



71st Conference of the Italian Thermal Machines Engineering Association, ATI2016, 14-16
September 2016, Turin, Italy

Rate-based approaches for the carbon capture with aqueous ammonia without salt precipitation

Stefano Lillia, Davide Bonalumi*, Gianluca Valenti

Politecnico di Milano, Dip. Energia, Via Lambruschini 4A, 20156, Milano, Italy

Abstract

The aim of this paper is the evaluation of the influence of the kinetic of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ reactions in the absorber with respect to the electric power losses due to the steam bleeding from the turbine for the regeneration of the solvent. The results exposed conclude that there are few works about the kinetic of the aqueous reaction of the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ and data from the literature are not in agreement among them probably due to a dependence of the kinetic constants on the ammonia concentration in the liquid. The kinetic parameters have a strong influence on the specific electric power losses.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the Scientific Committee of ATI 2016.

Keywords: carbon capture; CO_2 capture; aqueous ammonia; kinetics; absorption rate; rate-based simulation;

1. Introduction

The world energy production is expected to turn more and more sustainable in the future. The post-combustion carbon capture with aqueous solutions can be a viable option for mitigating the emission of carbon dioxide from fossil fuel power plants because of its applicability to both existing and new plants with moderate modifications to the power block. These carbon capture technologies can be accomplished by chemical absorption.

* Corresponding author. Tel.: +39-02-2399-3817; fax: +39-02-2399-3913.
E-mail address: davide.bonalumi@polimi.it

Nomenclature		
Equipment abbreviations		Symbols
ABS	Absorber	K Ammonia to carbon dioxide ratio [-]
CL	Air-cooler	$\%NH_3$ Ammonia initial concentration [-]
HX	Heat exchanger	rec. Recycling fraction [-]
PM	Pump	k_2 Arrhenius constant [kmol/(m ³ *s)]
REB	Reboiler	r Reaction rate [kmol/(m ³ *s)]
REG	Regenerator	A Arrhenius preexponential factor [kmol/(m ³ *s)]
COND	Condenser	E_A Activation energy [cal/mol]
Acronyms		T Temperature in Kelvin
CAP	Chilled Ammonia Process	R Universal gas constant
USC	Ultra Super Critical	C_i Concentration of i specie

Currently, the state of the art is the post-combustion layout based on the chemical Monoethanolamine (MEA) as reported in the document of the EBTF [1]. Alternatively to amines, the process named Chilled Ammonia Process (CAP) is considered a feasible option. Previous works proposed by Valenti *et al.* [2] show more attractive results for an ammonia-based capture plant with respect to a MEA-based one.

The chilled conditions of those studies include salt precipitation that can represent a complication in the management of the plant. Bonalumi *et al.* [3] show attractive results for an ammonia based capture plant operating in cooled condition that, contrary to the Chilled Ammonia Process, has not salt precipitation without losses in efficiency. Bonalumi *et al.* [3] show also a parametric investigation on a layout simulated in Aspen Plus with an equilibrium approach of chemical reactions in order to find the set of parameters that minimize the electric losses.

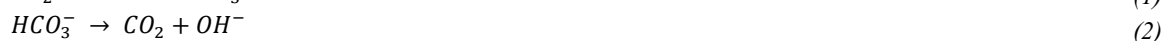
The objective of this work is the evaluation of the influence of the kinetic of the NH_3 - CO_2 - H_2O reactions in the absorber with respect to the electric power losses due to the steam bleeding from the turbine to the regenerator reboiler in order to provide the heat for the regeneration of the solution. A parametric analysis of the process determinates how strong the influence is of the kinetic parameters on the results and if the equilibrium approach to simulate the absorber applied by Bonalumi *et al.* [3] returns the same trend.

This work reviews first the bibliography about the kinetic of the absorption reaction in the NH_3 - CO_2 - H_2O system. Only few experimental works are available in literature: Pinsent *et al.* [4,5], Puxty *et al.* [6], Wang *et al.* [7] and Jilvero *et al.* [8] studied the kinetic of the NH_3 - CO_2 - H_2O system.

The information retrieved from the literature is employed in the Aspen Plus environment to assess the influence of the different values of the kinetic parameters on the performance of the carbon capture plant. The Aspen Plus model is composed by a conventional absorption-regeneration layout. In contrast, the steam turbine of the USC power plant is modelled in an approximate manner to calculate the electric loss of the steam turbine due to the steam bleeding.

2. Bibliographic review on kinetics

This paragraph contains a bibliographic review about the kinetic of the reaction of the system NH_3 - CO_2 - H_2O in order to summarize the results retrieved from the literature. There are few works about the kinetics studies about the chemical system NH_3 - CO_2 - H_2O . The system has rigorously a large amount of reaction, however, only the kinetic of two of these influences significantly the kinetic of the overall. In fact, Jilvero *et al.* [8] consider only the kinetic of the reaction (1-4) in order to implement them in the adsorption column model.



The kinetic of the reaction (1) is studied by Pinsent et al. [4] by the rapid thermal method over the range 0 to 40 °C (273-313 K). The rapid thermal method of measuring the velocity of rapid reactions in solution. The fitting of the data yields the Arrhenius constant with a second order kinetic of reaction as shown by equations (5-6):

$$\frac{-dCO_2}{dt} = r = k_2 * [CO_2][OH^-] \quad (5)$$

$$k_2 = A * e^{\frac{-E_A}{RT}} \text{ with } A = 4.32 * 10^{13} \frac{kmol}{(m^3 * s)} \text{ and } E_A = 13249 \frac{cal}{mol} \quad (6)$$

The kinetic of the reaction (3) is studied by Pinsent et al. [5], Puxty et al. [6], Wang et al. [7] and Jilvero et al. [8] in four different methods. Pinsent et al. [5] study the kinetic of the reaction (3) by the rapid thermal method with an ammonia concentration between 0.027 mol/L and 0.19 mol/L.

Puxty et al. [6] study the kinetic of the reaction (3) by measuring the rate of CO₂ absorption into a falling thin film using a wetted wall column for aqueous ammonia between 0.6 mol/L and 6 mol/L, 5–20 °C (278-293 K) and initial thin liquid film CO₂ loading between 0 mol_{CO2}/mol_{NH3} and 0.8 mol_{CO2}/mol_{NH3}.

Wang et al. [7] study the kinetic of the reaction (3) by the stopped flow apparatus in the range of temperature between 15°C and 45°C (288-318 K). In fact, the range of ammonia concentration is between 2.0 mmol/L and 16 mmol/L and the initial CO₂ between 3 mmol/L and 10 mmol/L.

Jilvero et al. [8] study the kinetic of the reaction (3) by a different approach with respect to the works quoted previously. In their work Jilvero et al. implement in Aspen Plus an adsorption column taking all the design parameters from the Munmorah Aqueous Ammonia pilot. Consequently, they fit the kinetics parameters of the reaction (3) with the experimental data from the pilot plant, proposing different Arrhenius parameters with respect on the other works.

In summary Table 1 reports the Arrhenius constant found by the cited works while Figure 1 shows the trends of the Arrhenius constant with respect of the reciprocal of the temperature and how Arrhenius law fit data in each work.

The Figure 1 indicates that Arrhenius law fits well the experimental data in each work but the results from each work are different among them. Especially, the results from Pinsent et al. and Wang et al. are in agreement between them, but different from the results by Puxty et al. and Jilvero et al. The results from Pinsent et al. and Wang et al. are determined by experimental data measured with low ammonia concentration, while Puxty et al. and Jilvero et al. by experimental data measured at high ammonia concentration. This could be the reason that explains the differences among the different results, probably there is a dependence of the kinetic parameters by the ammonia concentration.

$$\frac{-dNH_3}{dt} = r = k_2 * [NH_3][CO_2] \quad (7)$$

$$k_2 = A * e^{\frac{-E_A}{RT}} \quad (8)$$

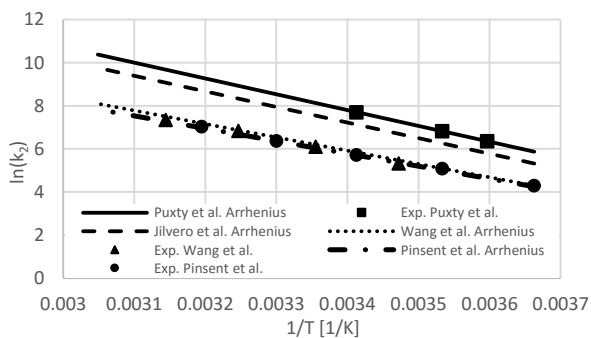


Figure 1. Comparison among the k_2 equations and experimental data.

Table 1. Arrhenius parameters of the reaction rates from the experimental works quoted. The parameters are presented in molarity basis.

Reaction	Source	Arrhenius parameters of k_2	
		A [kmol/(m ³ s)]	E _A [cal/mol]
(3)	Pinsent et al. [5]	1.35*10 ¹¹	11 585
(3)	Puxty et al. [6]	1.66*10 ¹⁴	14 577
(3)	Wang et al. [7]	5.01*10 ¹¹	12 279
(3)	Jilvero et al. [8]	6.51*10 ¹³	14 362

3. Modeling

The aim of this paper is the evaluation of the influence of the kinetic of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ reactions in the absorber with respect to the electric power losses due to the steam bleeding from the turbine to the regenerator reboiler in order to provide the heat for the regeneration of the solvent. As Figure 1 shows, the Arrhenius parameters from Pinsent *et al.* and Wang *et al.* return the same results, so the results of the simulations with Wang *et al.* parameters are not provided in the article because equal to the results found with Pinsent *et al.* parameters.

3.1. Absorption chemistry

The reaction characteristics of the absorbents in post-combustion capture are “liquid-film-controlled”. The absorber, that works without salt precipitation, is a packed column filled with a structured packed material (Mellapak 250Y) as proposed in [8]. This configuration is the best solution in order to maximize the surface-volume ratio and consequently to maximize the mass transport of the CO_2 from the gas to the liquid phase.

The thermodynamic model used for the electrolyte system is the Extended UNIQUAC proposed by Thomsen and Rasmussen [9]. It is implemented within the code Aspen Plus, and it is able to describe the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system. The Extended UNIQUAC model calculates the mixture properties and the equilibrium of the following reactions:



The absorber is modeled with a rate-based approach by introducing the kinetic coefficients for the backward and forward reactions of the reactions (12-13). The backward and forward reactions of the reaction (12) are the reactions (1-2) and the backward and forward reactions of the reaction (13) are the reactions (3-4). The reaction rates in Aspen are presented on a molarity base with the equation (14).

$$r = A * T^n * e^{\frac{-E_A}{RT}} \prod_{i=1}^{i=N} C_i^{\alpha_i} \quad (14)$$

Table 2 reports the reaction rate coefficient from the works by Pinsent *et al.*, Puxty *et al.* and Jilvero *et al.*

For the calculations of the mass and heat transfer phenomena inside the column with the structured packed are implemented within Aspen Plus V8.4 models specific for the Mellapak 250Y.

Table 2. Reaction rates of the reactions (1-4) considered in the present work.

Reaction	Surce	n	A [kmol/(m ³ *s)]	E _A [cal/mol]
(1)	Pinsent et al. [4]	0	4.32 * 10 ¹³	13 249
(2)	Pinsent et al. [4]	0	2.80 * 10 ¹³	25 818
(3)	Pinsent et al. [5]	0	1.35 * 10 ¹¹	11 585
(4)	Pinsent et al. [5]	0	1.03 * 10 ¹⁹	16 180
(3)	Jilvero et al. [8]	0	6.51 * 10 ¹³	14 362
(4)	Jilvero et al. [8]	0	4.97 * 10 ²¹	18 957
(3)	Puxty et al [6]	0	1.66 * 10 ¹⁴	14 577
(4)	Puxty et al. [6]	0	1.27 * 10 ²²	19 172

3.2. Electric power losses assumptions

The effect of the steam extraction on the power generation is computed starting from a typical expansion curve of a low pressure turbine. The curve is assumed to be a straight segment connecting inlet and outlet of the turbine on an entropy-enthalpy diagram (Figure 2). The extraction pressure along the curve is determined by the regeneration temperature allowing for a minimal temperature difference in the reboiler of 5°C. The extracted mass flow rate is defined by the energy balance over the reboiler for a given heat duty. The electric loss due to the steam extraction is computed as the power that would be generated by the extracted steam from the extraction state to the outlet state. The expansion curve remains constant with the steam bleeding because the turbine is designed for a power plant integrated with the capture plant. The integration of the exiting condensate with the power block, such as in the deaerator or in the pre-heating line, is not considered now. The characteristic of the steam turbine are the same as the steam turbine of the EBTF [1]. The ratio of the electric power loss due to the steam extraction from the turbine and the heat duty as a function of the regeneration temperature is depicted in Figure 2.

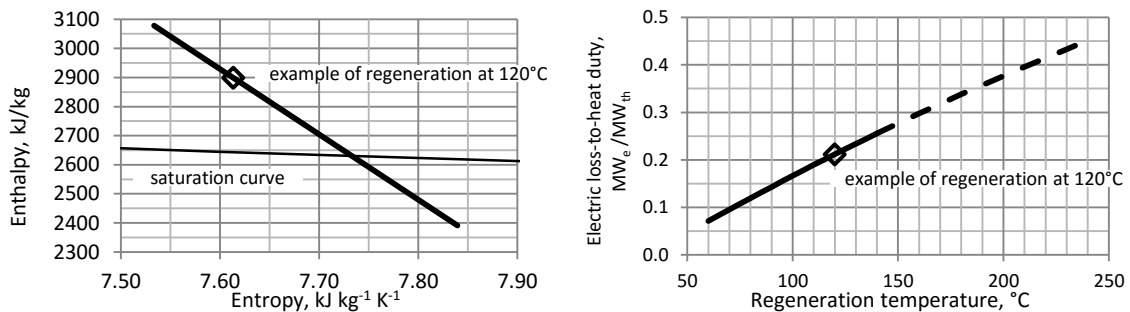


Figure 2. Left: expansion curve in the enthalpy-entropy diagram of the low pressure turbine from which the steam is extracted. Right: ratio of electrical loss-to-heat duty as a function of regeneration temperature. The diamond shows an example of a regeneration temperature at 120°C.

4. Case studies

4.1. Capture block

In this work the simulations with the rate-based approach of the capture plant are carried considering only the electric power losses due to the steam bleeding from the turbine to the regenerator. Figure 3 provides the process flow diagram. It is a simplified layout in order to focus the results on the dependence among the design parameters and the electric power losses. The layout is composed by: (i) the absorption column (ABS) implemented with a rate-based approach, (ii) a pump for the recycle on the top of the column (PM1), (iii) a pump (PM2) that increase the outlet rich flow of the column to the regeneration pressure, (iv) a recuperative heat exchanger (HX), (v) a regenerator simulated with an equilibrium based approach (REG), a condenser on the top (COND) and two air-coolers (CL1 and CL2) that cool the inlet flows in the absorber in order to reduce the temperature of the absorption process.

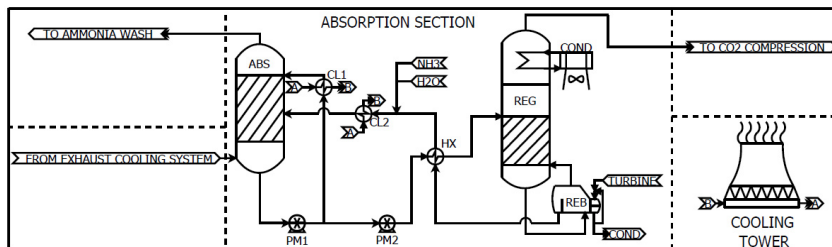


Figure 3. Process flow diagram implemented in Aspen Plus.

4.2. Design parameters

The design parameters are: (i) the kinetic parameters which describe the kinetic of the absorption reactions, (ii) ammonia-to-carbon dioxide ratio in the absorber, (iii) ammonia initial concentration in the aqueous solution (without considering the CO₂), (iv) recycling fraction of the rich solution to the top of the absorber. The ammonia-to-carbon ratio in the absorber is the ratio of the number of ammonia moles entering the reactor through the lean solution line and the number of carbon dioxide moles entering through the exhaust line.

The general assumption for the power plant are in Table 3. The values of (i) carbon capture efficiency, (ii) the regeneration pressure, (iii) the height of lean solution inlet at three fifth of the total height of the column, (iv) the minimum difference of temperature in the heat exchangers, (v) the condenser temperature and the outlet temperature from the air-coolers and the exhaust composition are taken from Bonalumi *et al.* [3]. Carbon capture efficiency is defined as the ratio of the flow rates [kmol/s or kg/s] of the carbon dioxide exiting the compression island and of that entering the capture plant.

The values of (i) the height of the column, (ii) the diameter of the column and (iii) the structured packed are deduced by Jilvero *et al.* [8] in order to respect the liquid on gas ratio inside the column. Aspen, in fact, during the simulation of the column model, controls that the liquid on gas ratio is physically correct for the considered geometry.

Table 3. General parameters adopted for simulations

Parameter	Unit	Value	Parameter	Unit	Value
<u>Overall parameters</u>			<u>Exhausts</u>		
Carbon capture efficiency	%	85	Mass flow rate	kg s ⁻¹	1
<u>Air coolers</u>			<u>Pressure</u>		
Fluid end temperature	°C	20	Temperature	°C	23
Relative pressure drop	%	0	CO ₂	%	14.90
<u>Column</u>			Inert (Ar, N ₂ , O ₂)		
Diameter	m	1	H ₂ O	%	2.00
Height	m	20	<u>Regenerator</u>		
Structured packed	NaN	Mellapak 250Y	Condenser temperature	°C	35
			Regeneration pressure	bar	5

5. Results and discussion

The Figure 4 (left) shows the carbon capture efficiency with respect to the lean CO₂ loading as a function of the three different kinetic models. The simulation considers only the absorber (without the regenerator) with an ammonia-to-carbon dioxide ratio in the absorber (K) of 5, ammonia initial concentration in the aqueous solution (%NH₃) of 7.5% and recycling fraction of the rich solution to the top of the absorber (rec.) of 0.5. These initial values of the design parameters are provided by Bonalumi *et al.* [3] as an optimal operating point derived from a parametric investigation of the plant simulated with an equilibrium-based approach.

Figure 4 (left) shows a strong dependence of the carbon capture efficiency on the kinetic parameters. In particular, there is a big difference among the kinetic parameters obtained by Pinsent *et al.* and the other two, as it was inferable in Figure 1. The Figure 4 (right) provides the results considering the whole plant (absorber and regenerator) described in Figure 3. The simulations have the same parametric set as before ($K=5$; %NH₃=7.5%; rec.=0.5), but in this case the carbon capture efficiency is fixed at 85% and the result is the specific electric power loss on the kilograms of CO₂ captured for the regeneration process.

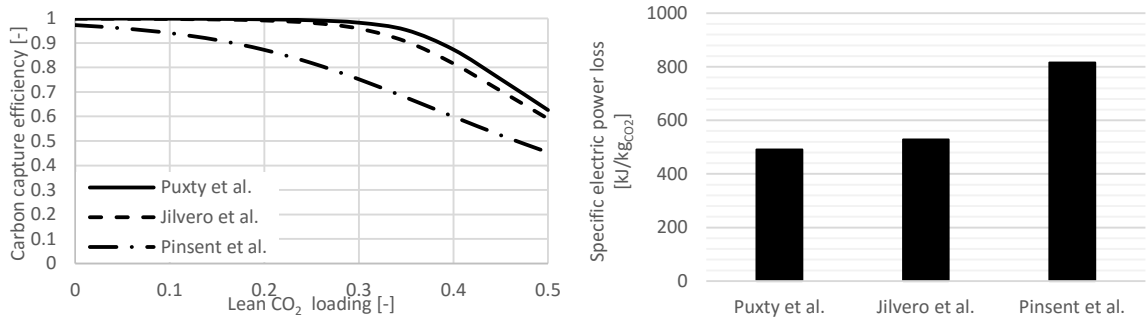


Figure 4. Left: carbon capture efficiency with respect to the lean CO₂ loading as a function of the three different kinetic models. Right: electric power loss with respect to the different set of kinetic parameters fixing the design parameters.

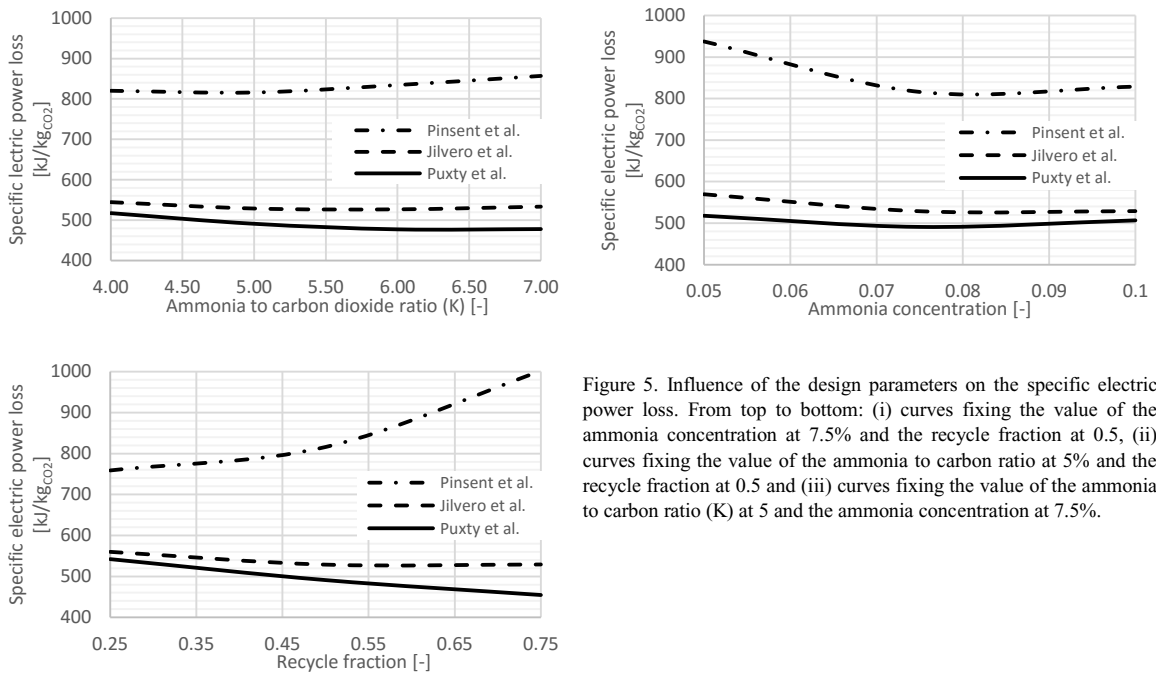


Figure 5. Influence of the design parameters on the specific electric power loss. From top to bottom: (i) curves fixing the value of the ammonia concentration at 7.5% and the recycle fraction at 0.5, (ii) curves fixing the value of the ammonia to carbon ratio at 5% and the recycle fraction at 0.5 and (iii) curves fixing the value of the ammonia to carbon ratio (K) at 5 and the ammonia concentration at 7.5%.

The results of the two graphs in Figure 4 are in agreement between them. In fact, with the Pinsent *et al.* parameters, the absorber requires a lean solution with a lower value of CO₂ loading to maintain constant the carbon capture efficiency. Consequently, the regenerator has to regenerate the rich solution out of the absorber to a high level of purity, so the heat required and the reboiler temperature increase and consequently also the electric power loss. For the same reason with Jilvero *et al.* parameters the consumption are a bit higher than with Puxty *et al.* parameters.

The parameters under analysis are: (i) the kinetic parameters, (ii) ammonia initial concentration in the aqueous solution, (iii) ammonia-to-carbon dioxide ratio in the absorber, (iv) recycling fraction of the rich solution to the top of the absorber. The graphics in Figure 5 describes the trend around the point selected by Bonalumi *et al.* [3] changing the parameters value in order to find local minimum of the electric power loss and investigate if the equilibrium-based approach and the rate-based one have similar trend.

Figure 5 shows that for the first two parameters (K and %NH₃) there is a minimum in the ranges considered. With the kinetic parameters used only slight variation is appreciable in the results and they are close to the values provided by Bonalumi *et al.* [3] adopting an equilibrium-based approach. Hence, the equilibrium-based approach for the

optimization process of a cooled ammonia plant returns trusted trends and results. The third graphic in Figure 5 shows a reduction of the electric consumption when the recycle fraction increase for the kinetic parameters provided by Jilvero *et al.* and Puxty *et al.*, but an opposite trend for the Pinsent *et al.* parameters. Jilvero *et al.* and Puxty *et al.* propose a faster kinetic, so the effect of the ammonia dilution due to the recycle is negligible while the increase of the mass transfer due to an increase of the mass flow has the effect to improve the CO₂ captured. On the other hand, Pinsent *et al.* provide parameters that determine a slower kinetic, so a higher recycle increase the ammonia dilution in the column and hinders the chemisorption of the CO₂. Consequently, the regeneration has to reduce the lean CO₂ loading in order to maintain the carbon capture ratio at 85%. The recycle fraction cannot be too much high because there is the risk for the column to be flood.

Finally, the specific heat duty of the regeneration, obtained for the optimized cases with the three different kinetics parameters and the one proposed by Bonalumi *et al.* can be compared. As expected, the lower result corresponds to the case simulated with an equilibrium-based approach (2.33 MJ/kgCO₂). Not too dissimilar values are obtained for the cases with the kinetics derived from Puxty *et al.* (2.46 MJ/kgCO₂) and Jilvero *et al.* (2.72 MJ/kgCO₂). The highest value is obtained from the parameters of Pinsent *et al.* (3.53 MJ/kgCO₂).

6. Conclusions and future works

The work proposes a study of the kinetics of the CO₂ absorption with aqueous ammonia solution applied in post-combustion carbon capture with different kinetic parameters of the reactions retrieved in the literature.

Based on the results exposed can draw the following conclusion:

- Data from the literature are not in agreement among them probably due to a dependence of the kinetic constants on the ammonia concentration in the liquid.
- The kinetic parameters have a strong influence on the specific electric power losses.
- The comparison of the results from the rate-based approach simulation with the results from an equilibrium-based approach concludes that the study of an absorption capture plant with an equilibrium-based approach is a valid assumption for a preliminary investigation and optimization process.
- The specific heat duty found with a fast kinetic are comparable with the heat duty found with an equilibrium-based approach.

Future works can provide an experimental investigation on the kinetic of reaction with respect on the ammonia concentration or a parametric analysis of a cooled ammonia carbon capture plant with a rate based approach.

References

- [1] EBTF, "D 4.9 European best practice guidelines for assessment of CO₂ capture technologies," pp. 1–112, 2011.
- [2] G. Valenti, D. Bonalumi, and E. Macchi, "A parametric investigation of the Chilled Ammonia Process from energy and economic perspectives," *Fuel*, vol. 101, pp. 74–83, Nov. 2012.
- [3] D. Bonalumi, G. Valenti, S. Lillia, P. L. Fosbøl, and K. Thomsen, "A Layout for the Carbon Capture with Aqueous Ammonia without Salt Precipitation," *Energy Procedia*, vol. 86, pp. 134–143, Jan. 2016.
- [4] B. R. W. Pinsent, L. Pearson, and F. J. W. Roughton, "The kinetics of combination of carbon dioxide with hydroxide ions," *Trans. Faraday Soc.*, vol. 52, no. 9, p. 1512, 1956.
- [5] B. R. W. Pinsent, L. Pearson, and F. J. W. Roughton, "The kinetics of combination of carbon dioxide with ammonia," *Trans. Faraday Soc.*, vol. 52, no. 2, p. 1594, 1956.
- [6] G. Puxty, R. Rowland, and M. Attalla, "Comparison of the rate of CO₂ absorption into aqueous ammonia and monoethanolamine," *Chem. Eng. Sci.*, vol. 65, no. 2, pp. 915–922, Jan. 2010.
- [7] X. Wang, W. Conway, D. Fernandes, G. Lawrance, R. Burns, G. Puxty, and M. Maeder, "Kinetics of the reversible reaction of CO₂(aq) with ammonia in aqueous solution," *J. Phys. Chem. A*, vol. 115, no. 24, pp. 6405–6412, 2011.
- [8] H. Jilvero, F. Normann, K. Andersson, and F. Johnsson, "The Rate of CO₂ Absorption in Ammonia—Implications on Absorber Design," *Ind. Eng. Chem. Res.*, vol. 53, no. 16, pp. 6750–6758, Apr. 2014.
- [9] K. Thomsen and P. Rasmussen, "Modeling of vapor–liquid–solid equilibrium in gas–aqueous electrolyte systems," *Chem. Eng. Sci.*, vol. 54, no. 12, pp. 1787–1802, Jun. 1999.