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## Kinetic study of a Layout for the Carbon Capture with Aqueous Ammonia without Salt Precipitation

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### Abstract

This paper focuses on carbon capture in an Ultra Super Critical power plant. The technology selected for CO<sub>2</sub> capture is based on cooled ammonia scrubbing in post-combustion mode, as recently investigated by the authors in another work. Here, a rate-based approach is adopted. In detail, a specific primary energy consumption for CO<sub>2</sub> avoided (SPECCA) of 2.77 MJ/kg<sub>CO2</sub> is calculated in case of 85% of CO<sub>2</sub> capture, with an ultimate power plant efficiency of 37.27%.

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*Keywords:* cooled ammonia; CO<sub>2</sub> capture; kinetics; NH<sub>3</sub>; Rate-based; SPECCA

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### 1. Introduction

The world energy demand will increase in the next decades and an important role will be played by the fossil fuels. Its application should be as sustainable as possible in the future. The post-combustion carbon capture with chemical absorption 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.

As reported in the document of the European Benchmark Task Force (EBTF) [1], the state of the art is the post-combustion layout is based on the chemical Monoethanolamine (MEA). Alternatively, to amines, the aqueous

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Nomenclature		Symbols	
Equipment abbreviations			
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

ammonia is considered a feasible option. Previous works proposed by authors [2] and [3] show more attractive results for an ammonia-based capture plant with respect to a MEA-based one.

The chilled conditions of those studies involve salt precipitation that can represent a complication in the management of the plant. Bonalumi *et al.* [4] present a parametric investigation on a layout without salt precipitation adopting cooled instead of chilled condition in the absorber. The equilibrium-based approach is conducted with the software Aspen Plus in order to find the set of parameters that minimize the electric losses.

The objective of this work is the evaluation of an ammonia-based capture plant with a rate-based approach. The kinetic of the  $NH_3$ - $CO_2$ - $H_2O$  reactions are reviewed by Lillia *et al.*[5]. The layout of the plant take inspiration from the previous work [4] and the design parameters are the ones obtained with the parametric study proposed in [5]. The Aspen Plus model comprises a complete simulation of the all sections of the capture plant from the exhaust cooling section to the  $CO_2$  compression one. The capture plant is integrated with the coal-fired described in the EBTF document. The steam turbine of the Ultra Super Critical (USC) power plant is modelled in an approximate manner to calculate the electric loss of the steam turbine due to the steam bleeding.

## 2. USC and CCS capture plant

The flue gas to be treated in the capture plant is obtained by a coal-fired power plant. The USC power plant adopted is the one described in [1]. Such document has the scope of establishing a consolidated common framework for international dissemination. The reference power plant has a net electric power output of 754 MWe and a net electric efficiency of 45.5%, both at nominal conditions. The carbon dioxide flow is about  $160.7 \text{ kg}_{CO_2}/s$  at a concentration of 15.2 vol. % on a dry basis. The reference capture plant is the cooled ammonia process proposed in [4].

The USC equipped with the CCS plant is divided into two major blocks: (i) the power and (ii) the capture block. The power block is treated as a whole, whereas the capture block is subdivided into islands: (i) exhaust chilling, (ii) absorption-regeneration-gas wash, (iii)  $CO_2$  compression and (iv) ammonia removal as proposed in Fig. 1.

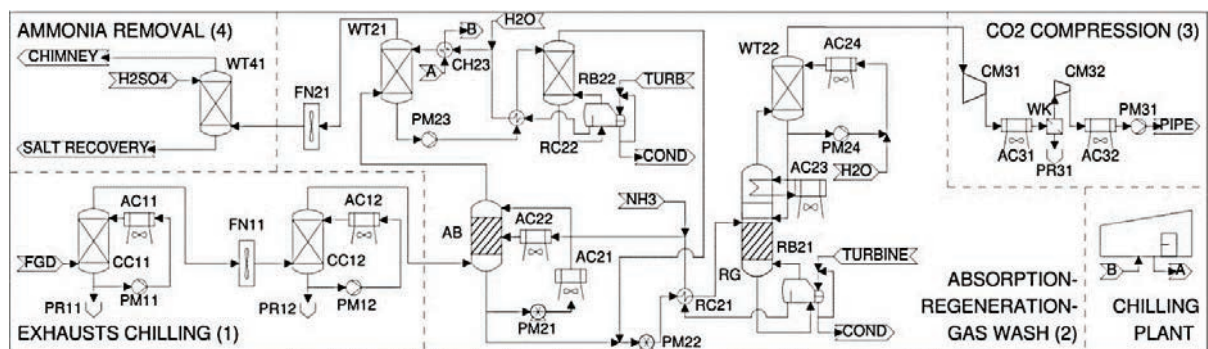
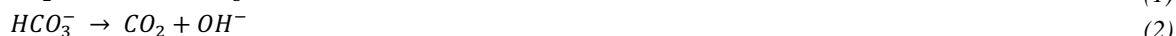


Fig. 1. Cooled layout: scheme of plant in with stages for the decreasing of the absorption temperature obtained with air coolers.

### 3. Kinetic and thermodynamic model

The simulation of the capture plant is work out with the software Aspen Plus in which the thermodynamic properties are obtained with the Extended UNIQUAC thermodynamic model. The last section (iv) ammonia removal is not simulated since it is supposed to reduce at trace the  $\text{NH}_3$  employing an acid water wash and does not affect in relevant manner the energy balance. The results of the integration of the capture plant with the reference EBTF case are simulated with a simplified model of the steam turbine.

There are few works about the kinetics studies about the chemical system  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ . Among the reactions that describe the system two of these influences significantly the kinetic of the overall process. Jilvero *et al.* [6] consider only the kinetic of the reaction (1-4) in order to implement them in the absorption column model.



The kinetic of the reaction (1) is studied by Pinsent *et al.* [7]. The kinetic of the reaction (3) is studied by Pinsent *et al.* [8], Puxty *et al.* [9], Wang *et al.* [10] and Jilvero *et al.* [6].

In the previous work [5] is evaluated 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 power plant integration. One of the conclusion is that the Arrhenius parameters from Pinsent *et al.* and Wang *et al.* return the same results. For this work are considered the values proposed by Jilvero *et al.* [6].

#### 3.1. Absorption chemistry

The reactions that occur in the absorber 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 [6] in order to promote the mass transfer of the gaseous  $\text{CO}_2$  to the liquid phase. The thermodynamic model used for the electrolyte system is the Extended UNIQUAC proposed by Thomsen and Rasmussen [11], it is validated for the current system in [4]. 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 (8)-(9). The backward and forward reaction of the reaction (8) are the reactions (1-2) and the backward and forward reactions of the reaction (9) are the reactions (3-4). The reaction rates in Aspen are presented on a molarity base with the equation (10).

$$r = A * T^n * e^{\frac{-E_A}{RT}} \prod_N^{i=1} C_i^{a_i} \quad (10)$$

Table 2 reports the reaction rate coefficient from the cited works.

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

Reaction	Surce	$n$	$A$ [kmol/(m <sup>3</sup> *s)]	$E_A$ [cal/mol]
(1)	Pinsent et al. [7]	0	$4.32 * 10^{13}$	13 249
(2)	Pinsent et al. [7]	0	$2.80 * 10^{13}$	25 818
(3)	Pinsent et al. [8]	0	$1.35 * 10^{11}$	11 585
(4)	Pinsent et al. [8]	0	$1.03 * 10^{19}$	16 180
(3)	Jilvero et al. [6]	0	$6.51 * 10^{13}$	14 362
(4)	Jilvero et al. [6]	0	$4.97 * 10^{21}$	18 957
(3)	Puxty et al [9]	0	$1.66 * 10^{14}$	14 577
(4)	Puxty et al. [9]	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 stream extraction from the turbine and the heat duty as a function of the regeneration temperature is depicted in Figure 2.

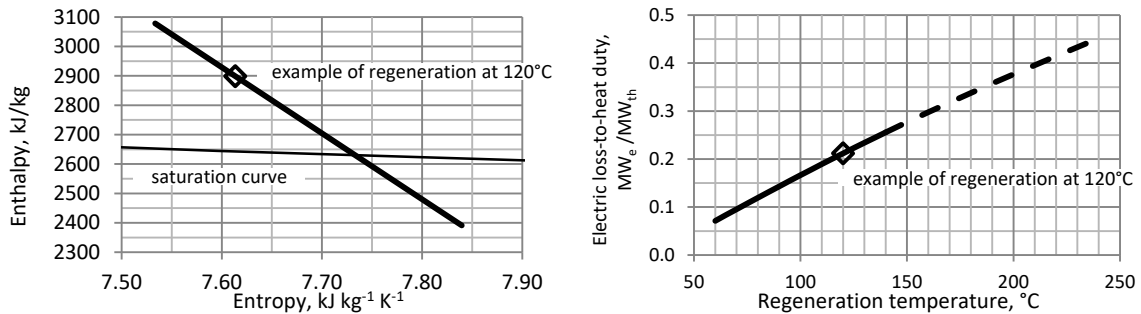


Figure 1. Left: expansion curve in the enthalpy-entropy diagram of the low pressure turbine from which the steam is extracted. Right: ratio of electrical loss-to-heat duty as a function of regeneration temperature. The diamond shows an example of a regeneration temperature at 120°C.

## 4. Case studies

### 4.1. Capture block

In this work the simulation with the rate-based approach of the capture plant is carried out considering not only the energy performances, but also the water and ammonia balance. A layout very similar to the one presented in [4] is proposed. It operates with the absorption stage in a cooled mode in which the cooling to 20°C of the streams entering the absorber is obtained exploiting the ambient temperature of 15°C. The temperature of the absorber is higher than 20°C, with this conditions is avoided the salts precipitation.

#### 4.2. Design parameters

The design parameters are: (ii) ammonia-to-carbon dioxide ratio in the absorber, (iii) ammonia initial concentration in the aqueous solution (without considering the CO<sub>2</sub>), (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 2. The values of (i) carbon capture efficiency, (ii) the regeneration pressure, (iii) the height of lean solution inlet in the absorber, (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.* [4]. 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.

Table 2. General parameters adopted for simulations

Parameter	Unit	Value	Parameter	Unit	Value
<u>Air coolers</u>			Composition:		
Fluid end temperature	°C	20	CO <sub>2</sub>	% (vol. wet)	13.73
Relative pressure drop	%	0	Inert (Ar, N <sub>2</sub> , O <sub>2</sub> )		76.54
Specific electric consumption	MW <sub>e</sub> MW <sub>th</sub> <sup>-1</sup>	0.02	H <sub>2</sub> O		9.73
<u>Ambient air</u>			<u>Heat exchangers</u>		
Temperature	°C	15	Minimum temperature difference	°C	5
<u>Chilling plant</u>			<u>Low pressure steam turbine</u>		
Coefficient of performance	MW <sub>th</sub> MW <sub>e</sub> <sup>-1</sup>	5	Inlet pressure	bar	4.5
Specific electric consumption	MW <sub>e</sub> MW <sub>th</sub> <sup>-1</sup>	0.20	Inlet temperature	°C	306
<u>Columns</u>			Outlet pressure		
Contact cooler pressure drop	bar	0.01	Outlet vapor title	%	93
Other column pressure drop	bar	0.03	Outlet velocity	m s <sup>-1</sup>	250
Absorber diameter	m	28	Generator efficiency	%	98
Absorber height	m	20	Isentropic efficiency	%	88
Absorber structured packed	Mellapak 250Y		<u>Motors</u>		
Scrubber diameter	m	28	Electro-mechanical efficiency	%	95
Scrubber height	m	7.5	<u>Pumps</u>		
Scrubber structured packed	Mellapak 250Y		Hydraulic efficiency	%	85
Regenerator condenser temperature	°C	35	<u>Reboiler</u>		
<u>Compressors</u>			Steam superheated temperature	°C	5
Isentropic efficiency	%	85	Steam subcooled temperature	°C	0
Last compressor end pressure	bar	80	<u>Reference power plant</u>		
<u>Fans</u>			Net electric power	MW <sub>e</sub>	754
Forced fan end pressure	bar	1.06	Net electrical efficiency, $\eta_{el,RIF}$	%	45,5
Induced fan end pressure	bar	1.06	Specific CO <sub>2</sub> emission, $E_{RIF}$	kg <sub>CO2</sub> MW <sub>e</sub> <sup>-1</sup>	763
Isentropic efficiency	%	90	<u>Pipeline</u>		
<u>Exhausts</u>			Delivery pressure	bar	110
Mass flow rate	kg s <sup>-1</sup>	782	<u>Targets</u>		
Pressure	bar	1.04	Max ammonia slip	ppmv	130
Temperature	°C	50	Treated gas	ppmv	10
			Compressed carbon dioxide	ppmv	5

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.* [6] in order to respect the liquid on gas ratio inside the column. The combination of the parameters used in for the proposed layout are proposed in Table 3.

Table 3. Selected parameters for Chilled and Cooled layout obtained by means the parametric analysis.

Parameter	Unit	Cooled ammonia
Ammonia initial concentration	%wt	7.5
Ammonia-to-carbon dioxide ratio	kmol kmol <sup>-1</sup>	5
Recycle	-	0.5
Height of lean inlet	m	12
Regeneration pressure	bar	5
Regeneration temperature	°C	111.8

## 5. Results and discussion

The results of the simulations of the capture plant layouts here investigated are integrated with the model of the power plant in order to assess the performance of the whole system.

### 5.1. Detailed integration of the capture plant with the power plant

The power consumptions of the capture plant integrated with the power plant are summarized in Table 4.

Table 4. Electric consumption for the proposed layout.

Electric power, MW <sub>el</sub>		Electric power, MW <sub>el</sub>	
<i>Exhaust cooling (1)</i>		PM22	2.251
AC11	2.351	PM23	0.002
AC12	0.132	PM24	0,012
FN11	4.177	Subtotal	<u>17.677</u>
PM11	0.592	<i>Power block</i>	
PM12	0.142	RB21	71.098
Subtotal	<u>7.394</u>	RB22	8.055
<i>ABS-RGN-GW (2)</i>		Subtotal	<u>79.153</u>
AC21	2.009	<i>CO<sub>2</sub> Compression (3)</i>	
AC22	4.742	AC31	0.326
AC23	1.414	AC32	0.957
AC24	0.019	CM31	15.421
CH21	2,288	CM32	14.825
FN21	3,821	PM31	0.652
PM21	1.120	Subtotal	<u>32.181</u>
		<b>TOTAL LOSS</b>	<b><u>136.405</u></b>

The electric consumption for the capture plants are reported in Table 4. The *Exhaust cooling* and the *CO<sub>2</sub> Compression* sections present the same values of previous investigation [4] and similar results are found for the *ABS-RGN-GW* sections. The *Power block* presents a higher energy demand with respect to previous work since the higher regeneration temperature. With respect to the previous work the absorber requires a lean solution with a lower value of CO<sub>2</sub> loading to maintain constant the carbon capture efficiency. Consequently, the regenerator has to regenerate the rich solution to a high level of purity, so the heat required and the reboiler temperature increase and consequently also the electric power loss.

## 6. Conclusions and future works

The work proposes an energy evaluation, with a rate-based approach, of the aqueous ammonia post-combustion carbon capture integrated with a USC. In Table 5 is proposed a comparison with the performances calculated with the equilibrium-based approach [4] and the rate-based-approach.

Based on the results exposed can draw the following conclusion:

- the overall energy balance for the kinetic study, compared with the equilibrium study, results penalized;
- the main request of energy is due to the need of an higher level of CO<sub>2</sub> purity in the lean stream;
- with respect to the results presented in the previous work the electric power loss for cooled cases is increased of about 5.5% and the SPECCA values pass from 2.58 to 2.77 MJ/kgCO<sub>2</sub>;
- 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;

Future works will be focused on investigations with rate-based approach based on experimental data. It is of interest a parametric analysis of both cooled and chilled conditions with an advanced layout of the capture plant.

Table 5. Performances of the compared capture plants.

Parameter	Unit	Chilled (equilibrium) [4]	Cooled (equilibrium) [4]	Cooled (kinetic)[this work]
Electric power loss	MWe	140.1	129.3	136.4
Net electrical power	MWe	613.9	624.7	617.6
Net electrical efficiency, $\eta_{el}$	%	37.05	37.70	37.27
Heat Duty specific	MJ/kgCO <sub>2</sub>	2.19	2.98	3.02
Specific CO <sub>2</sub> emission, $E$	kgCO <sub>2</sub> MWh <sub>e</sub> <sup>-1</sup>	141.4	138.9	141.2
SPECCA	MJ/kgCO <sub>2</sub>	2.86	2.58	2.77

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