Poly-Triazine-Thiophene Copolymer for Superior CO₂ Capture. *ACS Sustainable Chem. Eng.* **2016**, 4, 3697–3703.

[47] Martins, C.F.; Neves, L.A.; Estevão, M.; Rosatella, A.; Alves, V.D.; Afonso, C.A.M.; Crespo, J.G.; Coelhoso, I.M. Effect of water activity on carbon dioxide transport in cholinium-based ionic liquids with carbonic anhydrase. *Sep. Purif. Technol.* **2016**, 168, 74-82.

[48] Chinn, D.; Vu, Q.; Driver, M.S.; Boudreau, L.C. CO₂ removal from gas using ionic liquid absorbents. **2005**, US7,527,775 B2.

[49] Wang, L.; Zhang, Z.; Zhao, B.; Zhang, H.; Lu, X.; Yang, Q. Effect of long-term operation on the performance of polypropylene and polyvinylidene fluoride membrane contactors for CO₂ absorption. *Sep. Purif. Technol.* **2013**, 116, 300–306.

[50] Gomez-Coma, L.; Garea, A.; Irabien, A. Carbon dioxide capture by [emim][Ac] ionic liquid in a polysulfone hollow fiber membrane contactor. *Int J Greenh Gas Control.* **2016**, 52, 1-9.

[51] Luis, P.; Ortiz, I.; Aldaco, R.; Garea, A. Irabien A., Recovery of sulfur dioxide using non-dispersive absorption. *Int. J. Chem. React. Eng.* **2007**, *5*, 1-9.

[52] Luis, P.; Garea, A.; Irabien, A. Modelling of a hollow fibre ceramic contactor for SO₂ absorption. *Sep. Purif. Technol.* **2010**, 72, 174–179.

[53] Bounaceur, R.; Castel, C.; Rode, S.; Roizard, D.; Favre, E. Membrane contactors for intensified post combustion carbon dioxide capture by gas-liquid absorption in MEA: A parametric study. *Chem. Eng. Res. Des.* **2012**, 90, 2325-2337.

Figure captions:

Figure 1: Experimental setup.

Figure 2: Viscosity measurements.

Figure 3: Koverall (m s⁻¹) results.

Figure 4: Modelling results: profiles of dimensionless CO₂ concentration and process efficiency (%) along the fiber length assuming non-wetted mode.

Figure 5: Sensitivity analysis of mass transfer coefficient, K_{overall} (5a), and intensification factor (I) (5b).

Figure 6: Sensitivity analysis of length module, L

Figure 7: Sensitivity analysis as a function of the dimensionless Sherwood (7a) and Graetz numbers (7b).

Table captions:

Table 1: Hollow fiber membrane contactors characteristics.

Table 2: Influence of water content in the absorbent in the process efficiency.

Table 3: Kr (s^{-1}) Comparison between different K_{overall} (m s^{-1}) and Kr (s^{-1}) values using different hollow fiber membrane contactors.

Table 4: Comparison between experimental and simulation results and with other hollow fiber membrane contactors.



Figure 1.



Figure 2.



Figure 3.



Figure 4.



Figure 5.



Figure 6.



Figure 7

Membrane material	1AQ2-PVDF
Fiber o.d. do, (m)	7.7.10-4
Fiber i.d. d_i , (m)	4.51.10-4
Fiber length, $L(m)$	0.295
Number of fibers, <i>n</i>	11
Effective inner membrane area, $A (m^2)$	$4.60 \cdot 10^{-3}$
Porosity (%)	30
Packing factor	0.04
Tortuosity ^a	3.33

Table 1.

a Assumed 1/Porosity

Table 2.

Solvent	Efficiency (%)		
[emim][Ac]	$20.5^* \pm 2.27$		
[emim][Ac]+10%water	53.7±0.57		
[emim][Ac]+20%water	67.1±0.10		
[emim][Ac]+30%water	72.5±0.07		
[emim][Ac]+40%water	60.2±1.87		
*Ref. [14]			

Fiber Material	Solvent	Koverall 10 ⁻⁵ (m s ⁻¹)	Fiber Area/Shell volume, m ² m ⁻³	Kr 10 ⁻³ (s ⁻¹)	Ref
PVDF	[emim][Ac]	1.70	122.20	2.08	[14]
PVDF	[emim][Ac]+10%water	5.70	122.20	6.97	This work
PVDF	[emim][Ac]+20%water	8.21	122.20	10.0	This work
PVDF	[emim][Ac]+30%water	9.34	122.20	11.4	This work
PVDF	[emim][Ac]+40%water	6.81	122.20	8.32	This work
PP	[emim][EtSO4]	0.07	7200	5.04	[30]
PP	[emim][Ac]	0.19	7200	13.7	[30]
Ps	[emim][Ac]	0.26	421.43	1.10	[50]

Table 3.

Fiber	Salvant	$um(m,s^{-1})$	Experimental	Simulation	/Error/	Ref
Material	Solvent	um (m·s)	Efficiency (%)	Efficiency (%)		
PVDF	[emim][Ac]	$1.90 \cdot 10^{-1}$	20.5±2.27	20.9	0.4	[14]
	[emim][Ac]+10%water	$1.90 \cdot 10^{-1}$	53.7±0.57	54.5	0.8	This work
	[emim][Ac]+20%water	$1.90 \cdot 10^{-1}$	67.1±0.10	67.8	0.7	This work
	[emim][Ac]+30%water	$1.90 \cdot 10^{-1}$	72.5±0.07	72.6	0.1	This work
	[emim][Ac]+40%water	$1.90 \cdot 10^{-1}$	60.2±1.87	60.9	0.7	This work
Ps	[emim][Ac]	$7.58 \cdot 10^{-3}$	29.5±1.7	46.76	17.3	[50]
	[emim][Ac]	1.33.10-2	16.3	16.0	0.3	[30]
PP	[emim][EtSO4]	1.33.10-2	10.5	10.8	0.3	[30]
	[emim][EtSO4]	3.81·10 ⁻³	28.7	31.3	2.6	[30]

Table 4.