THEORETICAL AND EXPERIMENTAL STUDY OF NH₃ ABSORPTION INTO AMMONIA/WATER SOLUTION USING POLYMERIC POROUS MEMBRANES.

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ABSTRACT

This study aims at investigating experimentally and analytically the influence of temperature, pressure and solution velocity on the ammonia vapor mass transfer through a microporous hydrophobic membrane and the absorption into a thin film of ammonia/water solution. To achieve this objective, a mathematical model has been developed and a sensitivity analysis has been carried out in order to determine the influence of the solution mass flow rate, pressure and temperature in the mass and heat transfer processes. For validating the model, an experimental test bench has been designed and built and preliminary results have been obtained.

NOMENCLATURE

x	[-]	Ammonia mass fraction
m	[kg/s]	Mass flow rate
M	[g/mol]	Molecular weight
p	[Pa]	Pressure
T	[K]	Temperature
R	[J/K·mol]	Gas constant
dp	[m]	Pore diameter
J	[kg/m²·s]	Mass flux
H	[J/kg]	Specific enthalpy
Dh	[m]	Hydraulic diameter

Special characters

τ	[-]	Tortuosity factor
ε	[-]	Membrane porosity
δ	[m]	Membrane thickness
μ	[Pa·s]	Viscosity
ε	[-]	Membrane porosity
ρ	[kg/m³]	Density

Subscripts

BL	Bulk liquid
BG	Bulk gas
vap	Vaporization
MM	Membrane
abs	Absorption

INTRODUCTION

Last decades membrane technology has been widely studied and used for improving mass transfer processes in a variety of sectors such as environmental engineering (water and polluted effluents treatments, CO_2 capture, etc.), food industry (concentration / purification products), biotechnology, etc. However, the application of membrane technology in the energy sector, specifically in the field of absorption refrigeration technology, it is quite recent. Membranes have a very good potential in this field due to the lower size and weight of the modules but keeping a high surface area. These advantages make membranes as great candidates for being used in absorption refrigeration cycles driven by exhaust gases of the engines of some mode of transport (boats, planes, etc).

Recently, several authors have studied the absorption and desorption processes with working fluids typically used in absorption cycles. Regarding lithium bromide-water mixture, Ali and Schwerdt [1] determined experimental and theoretically the desired membrane characteristics for absorption chiller applications: high permeability to the refrigerant (water vapour), hydrophobic to the aqueous solution with high liquid entry pressure to avoid wettability of the membrane pores and no capillary condensation of water vapour to avoid blocking of the pores. For practical use, the membrane should have a thin hydrophobic microporous active layer with a thickness up to 60 μm, mean pore sizes around 0.45 μm and a porosity of up to 80%. In a subsequent study, Ali [2] designed a compact plate-and-frame absorber possessing a hydrophobic microporous membrane contactor. The results obtained clearly indicate that the aqueous solution channel thickness is the most significant design parameter that affects the absorber size compactness. Yu et al. [3] also concluded that the solution film thickness and velocity are the critical parameters that affect the absorption rate. The results obtained by Ali also show that the countercurrent refrigerant flow with the aqueous solution has positive effect on the absorber size compactness. Wang et al. [4] studied the application of vacuum membrane distillation to lithium bromide absorption refrigeration system. They used a hollow fibber membrane module made by polyvinyldene fluoride as a desorption device. The main conclusion of that work was that vacuum membrane distillation is an efficient, light and cheap desorption mode. Isfahani et al. [5] went one step forward and studied the efficacy of highly porous nanofibrous membranes for application in membrane based absorbers and desorbers. An experimental plant with all the main components present in the absorption refrigeration systems (evaporator, absorber, desorber and condenser) was set

up. Significantly higher absorption and desorption rates than in the conventional falling film absorbers and desorbers were achieved.

Regarding ammonia/water mixtures, Chen *et al.* [6] proposed and studied via mathematical simulation the integration of the heat exchanger inside the membrane module. Due to the application of this innovative hybrid hollow fibber membrane absorber and heat exchanger (HFMAE) in a typical ammonia/water absorption chiller, an increase of COP by 14.8% and the reduction of overall system exergy loss by 26.7% was obtained. Finally, Schaal [7] carried out several lab-scale experiments with different prototypes of membrane absorbers. Furthermore, a stable operation in an ammonia/water absorption refrigeration plant was accomplished. The main advantage of the membrane absorbers compared to other absorption technologies like plate or shell and tube absorbers is the reduction of size and weight due to the higher surface areas per volume unit than membranes offer. This advantage was pointed up and quantified in Schaal: Membranes can reduce the absorber size up to a factor of 10 compared to plate absorbers and even 100 times compared to shell and tube absorbers.

In this work, a theoretical and experimental study of the ammonia/water absorption process in an adiabatic membrane absorber has been carried out. Most of the studies presented are referred to the H_2O/LiBr mixtures and just a few have NH_3/H_2O as a working mixture. In this work, a new theoretical model has been developed using different assumptions and equations than the ones presented in Schaal and Chen *et al*. Also, a different membrane module has been used for the experimental work (flat sheet membrane instead of using a hollow fiber membrane module). The study has been divided into two main parts: First, a theoretical modelling using Engineering Equation Solver (EES) has been developed and a sensibility analysis of the key parameters of the absorption process has been carried out. Secondly, a pilot plant scale flat sheet membrane absorber test bench has been designed, built and tested for studying the ammonia absorption process. Validation of the theoretical model with the experimental results is the last part of this work.

EXPERIMENTAL SET-UP

A pilot plant scale membrane absorber test bench has been set up for studying the ammonia vapour absorption process into ammonia/water solution using polymeric porous membranes as a contactor. The plant consists of two tanks; one for the weak solution (lower ammonia concentration) and the other one for the strong solution that leaves the membrane absorber (higher ammonia concentration). It has in turn a solution diaphragm pump (Weimer Hydra-Cell series D03), two filters (90 and 7 microns) for preventing any solid particles soiling the membrane, a water bath for adjusting the inlet temperature of the solution, two Coriolis flowmeters whose density measurement allow us to determine the ammonia concentration and the flow rate, a mass flow controller for controlling the ammonia vapour flow rate and a reverse osmosis membrane module (Sterlitech SEPA CF Module). Due to the fact that there are no commercial membrane modules available in the

market for this specific application, the membrane module had to be previously modified in order to meet the requirements of the absorption process. These modifications are explained below. The membrane used is a hydrophobic PTFE laminated membrane (Sterlitech) with an average pore size of 0.05 μm. The thin active layer (PTFE) is laminated onto a polypropylene 0.18 mm layer. Finally, several pressure and temperature sensors located in different key points of the plant enable us to determine the heat exchanged in the absorption process. The detailed system diagram is shown in greater detail in **Figure 1**.

In **Figure 2** it can be observed a scheme of the reverse osmosis flat sheet membrane module. The ammonia/water weak solution enters in the membrane module and is homogeneously distributed all along the membrane surface, where the absorption process takes place. Then, the ammonia/water solution exits the absorber at higher concentration and temperature. The ammonia vapour from the ammonia bottle enters in the module, filling the pores of the membrane and being absorbed by the solution in the liquid interface. The valve V_1 (**Figure 1**) remains closed during the experiments so it can be considered that all the ammonia entering the module is absorbed in the solution. The driving force of the absorption process is the difference between the saturation pressure of the ammonia water mixture and the operation pressure. It is important to control the pressure on both sides of the membrane module for preventing liquid breakthroughs inside the pores when $P_{liq}>P_{gas}$ [7]. Otherwise, mass transfer process is improved when $P_{liq}<P_{gas}$ but a two phase flow is obtained and this situation is not proper for the application of this membrane absorbers in an absorption refrigeration cycle.
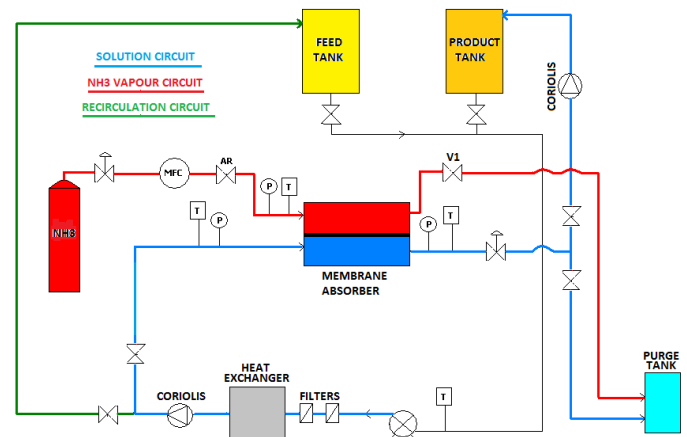
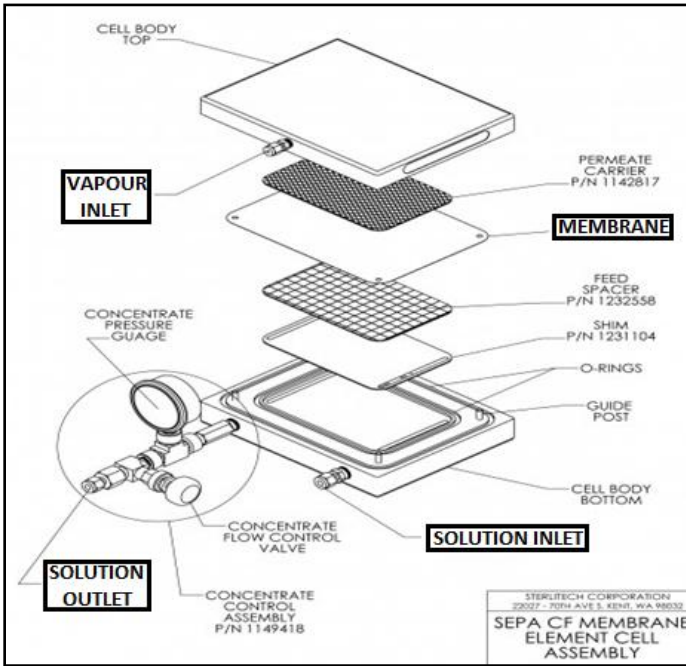**Figure 1** Pilot plant membrane absorber test bench.

Figure 2 SEPA-CF membrane element cell assembly

MODELLING

A theoretical model using Engineering Equation Solver (EES) was developed in order to study the adiabatic absorption process when a microporuous membrane is used as a contactor. Essentially the model determines the amount of ammonia absorbed (mass transfer process)and the heat exchanged during the absorption process. Feed inlet conditions (pressure, temperature and ammonia concentration) are input data. The flat sheet membrane module (14.6cm x 9.5cm) was discretized in 146 elements and the mass and energy balances, transport equations and equilibrium conditions were applied to each one of the elements.

Ammonia/water mixture properties

Density and enthalpy were taken from Ibrahim [8], thermal conductivity was calculated using Bohne equation [9] and the viscosity, heat capacity and diffusion coefficient of ammonia in water were calculated from Conde [10].

Interface modelling

Two transport resistances have considered for modelling the ammonia flow across the membrane: the resistance liquid boundary layer and the transport resistance across the pores of the membrane. Resistance in the vapour boundary layer is neglected due to the fact that pure ammonia in the gas side is considered.

Mass transfer across the porous membrane

Depending on the value of the Knudsen number, Kn (defined as the ratio of the molecule mean free path to pore characteristic diameter), different mechanisms by which vapour may be transported through the membrane are established: (i) Knudsen diffusion, (ii) viscous flux (Poiseuille flow) and (iii)

transition flow. The dusty-gas model assumes that the Knudsen diffusion resistance R_K is in parallel with the Poiseuille flow resistance R_P [11], obtaining:

$$\frac{1}{R_m} = \frac{1}{R_K} + \frac{1}{R_p} = C_m \tag{1}$$

In this model, a transition flow is considered and both resistances have been taken into account. The mass transport coefficient (C_m) according to the resistance analogy can be written as [11]:

$$C_m = \frac{M_{NH3}}{\tau \cdot \delta}\left(\frac{D_K}{R \cdot T_{BG}} + \frac{P_v \cdot B_0}{R \cdot T_{BG} \cdot \mu_{BG}}\right) \tag{2}$$

where P_v is the ammonia vapour pressure in the interface, T_{BG} the gas temperature and μ_{BG} the gas viscosity. Ammonia flow across the membrane (J) and Knudsen diffusion coefficient (D_k) are shown in equations (3) and (4) respectively [11]:

$$J = C_m \cdot (p_{m2} - p_{m1}) \tag{3}$$

being p_{m2} the ammonia vapour pressure. Taking into account that we are considering pure ammonia in the gas side, p_{m2} is equal to the gas pressure. p_{m1} is the partial pressure of ammonia vapour at the interface and it is calculated at every element of the discretized membrane module because temperature and composition are changing along the module.

$$D_K = K_0\left(\frac{8 \cdot R \cdot T_{BG}}{\pi \cdot M_{NH3}}\right)^{0.5} \tag{4}$$

where K_0 and B_0 are previously determined:

$$K_0 = \frac{\varepsilon \cdot d_p}{3\tau} \tag{5}$$

$$B_0 = \frac{\varepsilon \cdot \left(\frac{d_p}{2}\right)^2}{8\tau} \tag{6}$$

Mass transfer in the liquid phase

Using the film theory [12], the ammonia concentration in the interface (x_{m1}) can be calculated from a mass balance across the solution concentration boundary layer as:

$$x_{m1} = x_{BL} \cdot exp\left(\frac{J}{\rho \cdot K_b}\right) \tag{7}$$

where ρ is the density of the solution, x_{m1} the ammonia concentration on the liquid interface boundary layer and K_b the mass transfer coefficient between the solution-vapour interface layer and the bulk solution. It is calculated by formula presented by Gabelman and Hwang [13] for rectangular membrane module (Eq. 8).

$$Sh = \frac{K_B \cdot D_h}{D_{BL}} = 0.18 Re^{0.86} Sc^{0.33} \tag{8}$$

where D_{BL} is the diffusion coefficient of ammonia in water.

The mass flow rate of the ammonia (vapour) absorbed is determined by:

$$m_{abs} = J \cdot dA \tag{9}$$

where dA is the discretized membrane area. Finally, the total and species mass balances are presented:

$$m_{BL}[n+1] = m_{BL}[n] + m_{abs} \tag{10}$$

$$m_{BG}[n+1] = m_{BG}[n] - m_{abs} \tag{11}$$

$$m_{BL}[n+1] \cdot x_{BL}[n+1] = m_{BL}[n] \cdot x_{BL}[n] + m_{abs} \tag{12}$$

Heat transfer

Adiabatic absorber is considered; all the heat released during the absorption process is completely transferred to the liquid and vapour phase, neglecting heat losses to the surroundings [7]. Energy balance for the liquid and the vapour side are shown in equations (13) and (14) respectively.

$$m_{BL}[n] \cdot H_{BL}[n] + m_{abs} \cdot (\Delta h_{vap}[n] + h_{abs}) = m_{BL}[n+1] \cdot H_{BL}[n+1] + U \cdot dA \cdot (T_{BL}[n] - T_{BG}[n]) \tag{13}$$

$$m_{BG}[n] \cdot H_{BG}[n] + U \cdot dA \cdot (T_{BL}[n] - T_{BG}[n]) = m_{BG}[n] \cdot H_{BG}[n+1] \tag{14}$$

U is the overall heat transfer coefficient (Eq. 15), Δh_{vap} is the ammonia vaporization enthalpy at T_{ml} and h_{abs} is the heat released in the absorption process.

$$\frac{1}{U} = \frac{1}{\alpha_{BL}} + \frac{\delta}{k_{MM}} + \frac{1}{\alpha_{BG}} \tag{15}$$

where k_{MM} is the membrane thermal conductivity, obtained using Eq. (16). α_{BL} and α_{BG} are the heat transfer coefficients in the liquid and gas phases respectively and obtained using the analogy between the heat and mass transfer [1].

$$k_{MM} = \varepsilon \cdot \lambda_{BG} + (1 - \varepsilon) \cdot \lambda_{MM} \tag{16}$$

where λ_{BG} and λ_{MM} are the thermal conductivity of the bulk gas and the membrane respectively.

RESULTS

The results obtained in the simulation using the model previously described are studied in this section. The inlet conditions for the base case study are shown in **Table 1**.

Table 1. Inlet values for the simulation base case study.

p (bar)	T_s (ºC)	T_v (ºC)	m_s (kg/h)	x_s
3	30	18	30	0.42

whereT_s and T_v are the inlet solution and vapour temperatures, respectively, m_s the solution flow rate, x_s the ammonia concentration and p the pressure for the liquid and vapour streams. The effect on the heat and mass transfer processes of the variations in the mass flow rate (20-50 kg/h), inlet temperature (20-35 ºC) and pressure (2.5-4 bar) was studied.

Mass transfer

Figure 3 shows the effect of the solution mass flow rate in the mass transfer process. It can be clearly seen that for the range studied, the higher flow rate the lower is the ammonia concentration at the outlet of the membrane absorber (lower Δx). This fact can be explained by the dilution effect produced when the ammonia vapour crossing the membrane is absorbed in a bigger amount of solution as a result of the increment in the flow rate. On the other hand, the ammonia flux across the membrane (J) increases when solution flow rate increases. This behaviour can be explained because if the concentration of the solution is decreasing (**Fig. 3**), the partial pressure of the ammonia vapour at the interface is also decreasing. Looking at Eq. 3 we can conclude that the lower p_{ml}, the bigger is the pressure difference and the higher is the ammonia flux across the membrane. That is to say, increasing the solution flow rate the mass transfer process driving force is also enhanced.
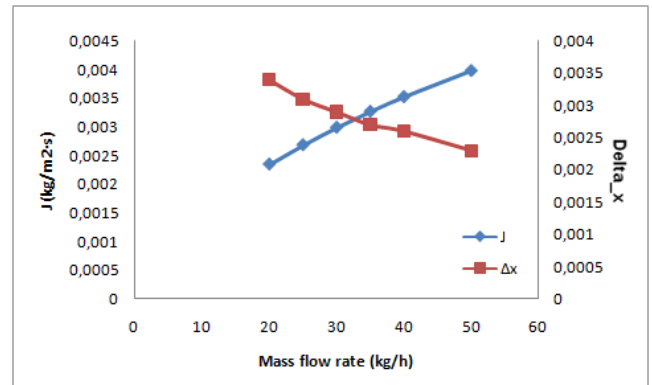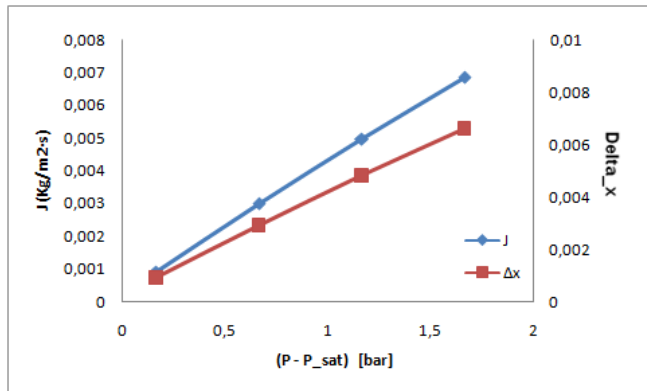

Figure 3.Ammonia flux and ammonia concentration difference at different feed flow rates.

The effect of the inlet temperature and pressure in the mass transfer process can be observed in **Figure 4** and **Figure 5** respectively. As expected, the farther feed inlet conditions are from the saturation point, the higher ammonia flux across the membrane. It increases in a very significant way because the driving force ofthe absorption process is enhanced. That is why the higher the pressure and/or the lower the temperature, the higher is the mass transfer obtained. Taking into account that in this case the solution flow rate is kept constant, the outflow of the absorber will be more concentrated due to the higher ammonia flux crossing the membrane.
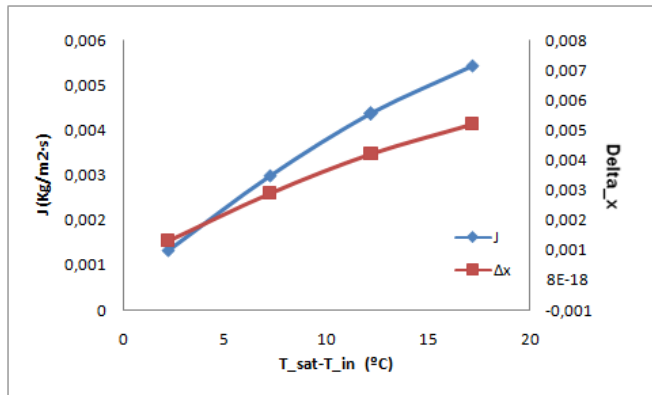
Figure 4.Ammonia flux and ammonia concentration difference at different inlet temperature.

Figure 5.Ammonia flux and ammonia concentration increment in the absorber at different pressure levels.

Heat transfer

Finally, the influence of the inlet conditions on the heat transfer process is studied. In **Figure 6,** temperature difference between inlet and outlet solutions in the absorber is presented. For this purpose, the following feed inlet conditions are varied; mass flow rate, pressure and temperature.
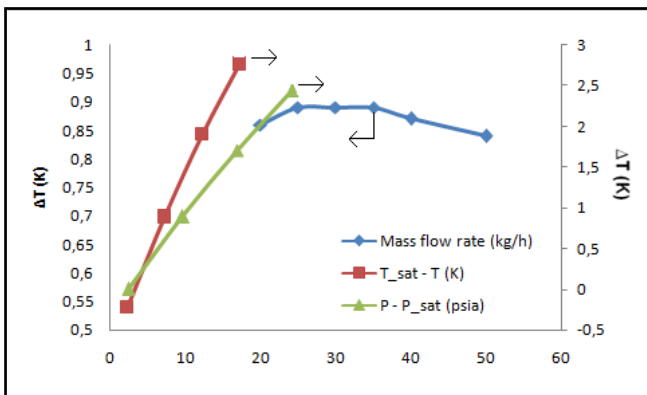
Figure 6. Temperature difference in the absorber ($\Delta T=T_{out}-T_{in}$) at different inlet operating conditions; mass flow rate, temperature and pressure.

As expected, it can be clearly observed that temperature and pressure have the strongest influence in heat and mass transfer

processes. The farther from the saturated conditions, the bigger ΔT and Δx at the absorber outlet are reached because the mass transfer process is improved due to the driving force difference. That is to say, the better mass transfer leads to a bigger amount of heat released in the absorption process and therefore a higher outlet temperature.

Regarding to the mass flow rate influence in the heat transfer, there is a maximum ΔT obtained when m ≈ 30 kg/h and then the temperature difference slowly decreases. This effect can be explained because when the mass flow rate is increased, J also increases (**Fig. 3**) and that would mean higher absorption heat and higher outlet temperature. However, an increase of the mass flow rate also means that there is more amount of liquid that has to be heated, so after reaching the maximum ΔT, subsequent increases in the mass flow rate will lead to lower ΔT because the absorption heat is not enough for keeping or increasing the outlet temperature.

Model Validation. Preliminary experimental results

The model developed has been validated with the preliminary results obtained in the membrane absorber test bench. Experiments were carried out at different mass flow rates (27-48 kg/h) but keeping constant the pressure at 3 bar and the inlet temperature of the solution at 30 ºC. The ammonia flux obtained in the experiment is shown in **Figure 7** and the ammonia concentration difference between the inlet and the outlet solution in the absorber is presented in **Figure 8**.
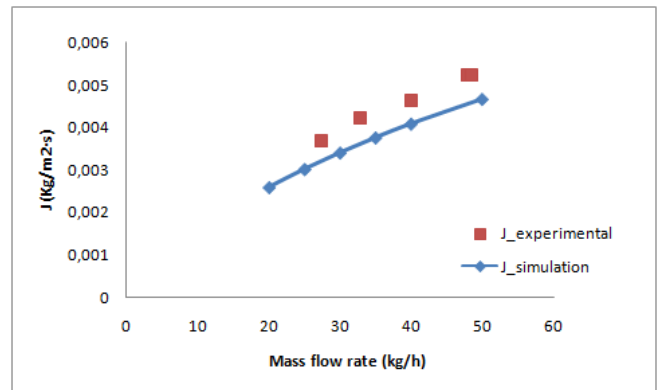
Figure 7. Ammonia flux through the membrane at different mass flow rates.
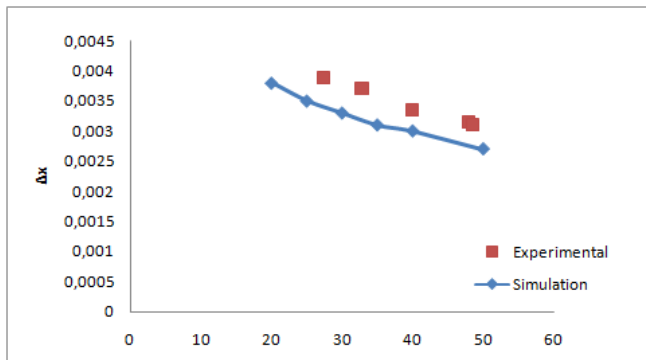
Figure 8. Ammonia concentration increment in the absorber at different mass flow rates.

Comparing the preliminary experimental results and the theoretical ones, it can be observed that same trend and similar values were obtained for the ammonia flux and Δx, but the experimental results are always higher than the ones predicted by the model. However, more experiments are planned for the next three months in order to complete the validation of the model in a wide range of the working conditions (pressure and temperature) and a deeper study of the model will be made in order to improve the simulation.

CONCLUSION

A theoretical model was developed in order to study the ammonia/water adiabatic absorption process when a microporuous flat sheet membrane is used as a contactor. First, a theoretical sensitivity analysis of the influence of the pressure, solution inlet temperature and mass flow rate in the absorption process was carried out. Regarding to the mass transfer process, it can be concluded that there is a strong influence of the pressure and temperature in the heat and mass transfer process. In the range studied, an increase in the mass flow rate causes a slightly improvement of the ammonia absorption flux. Finally, the model has been validated with the preliminary results obtained in an adiabatic membrane absorber. More experiments will be carried out for the next three months and the model will be improved using a more suitable Nusselt and Sherwood correlations for this process. It will be also studied and evaluated the effect of the mass transfer on the heat transfer process in order to improve the estimation of the heat transfer coefficient.

ACKNOWLEDGEMENTS

REFERENCES

[1] Ali, A.H., Schwerdt, P.; Characteristics of the membrane utilized in a compact absorber for lithium bromide-water absorption chillers. International Journal of refrigeration, 2008, 32, 1886-1896.

[2] Ali, A.H.; Design of a compact absorber with a hydrophobic membrane contactor at the liquid-vapor interface for lithium bromide-water absorption chillers. Applied Energy, 2010, 1112-1121.

[3] Yu, D., Chung, J., Moghaddam, S. Parametric study of water vapor absorption into a constrained thin film of lithium bromide solution. International Journal of Heat and Mass Transfer, 2012, Volume 55, Issues 21–22, 5687-5695.

[4] Wang, Z., Gu, Z., Feng, S., Li, Y.; Application of vacuum membrane distillation to lithium bromide absorption refrigeration system. International Journal of refrigeration, 2009, 32, 1587-1596.

[5] Isfahani, R.N., Sampath, K., Moghaddam, S.;Nanofibrous membrane-based absorption refrigeration system. International Journal of refrigeration, 2013, 36, 2297-2307.

[6] Chen, J., Chang, H., Chen, S-R. ; Simulation study of a hybrid absorber-heat exchanger using hollow fiber membrane module for the ammonia-water absorption cycle.International Journal of Refrigeration, 2006, 29, 1043-1052.

[7] Schaal, F. Membranabsorberfür die Absorptionskältetechnik. Dissertation, Universität Stuttgart (2008).

[8] Ibrahim, O.M., Klein, S.A."Thermodynamic Properties of Ammonia-Water Mixtures". ASHRAE Transactions, 1992, 9(1), 1495-1502.

[9] Cuenca, Y. Experimental Study of Thermal Conductivity of New Mixtures for Absorption Cycles and the Effect of the Nanoparticles Addition. Dissertation.University RoviraiVirgili, Tarragona (2013).

[10] Conde, M. Thermophysical properties of NH3 + H2O mixtures for the industrial design of absorption refrigeration equipment. Zurich: M.Conde Engineering, 2006, pp. 12-15.

[11] Venegas, M., de Vega, M., García-Hernando, N. Parametric study of operating and design variables on the performance of a membrane-based absorber. Applied Thermal Engineering, 2016, 98, 409-419.

[12] Martínez, L. Rodríguez-Maroto, J.M..On transport resistances in direct contact membrane distillation.Journal of Membrane Science, 2007, Volume 295, 28-39.

[13] Gabelman, A., Hwang, S-T.Hollow fiber membrane contactors. Journal of Membrane Science, 1999, Volume 159, 61-106.