CARBON DIOXIDE CAPTURE BY [emim][Ac] IONIC LIQUID IN A POLYSULFONE HOLLOW FIBER MEMBRANE CONTACTOR

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Abstract

CO_2 emissions have to be controlled and reduced in order to avoid greenhouse effect. This work reports an analysis of the efficiency of CO_2 separation using a hollow fiber membrane contactor and an ionic liquid. This process configuration contributes to the process intensification approach in the field of CO_2 capture and storage.

In this study, the ionic liquid 1-ethyl-3-methylimidazolium acetate, [emim][Ac], was used as absorbent due to its high solubility. The module selected was polysulfone (Ps) because it is a well characterized polymer that allows to operate at moderate temperatures. Results were compared to previous studies with a polypropylene module. The gas stream flowed through the inside of the hollow fibers. The CO_2 removal efficiency was obtained from experimental data, showing a temperature dependence: from 30 to 45.0 %, corresponding to 291 K and 348 K respectively, when the Ps contactor was used. The overall mass transfer coefficient $K_{overall}$ has also been evaluated.

In addition, a numerical analysis was carried out to study the performance of the membrane contactor for the CO_2 capture in order to estimate the process conditions to accomplish 90% CO_2 capture as a target to be competitive with the conventional absorption process.

Keywords: Carbon dioxide capture, hollow fiber membrane contactor, Polysulfone, [emim][Ac] ionic liquid.

1. *Introduction*

Climate change resulting from the presence of greenhouse gases is becoming a serious issue of the present century (Ahn et al., 2013). Over 80% of energy needs worldwide are nowadays supplied by fossil fuels (Korminouri et al., 2014) where combustion in power plants is the largest point source contributor to CO_2 emissions (Saeed and Deng, 2015; Mansourizadeh et al., 2014; Mansourizadeh and Ismail, 2011). The CO_2 capture and sequestration (CCS) is a concern globally today to reduce the impact on the atmosphere and protect humans against the risks associated with CO_2 pollution (Boot-Handford et al., 2014). Therefore, it is important to continue developing technologies to mitigate this issue. A wide range of technologies exist for CCS based on physical and chemical processes including absorption, adsorption, membranes and cryogenics (Rao and Rubin, 2002)). Considering the dependence on fossil fuels, capture and removal of greenhouse gases is an important subject to study (Korminouri et al., 2014). Three main methods can be identified on the capture of CO_2: pre-combustion, post-combustion and oxy-combustion.

For post-combustion capture, CO_2 at low partial pressure must be separated from flue gas after the fuel has been completely burned for energy conversion (Merkel et al., 2010). The typical conditions for post-combustion capture are 10-15% CO_2, 5-10% H_2O, 70-75% N_2 and lower concentrations of other components (Ramdin et al., 2012). In the 90% of the total post-combustion treatments the solvent used are alkanolamines (Albo and Irabien 2012). Previous works showed that process intensification can be performed in two steps to develop a zero solvent emission process (Albo et al., 2010): (i) replace conventional power stations by membrane processes, and (ii) use ionic liquids instead of alkanolamines.

Post-combustion carbon dioxide capture appears to be the most amenable strategy for integration with existing coal-fired power plants (Fernández-Barquin et al., 2015; Low et al., 2013; Dai et al., 2016). Membrane absorption has been identified as an effective approach for CO_2 capture, which combines the advantages of chemical absorption and membrane separation (Zhang et al., 2015). Membrane technology appears to be an attractive option in terms of energy saving, modularity, easy scaling up and control, such as those energy intensive based on wet scrubbing using aqueous amine solutions (Fernández-Barquin et al., 2016).

The properties of the membrane depend on the material, the structure and thickness, the configuration and the module and system design, which involve the existence of many variables that have to be studied. The common materials for CO_2 separating membranes are organic polymers, such as polysulfone (Ps), polyimide (PA), poly(ethylene oxide) and polycarbonate (PC) (Luis et al., 2012; Wang et al., 2014). In the present work, polysulfone (Ps) was chosen because it is a well characterized polymer (Scholes et al., 2010). Ps is an asymmetric nonporous polymeric material applied for CO_2 capture and has been extensively studied for gas permeation and separation, because of its low permeability and comparatively high selectivity, which bring it close to Robeson's upperbound limit (Casado-Coterillo et al., 2012). This material has also excellent mechanical strength, high thermal and chemical stability and is not necessarily considered as hydrophobic (Korminouri et al., 2015; Nabian et al., 2015). The above properties of this polymer provide a potential application in the membrane gas absorption processes (Mansourizadeh and Ismail, 2010).

In terms of long-term stability, membrane materials with suitable glass transition temperature (Tg) needs to the applied. For the CO_2 off-shore removal from natural gas, membrane with moderate Tg can be used since the separation can be carried out at room temperatures. However, for the CO_2 capture from flue gases, membranes with high Tg may need to be applied because flue gases are often emitted at high temperatures. For such applications, PTFE, polyimide and polysulfone polymers are more appropiate than PE and PP polymers which have very low Tg values (Li and Chen, 2005).

Since the 1980s, membrane contactors have been highly regarded due to several advantages over traditional equipment (Mehdipour et al., 2014). In hollow fiber membrane contactors, the two phases (gas and liquid) contact together without dispersing via membrane, which provides higher interfacial area, and independent control of the liquid and gas flow rates. Ideally, the membrane is porous and hence CO_2 transfer through the membrane is rapid because the pores are gas filled. This ensures a high overall mass transfer and therefore a small membrane contactor area. For this reason, membrane contactors have high specific surface area and can be made modular. Hence scaling up or down is relatively easy. Finally, the mass transfer occurs by diffusion across the two phases (Albo et al., 2010; Albo and Irabien, 2012; Rahbari-Sisakht et al., 2013a; Scholes et al., 2015).

One of the key factors in the separation of CO_2 for gas mixtures is the type of the absorbent or solvent (Reza-Razavi et al., 2013). Ionic liquids (ILs) are compounds that have created enormous interest in recent years as solvents for gas recovery (Albo and Irabien, 2012) ILs are salts, which consist exclusively of ions, with a melting point lower than 100 °C (Albo et al., 2011). ILs have several properties that make them useful for carbon dioxide capture such as (nearly) negligible volatility, high thermal stability, nonflammability, tunability, solvation properties, and high CO_2 solubility (Ramdin et al., 2012). The combination of these features can bring new opportunities in the use of IL-based membranes and processes in CO_2 separation applications, which are more energy efficient and environmentally friendly compared with the current commercial separation technologies. The use of ILs in membrane processes has been a research highlight in recent years. A comprehensive review of these research efforts is reported by Dai et al., 2016.

Ionic liquids containing a carboxylic anion are more biodegradable and less toxic than most other ILs (Chen et al., 2014). Moreover, the 1-ethyl-3-methylimidazolium acetate [emim][Ac] possess physical and chemical absorption, that coupled with its high CO_2 solubility make the [emim][Ac] a promising absorbent. Chemical absorption is useful for ILs because of the mechanism leading to a greater absorption capacity of the gas (Pinto et al., 2014).

In the present work, the study of the CO_2 capture in a polysulfone hollow fiber membrane contactor was carried out at different temperatures using as solvent the ionic liquid [emim][Ac]. The possibility to significantly intensify gas-liquid absorption processes thanks to the membrane contactor has been proposed. In addition, a simulation task was accomplished in order evaluate the set of conditions (i.e. membrane mass transfer coefficient, membrane dimensions, module design) for a significant intensification effect compared to a packed column configuration.

2. *Materials and Methods*

Table 1: Ps and PP membrane contactor characteristics.

Membrane material	Ps	PP
Fiber o.d. d_o, (m)	$1.3 \cdot 10^{-3}$	$3 \cdot 10^{-4}$
Fiber i.d. d_i, (m)	$7 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$
Fiber length, L (m)	0.347	0.115
Number of fibers, n	400	2300
Effective inner membrane area, A (m^2)	0.18	0.18
Porosity (%)	43	40
Packing factor	0.43	0.39
Tortuosity[a]	2.33	2.50

aAsummed as 1/Ɛ

Carbon dioxide (99.7 ± 0.01 vol.%) and pure nitrogen (99.999 ± 0.001 vol.%) were purchased from Air Liquide (Spain). The gas stream was composed by 15% carbon dioxide and 85% nitrogen. The [emim][Ac] ionic liquid was supplied by Sigma Aldrich (Spain). The 1-Ethyl-3-methylimidazolium acetate [emim][Ac] (≥90%) (IL) was chosen because of its high CO_2 solubility. Previous works reported values of the [emim][Ac] high CO_2 solubility (Gurau et al., 2011; Ramdin et al., 2012; Papatryfon et al., 2014). To ensure that the ionic liquid is suitable for our process despite its relatively low purity, solubility rates were measured and, compared with literature data, similar values were obtained. Ps hollow fiber membrane contactor was provided by VWR International Eurolab, S.L. (Spain). The main characteristics of this hollow fiber are shown in Table 1.

Table 2: Viscosity values as function of temperature (Freire et al., 2011).

T (K)	Viscosity (cP)
291	249
298	144
318	48
333	26
348	16

To ensure the stability of the ionic liquid for the temperature interval of the CO_2 capture experiments, up to 350 K, the thermogravimetric analysis was performed in a TGA-60H Shimazdu Thermobalance. Figure 1 shows the decomposition temperature. The [emim][Ac] remains without losing its properties until 440K. Table 2 shows the different viscosity values reported by Freire et al., (2011) as a function of temperature.

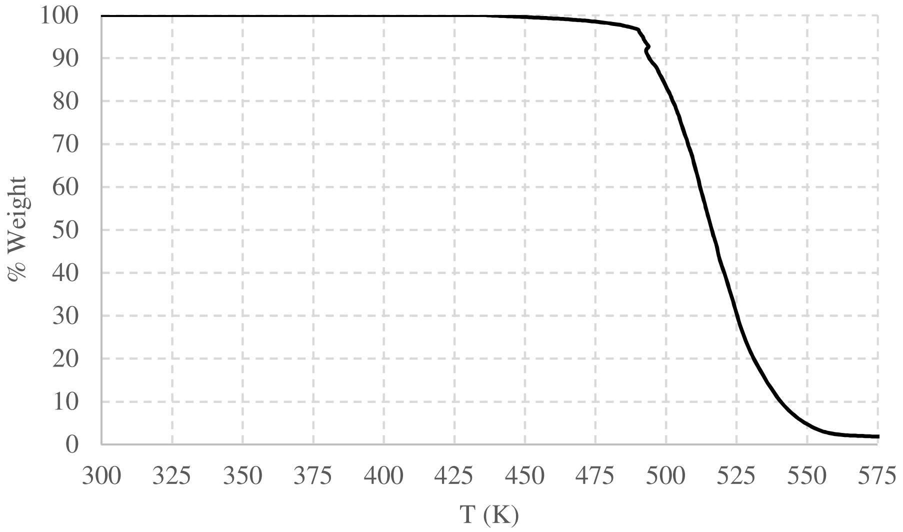


Figure 1: TGA analysis for the [Emim][Ac] ionic liquid.

The experimental setup of the CO_2 capture with [emim][Ac] in the hollow fiber membrane contactor is shown in Figure 2. The gas flow rate operated at 70mL min^{-1}. The feed gas was adjusted by a mass flow controller (Brook instrument MFC 5850, Emerson Process Management Spain). The gas stream flowed through the inside of the hollow fibers and the [emim][Ac] ionic liquid flowed countercurrently through the shell side. The IL was pumped at 50 mL min^{-1}. The temperature was controlled by a Memmert UNE 200 convection oven.

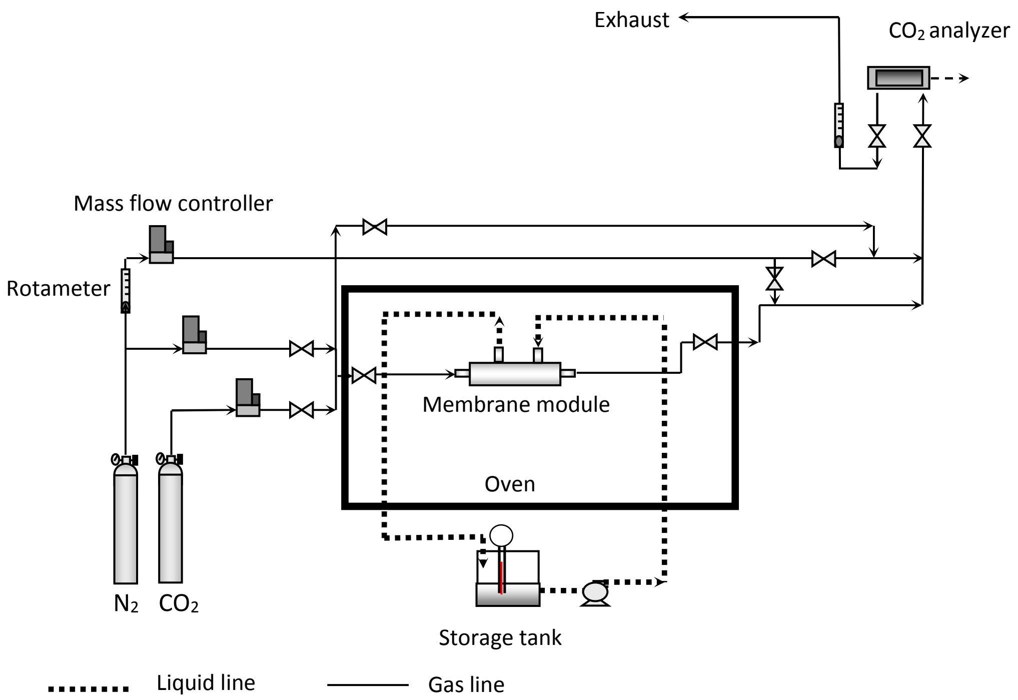


Figure 2: Experimental set-up of the CO_2 capture system at laboratory scale.

The CO_2 concentration in the outlet gas stream was continuously monitored by sampling a fraction of the stream through an analyzer (Emerson Process, Rosemount Analytical NGA 2000) each 15s. This analyzer is based on non-dispersive infra-red (NDIR) spectroscopy. The steady state was determined by a constant carbon dioxide concentration in the exit gas stream.

3. Results and discussion

3.1 Carbon dioxide capture

Carbon dioxide absorption in 1-ethyl-3-methyl imidazolium acetate was performed in a polysulfone hollow fiber membrane contactor in order to evaluate the process efficiency and compare the results with the previous data reported in the literature.

The outlet concentration of carbon dioxide at pseudo-steady-state in terms of efficiency (%) was calculated according to equation 1:

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

where $C_{CO2,out}$ is the outlet analyzer concentration and $C_{CO2,in}$ is the inlet concentration (15%). The outlet concentration of carbon dioxide was calculated as $C_{CO2(g),out}$/ $C_{CO2(g),in}$ at pseudo-steady state, ranged between 0.55 and 0.7, which indicates a process efficiency of around 30-45% (291-348 K) according to equation 1, for a gas stream contained 15% carbon dioxide and 85% nitrogen.

Figure 3 represents the experiments continuously monitored at different temperatures; 291, 298, 318, 333 and 348 K with a gas flow rate of 70 mL min^{-1}. Pseudo-steady state was obtained after 50 minutes maximum operating time.

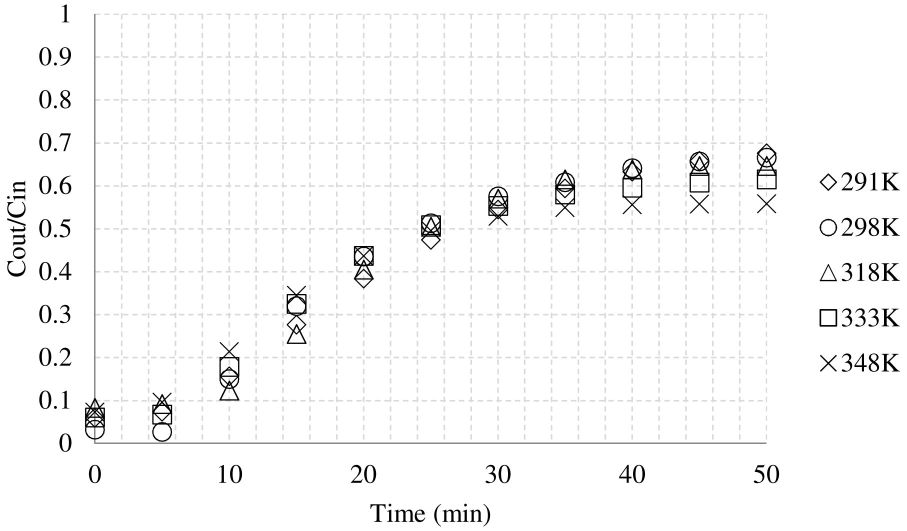


Figure 3: CO_2 outlet concentration (dimensionless) vs time at different temperatures.

Table 3: Process efficiencies in CO_2 capture experiments at different temperatures.

T (K)	Efficiency (%)
291	29.5±1.7
298	33.1±2.6
318	37.4±1.9
333	38.5±2.2
348	44.2±3.5

Table 3 indicates the different efficiency values in the temperature interval 291-348 K. Each experiment was replicated three times under the same operating conditions and the average value was calculated. As it can be seen, the experimental errors are less than 3.5% in all the cases. The efficiency increases when the temperature raises, being favored the chemical reaction.

The efficiency results showed in Table 3 were also compared with previous data reported in the literature (Gomez-Coma et al., 2014). Figure 4 presents the polysulfone results and the results with a polypropylene (PP) hollow fiber membrane contactor.

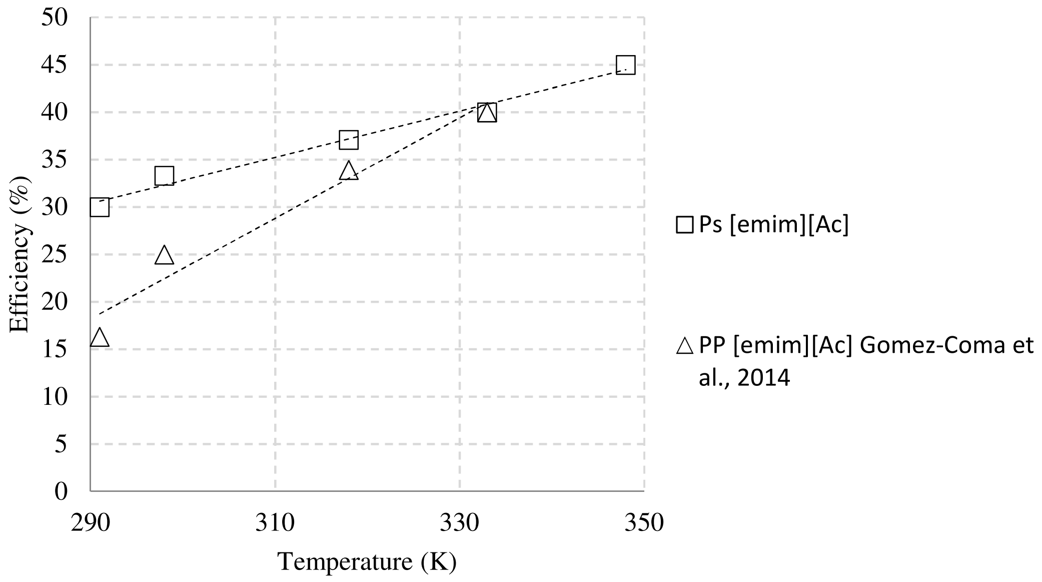


Figure 4: Comparison between Ps and PP hollow fiber membrane contactors: CO_2 capture efficiencies (%) at different temperatures.

Table 1 shows also the main characteristics of the PP hollow fiber membrane contactors too. It should be noted that PP and Ps membrane contactors have the same effective inner membrane area (0.18 m^2).

The Ps results achieve higher CO_2 capture efficiencies at the same temperatures than PP hollow fiber membrane contactors:using the [emim][Ac] ionic liquid, the efficiencies were 30% and 16% (291K) with Ps and PP respectively. In addition, the polypropylene hollow fiber membrane contactors are limited by temperature: with polysulfone membranes, the temperature could reach higher values and therefore higher efficiencies (Fig. 4).

The thermal stability of the membrane is an important issue. Under high temperatures, the membrane material may undergo degradation or decomposition. The extent of membrane change depends of the glass transition temperature T_g for amorphous polymers or the melting point T_m for crystalline polymers. Over these temperatures, the properties of the polymers change significantly. The glass transition temperatures for the commonly used polymers, in CO_2 membrane contactors, are referenced by Li and Chen (2005). Taking into account the Tg data, the higher values correspond to PTFE, polyimide, and polysulfone polymers which are the preferred in terms of long-term stability, while PE and PP polymers have very low Tg values.

For the CO_2 absorption from flue gases, membranes with high Tg may need to be applied because flue gases are often emitted at high temperatures. In this scenario, thermal stability of the membrane material may be the key factor for the membrane performance. This fact supports the selection of the polysulfone membrane contactor for the CO_2 capture.

3.2. Mass transfer description

The overall mass transfer coefficient, $K_{overall}$ was calculated as (Gomez-Coma et al., 2014; Albo and Irabien 2012):

$$N_{CO_2,g} = \frac{Q_g}{A}\left(C_{CO_{2,in}} - C_{CO_{2,out}}\right) = K_{overall}\frac{\Delta ylm \cdot P_T}{RT} \qquad (2)$$

where Q_g represents the gas flow rate ($m^3\ s^{-1}$), A is the membrane area (m^2), P_T is the total pressure in the gas phase, and Δylm is the logarithmic mean of the driving force based on the gas phase molar fractions.

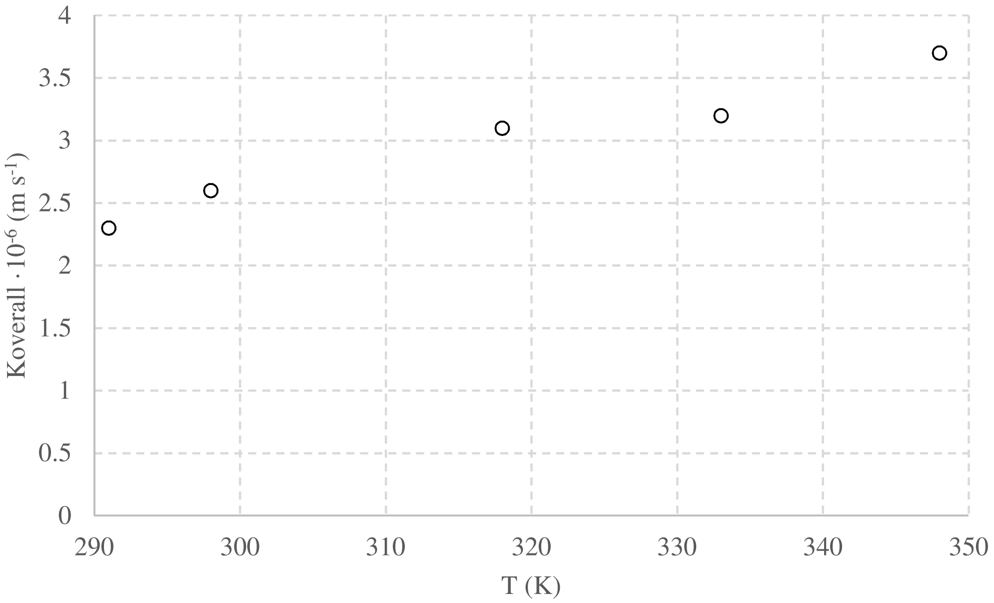


Figure 5: $K_{overall}$ values at different temperatures.

Figure 5 shows the overall mass transfer coefficients obtained at different temperatures from 303K to 348K when the Ps contactor was used. The $K_{overall}$ takes values between $2.3 \cdot 10^{-6}$ and $3.7 \cdot 10^{-6}$ m s^{-1} in the range of temperature from 291 to 348K. The $K_{overall}$ values increase significantly as the temperature rises: an increment of 60% in the temperature range 291-348 K is accomplished. However, the absorption rate did not increase as expected for a process dominated by a chemical reaction. This could be attributed mainly that temperature favors the CO_2 capture but impacts on other factors such as solubility, viscosity and diffusivity. Thevalues of the overall mass transfer coefficient presented in this work, are higher than other values reported in the previous literature for other fiber materials and traditional solvents such as MEA (Rahbari-Sisakht et al., 2013b; Boributh el., 2013). This point is crucial due to the advantages of ionic liquids; e.g. negligible vapour pressures, high thermal, electrochemical and chemical stability and loss less regenerative abilities.

The interaction between CO_2 and the ionic liquid may be described by chemisorption as proposed by Gurau et al. (2011) for ILs with anions of remarkable basicity, The crystal structure demonstrated the formation of the imidazolium carboxylate and the role of acetate in complexing acetic acid.

The description of mass transfer by means of the resistance in series was evaluated. The hollow fiber configuration was selected where the liquid phase flows in the shell side and the gas phase flows through the lumen side. The gas–liquid interface was located on the outer diameter of the tubes. Considering chemical reaction in the liquid side (expressed by the enhancement factor, E) the equation is the following (Eq. 3) (Ortiz et al., 2010; Luis and Van de Bruggen 2013).

$$\frac{1}{K_{overall}} = \frac{d_0}{k_g\, d_i} + \frac{d_0}{k_{mg}\, d_{lm}} + \frac{1}{k_l\, H_d\, E} \tag{3}$$

where d_{lm} is the log mean diameters in (m) of the hollow fiber, H_d represents the dimensionless Henry constant and k_g, k_{mg}, k_l, are the individual mass transfer coefficients of the gas phase, membrane and liquid phase, respectively (m s^{-1}).

Table 4: Contributions to mass transfer. CO_2 absorption with [emim][Ac] in the Ps membrane module.

T (K)	$R_{total}\cdot 10^{-5}$ (s m^{-1})	R_g (s m^{-1})	R_m (s m^{-1})	$R_l\cdot 10^{-5}$ (s m^{-1})
291	4.55	23	77	4.5
298	4.03	22	76	4.0
318	3.30	20	72	3.3
333	2.86	18	69	2.9
348	2.34	17	67	2.3

The overall mass transfer coefficient, $K_{overall,}$ is given by the summation of the resistances in the gas (R_g), membrane (R_m) and liquid (R_l) film (Gomez-Coma et al., 2016; Luis et al., 2009; Ortiz et al., 2010). Table 4 shows the calculated resistances, pointing out that the liquid phase produces the main resistance to mass transfer (nearly

100%), in concordance with previous studies (Gomez-Coma et al., 2014; Gomez-Coma et al., 2016b; Ortiz et al., 2010; Luis et al., 2009).

Taking into account that membrane contactors are considered to be the most promising strategy to achieve intensified CO_2 capture by gas-liquid absorption, the intensification effect was also quantified. The intensification factor I is expressed by the volumetric absorption capacity of a membrane contactor divided by the average volumetric absorption capacity of a packed column. This value has a reference value in a classical packed column estimated around 1 mol CO_2 $m^{-3}s^{-1}$, using MEA 30 wt% solution as solvent (Bounaceur et al., 2012; Favre 2011).

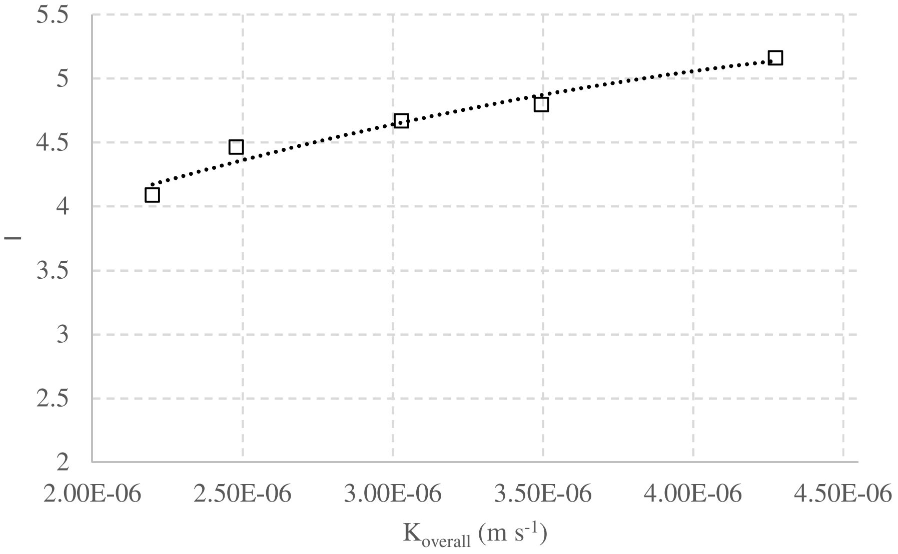


Figure 6: Intensification factor values at different $K_{overall}$ according to Figure 5.

Figure 6 presents the different values of I according to the $K_{overall}$ achieved. Values of I upper than 4 were obtained in all the cases. For a value of $3.73 \cdot 10^{-6}$ m s^{-1} (348 K), an intensification factor of 5.2 was reached. Thus, these values evidence the use of a Ps hollow fiber membrane contactor and the ionic liquid [emim][Ac] as a promising alternative to the conventional CO_2 capture carried out in packed columns.

3.3 Simulation task to estimate mass transfer and operational effects.

A numerical analysis was accomplished to study the performance of a polysulfone hollow fiber membrane contactor for the removal of CO_2 when the [emim][Ac] ionic liquid is used as absorbent. A sensitivity analysis related to the process efficiency was performed to show the influence of the module length and the mass transfer coefficient on the CO_2 capture efficiency, and to determine the required values for achieving a 90% efficiency as a design target.

The optimal design of a membrane contactor should address the interplay between membrane (mass transfer coefficient), fiber dimensions, and module configuration to achieve target performance in areas, such as maximal process intensification with minimal energy requirements (Zhao et al, 2016).

The modelling of the CO_2 capture using the Polysulfone hollow fiber membrane module was considered for both wetted and non-wetted operating modes. In a non-wetted operating mode, the carbon dioxide transfers to the liquid phase by diffusion through the pores filled with gas. Otherwise, in a wet operating mode the pores are filled with the liquid (Luis et al., 2007; Luis et al., 2010). The modelling of the CO_2 transferred from the gas phase to the liquid phase through the membrane barrer was carried out using Aspen Custom Modeler software (Aspen Technology Inc.).

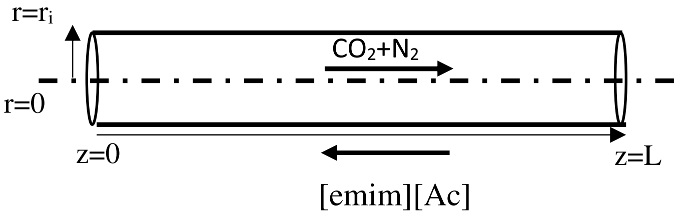


Figure 7: Coordinates of a fiber in the hollow fiber contactor.

The radial and the axial coordinates of the fiber are presented in the Figure 7. Radial position r=0 is pointed as the center of the fiber and the axial distance of z=0 represents the initial position of the gas in the fiber.

The equation 4 describes the differential mass balance of CO_2 in the gas phase in dimensionless form. This equation was based on the following assumptions: a negligible concentration of the soluble gas in the absorption liquid, a steady state and isothermal conditions, no axial diffusion, ideal gas behavior, tube side and shell side constant pressures and the velocity is fully developed in a laminar flow (Luis et al., 2007; Luis et al., 2010, Gomez-Coma et al., 2016b).

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

The dimensionless variables were defined as:

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

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

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

In order to solve the equation 4, the boundary conditions used were the following:

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

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

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

where Gz and Sh are the Graetz and Sherwood number respectively (Gomez-Coma et al., 2016b).

Finally the CO_2 concentration at the outlet of the module is calculated as dimensionless mixing cup (Equation 7):

$$\bar{C}_{CO_2=L} = 4\int_0^1 \bar{C}_{CO_2}\,[1-\bar{r}^2]\bar{r}\,d\bar{r} \tag{7}$$

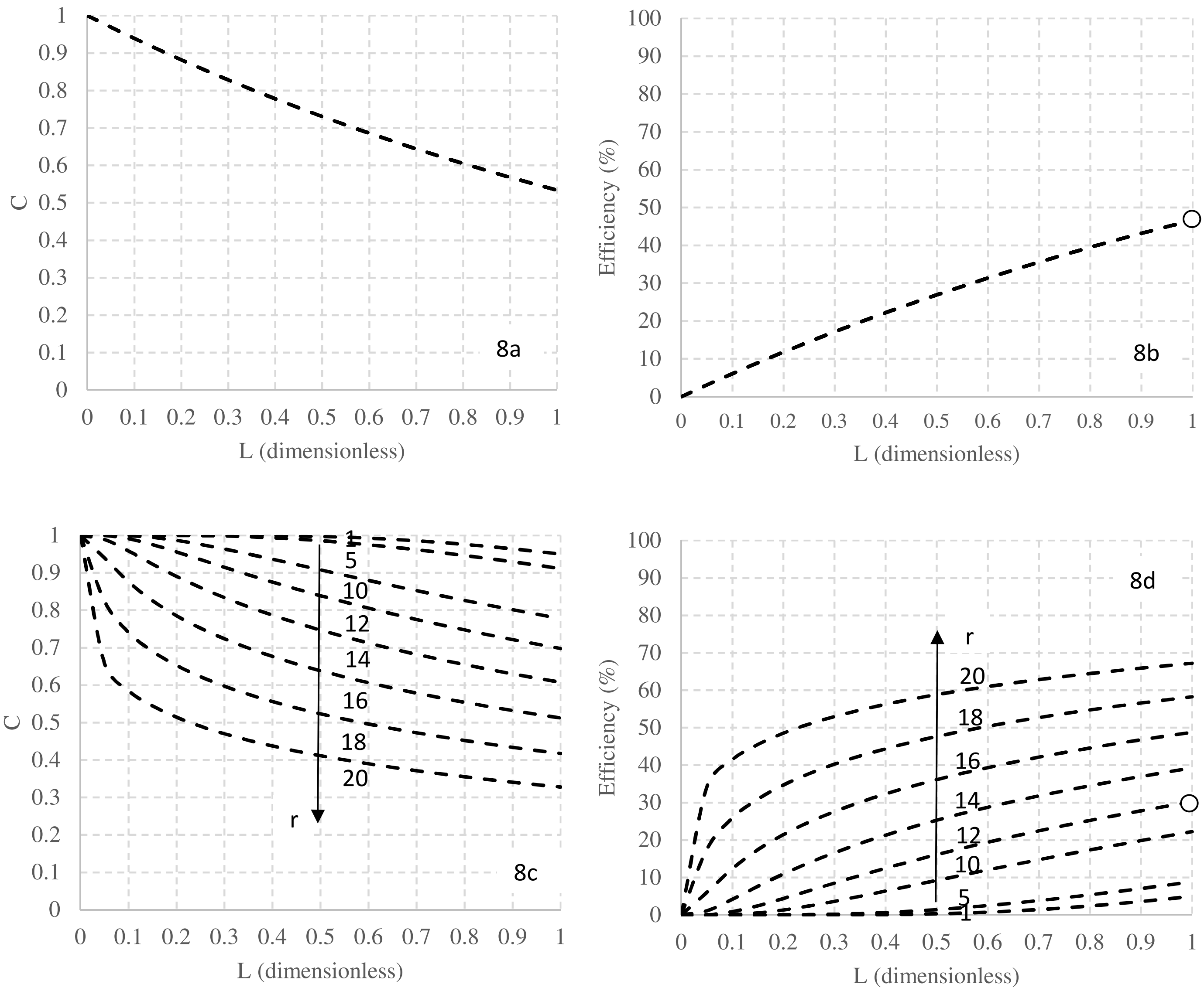


Figure 8: Modelling results: profiles of dimensionless CO_2 outlet concentration (8a, 8c) and process efficiency (%) (8b, 8d) in non-wetted model and wetted model along the fiber length. Node 1: r=0; Node 20: r=1.

The modelling results using a gas flow of 70mL min^{-1} and the different parameters of the Ps hollow fiber membrane contactor (specified in Table 1) were shown in Figure 8. Different nodes in the radial dimension are shown in these figures, from the center of the fiber (r=0) to the membrane layer (r=1). In the present study, there is non-wetted model because of the fact that ionic liquid presents hydrophilicity. However, the two different scenarios (non-wetted and wetted) have been shown in order to explain the nodes behavior in both cases and to quantify the possible effect of wetting on the process efficiency.

The Figures 8a and 8b are focused on a non-wetted operating mode. In this operating model there is not axial diffusion thus all nodes concur. In order to show the differences when wetted mode occurs, Figures 8c and 8d were presented. In this last case, there is axial diffusion and therefore the nodes were differentiated. Figures 8a and 8c show the dimensionless carbon dioxide concentration along the dimensionless length. On the other hand, Figure 8b and 8d use the same abscissa but in this case, what is represented is the efficiency (%). Under the operating conditions covered in this study, the process efficiency decreased a 20 % if the pores of the membrane get wet, respect to a non-wetted mode. Note that both Figures 8b and 8d appear with the CO_2 efficiency calculated based on the dimensionless mixing cup (Eq. 7).

An analysis of the set of conditions to be fulfilled in terms of membrane material (i.e. mass transfer coefficient), fiber dimensions and module packing, in order to ensure a significant intensification effect, is an objective that should be considered to offer a evaluation of the interest and limitations of the different membrane materials, fibers and modules which are reported for this application.

In order to estimate the mass transfer effect on the CO_2 capture efficiency, a sensitivity analysis was performed. As previous works, a value of 90% efficiency was pointed as design target (Yeon et al., 2005; Paul et al., 2007; Zhang et al., 2008; Favre, 2011; Wang et al., 2013). On this basis, the aim of this simulation is to obtain the parameters required to reach this efficiency, in order to provide a cleaner process without solvent losses, non-toxic and lower equipment. Please noted that the ILs are non-volatile, the [emim][Ac] is non-toxic (Alvarez-Guerra and Irabien 2011) and hollow fiber membrane contactors have high specific surface area per unit volume.

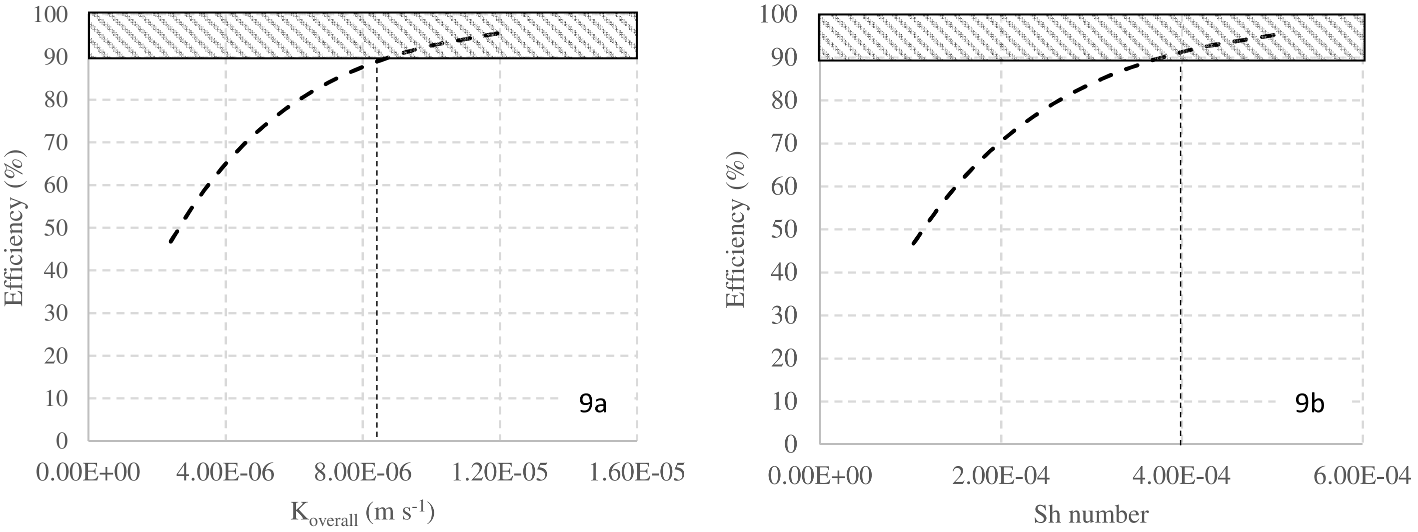


Figure 9: Sensitivity analysis of overall mass transfer coefficient, $K_{overall}$ (9a), and the corresponding Sherwood number (9b).

Figure 9 modifies the overall mass transfer coefficient, $K_{overall}$, from a reference value of $2.4 \cdot 10^{-6}$ m s^{-1} (291K), that can be required to obtain high efficiencies. As it can be seen from Figure 9a, values upper than $9.0 \cdot 10^{-6}$ m s^{-1} reached efficiency values higher than 90%.

Moreover, a more detailed analysis was carried out in figure 9b. The dimensionless Sherwod number was analyzed. Maintaining a fixed dimensionless Graetz number with a value of $6.6 \cdot 10^{-4}$ when the Sherwood number takes values higher than $4 \cdot 10^{-4}$ the design target is accomplished.

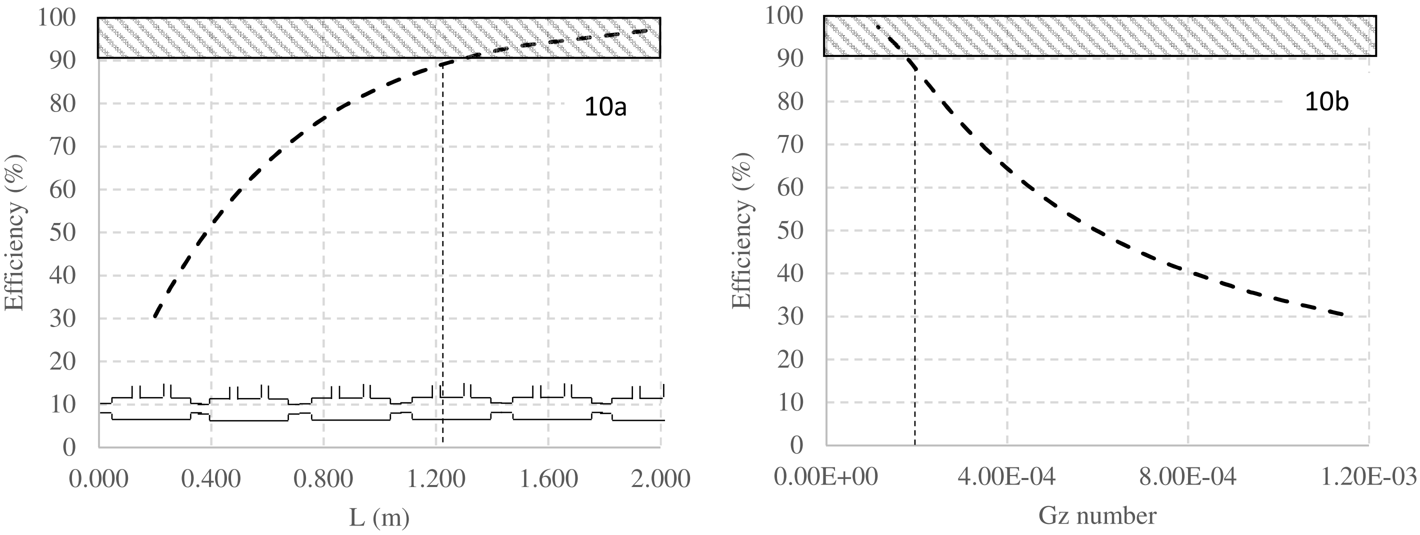
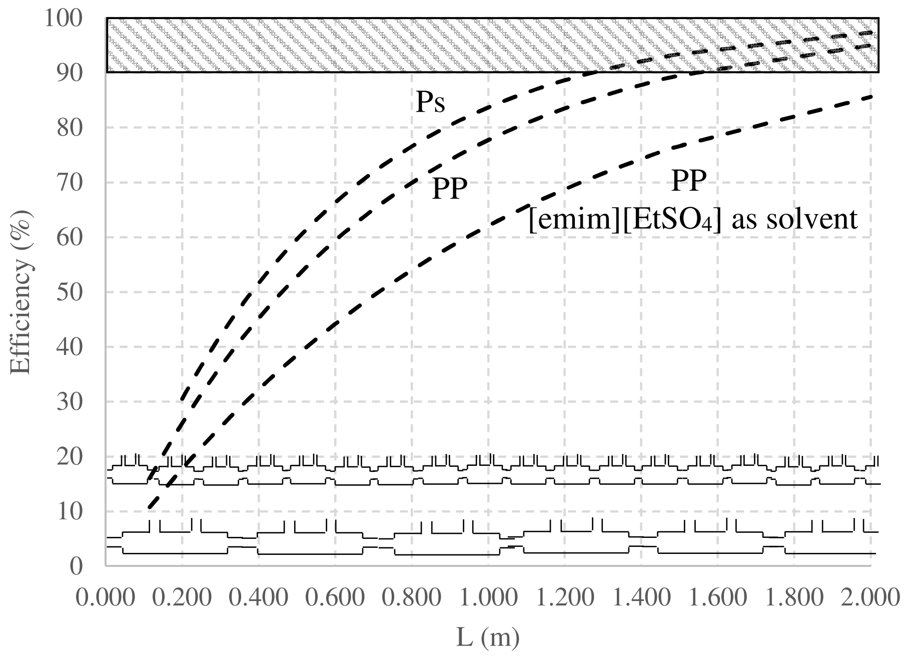


Figure 10: Sensitivity analysis of length module, L (10a), and the corresponding Graetz number (10b).

Taking into account the option to implement a multi-stage network of membrane modules for a high efficiency objective, the fiber length was also modified in order to estimate the number of hollow fibers membrane contactors were necessary to connect in series to achieve a CO_2 capture efficiencies, upper 90%. Figure 10a shows the influence of fiber length. Four Ps hollow fiber membrane contactors will be necessary to couple in series to reach a CO_2 free gas flow. In this sense, this work proposes a post-combustion process based on a set of four Ps membrane modules in series (total length 1.4 m) and a number of these sets in parallel that can be estimated from the basis of flue gas flowrate required (Hoff and Svensen 2013). Furthermore, keeping fixed the dimensionless Sherwood number, the Graetz number was varied (Figure 10b). Graetz values smaller than $2.53 \cdot 10^{-4}$ provide efficiencies higher than 90%.



*Q_g: 70 ml min^{-1}; um Ps: $7.58 \cdot 10^{-3}$ m s^{-1} PP: $1.33 \cdot 10^{-2}$ m s^{-1}.

Figure 11: Quantity of hollow fiber membrane contactors required to achive 90% efficiency for different materials.

The number of hollow fiber membrane contactors required to connect in series were compared with previous data reported in the literature (Gomez-Coma et al., 2014). Figure 11 shows the different quantity of membrane contactors needed to achieve the design target (90% efficiency). Ps hollow fiber membrane contactor requires fewer modules in series than using PP modules, which leads to a significant saving in size equipment to achieve high efficiencies.

Further work on membrane contactors should be aimed at optimizing membrane geometry and module design, which is essential for successful scale-up. Operating in more turbulent flow conditions produces greater mass transfer. However, the shorter residence time that results from a greater solvent flow results in lower solvent loadings. At an industrial scale this must be compensated by multiple passes through membrane modules in series, to ensure that a full solvent loading is achieved. The estimation of capture costs should take into account some target values, such as the DOE`s goal in 2025 of \$40/tonne CO_2.

4. *Conclusions*

Carbon dioxide capture in a polysulfone (Ps) parallel-flow membrane contactor when the ionic liquid 1-ethyl-3-methylimidazolium acetate [emim][Ac] is used as the absorption liquid has been studied by means of efficiency and overall mass transfer coefficient, $K_{overall}$. Taking into account that thermal stability of the Ps polymer, that allows its use for the CO_2 absorption from flue gases, often emitted at moderate temperatures, the influence of the temperature has been quantified.

An efficiency of 45% has been achieved when the temperature rises to 348K. On the other hand, working at 318K the efficiency is higher than with other materials such as polypropylene (PP) comparing the same effective area and the same solvent.

The overall mass transfer coefficient takes values between $2.3 \cdot 10^{-6}$ and $3.7 \cdot 10^{-6}$ m s^{-1} in the range of temperature from 291 to 348K, which are competitive with other values reported in previous literature. The absorption rate does not increase as expected for a chemical reaction. This is because of the fact that temperature favors the CO_2 capture but impacts on other factors such as solubility, viscosity and diffusivity.

Finally, a theoretical simulation using a base case was carried out. Taking into account a target value of 90% CO_2 capture, (i) the mass transfer coefficient should be higher than $9 \cdot 10^{-6}$ $m \cdot s^{-1}$, or (ii) four Ps hollow fiber membrane modules disposed in series were necessary (corresponding to a total length 1.4 m), being proposed for the scaling-up a network of modules in series and as many in parallel as the flue gas flow rate increases. In addition, a comparative with other materials have performed. Polysulfone hollow fiber contactor results much more competitive than PP hollow fiber membrane contactors to achieve 90% efficiency. This fact and the thermal stability of the Ps polymer, which is important of the long-term use, support the selection of the polysulfone membrane contactor for the CO_2 capture.

Further work on membrane contactors should be aimed at optimizing membrane geometry and module design, which is essential for successful scale-up. The new IL-based absorbents coupled with smart design of the membrane processes and development of more compatible membrane materials offer a competitive alternative to the conventional packed column design.

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