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# Modeling of Ultra Super Critical power plants integrated with the Chilled Ammonia Process

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#### Abstract

As carbon dioxide anthropogenic generation and climate change appear to be correlated, carbon capture becomes necessary, in particular if applied to coal-fired power plants. The Chilled Ammonia Process (CAP) is a promising technology to be proved for the purpose. This work investigates the integration of Ultra Super Critical (USC) power plants with CAP, conducting a parametric investigation on the design parameters to find the optimum and analyzing then on the details of the power block. The commercial code Aspen Plus and the in-house research code GS are employed. With respect to a reference plant, carbon capture reduces the net electrical power by 19% and the net electrical efficiency by 8.5 percent points. The performance index SPECCA is also utilized. The optimum SPECCA is 3.18 MJ/kg<sub>CO2</sub>, which is to be compared to 4.2 MJ/kg<sub>CO2</sub> for conventional amine. (c) 2011 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: Ultra Super Critical; post-combustion; Chilled Ammonia Process.

## 1. Scope and methodology

The ongoing scientific discussion does not focus on whether fossil fuels will have to meet the short- and the midfuture energy demand, but rather on how they will be most effectively exploited in doing so, in terms of the overall efficiency and the environmental impact. In this scenario, coal will play most likely a primary role, being the most abundant and diffuse of all fossils. As carbon dioxide anthropogenic generation and climate change appear to be correlated, carbon capture becomes necessary. The chemical absorption in ammonia aqueous solutions applied to conventional steam cycles, a process commercially named Chilled Ammonia Process (CAP), is a promising technology still under numerical modeling and pilot testing.

As a continuation of a previous investigation [1], this work simulates in greater details the integration between modern Ultra Super Critical (USC) power plants and the conventional layout for CAP, which was implemented by the company Alstom in the pilot plant that has recently concluded the experimental operation, [2], but outdated by a

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modified version for the plants that will be built [3]. The numerical results referred to the former layout have the advantage of being comparable against the experimental results, which however have been limitedly diffused so far.

The scope of this work is (i) to identify the design parameters of the capture block and (ii) to quantify their influence on the performance indexes of the overall plant through a parametric investigation in order to determine an optimal set of values. Moreover, it is (iii) to model precisely the integration between the carbon capture and the power generation through a specific investigation of the base case. For the sole parametric analysis, the power block is simulated in an approximate manner in order to handily estimate the electrical power loss due to the steam extraction. Subsequently, the detailed model of the power block is coupled to the optimal capture block, forming the base case for this study. The commercial software Aspen Plus, version 2006.5, and the GS in-house software, which has been developed for over two decades of research in the field of power plant design [4], are employed.

## 2. Models and simulations

The overall plant consists of a power block and a capture block. The power side includes a Flue Gas Desulfurization (FGD) from which the exhausts are directed to the capture side. The power block, either in the approximated model or in the detailed one, is treated as a whole system whereas, in contrast, the islands comprising the capture block are simulated separately. These islands are: (i) exhaust chilling, (ii) carbon dioxide absorption, regeneration and gas washing (which will be shorten as abs/reg/wash in the following) and (iii) carbon dioxide compression. The general assumptions for this study are reported in Table 1.

## 2.1. Power block for the parametric investigation

The effects of the steam extraction on the power generation within the parametric investigation are computed starting from a typical expansion curve of a Low Pressure (LP) turbine. The extraction pressure is determined by the regeneration temperature allowing for a minimal temperature difference between the condensing steam and the solution. Prior to entering the reboiler, the steam is attempered with part of the liquid water exiting the reboiler itself. The possibility of a further integration with power block, by exploiting the exiting liquid water for other purposes, such as in the deaerator or in a pre-heating line, is not considered in this model. The numerical assumptions for this model are included in Table 2.

## 2.2. Power block for the base case investigation

As explained, the base case capture block is integrated with a detailed model of the power block forming the base case investigation. The reference plant, that is not equipped with carbon capture, is based on an USC boiler. For the case of carbon capture, the steam for the reboiler is extracted from the turbine cross-over and, once exploited, redirected into the water pre-heating line. The general arrangement layout for these plants is based on an inland site with natural draft cooling towers and delivery of the coal by rail. Assumptions regarding site conditions (ambient temperature, cooling water temperature, etc), equipment efficiency are based on the common framework documents of the EBTF (European Benchmark Task Force) [5].

## 2.3. Exhaust chilling island

Flue gases from the FGD are chilled by way of three contact coolers operating in series and at decreasing temperature levels. The first cooler works with an ambient air-cooled water loop, the other two with closed chilled water loops. The evaporation temperature of the coldest chiller varies in a manner explained in section 2.6, whereas the evaporation temperature of the other chiller is managed to divide equally the load over the two chillers. Since exhausts from the FGD are saturated, each contact cooler loop has a purge to evacuate the condensing water. Between the second and the third contact coolers, a fan is placed to outset the pressure losses of all coolers and absorber. This island is modeled in Aspen Plus employing the Peng-Robinson Equation Of State (EOS). The exhaust characteristics are depicted in Table 3.

#### 2.4. Carbon dioxide absorption/regeneration/washing

The thermodynamic electrolyte model and library employed are those built in Aspen Plus [6]. The validation of the binary systems,  $CO_2$ -H<sub>2</sub>O and NH<sub>3</sub>-H<sub>2</sub>O, in the region of interest against experimental data from the open literature is conducted [7-18]. For the sole NH<sub>3</sub>-H<sub>2</sub>O, the validation against computed data from the code Refprop is also conducted [19]. Just a limited number of results from this validation are visualized in Figure 1, showing a good agreement between computed and measured values, which is in general true for the other cases not illustrated here. The validation against the ternary system is not executed but will be attempted in the future [20]. The Aspen Plus model for application to amine and ammonia is under analysis worldwide. Regarding the ammonia application, type of precipitated salts, list of reactions and their equilibrium constants are in the focus of those studies. The first results are only currently being published, [21], and hence the model accuracy is still relatively uncertain.

The capture layout is conventional and derived from [2]. It comprises an absorber and a regenerator with, interposed, a recuperative heat exchanger as well as a pump on the rich solution entering the recuperator and a chilling exchanger on the lean solution exiting the recuperator. For difficulties in converging the simulation, the absorber and the regenerator are not modeled as columns but as three flash drums connected in series each. For keeping the absorber cold, being the absorption reaction exothermal, a great portion of the rich solution is chilled and recycled to the absorber. The evaporation temperature of the two chillers serving the lean and rich solutions into the absorber varies as outlined in section 2.6. Both gas streams exiting from the absorber and the regenerator are washed with chilled and cooled water respectively to recover the ammonia. This third chiller has an evaporation temperature constantly set at -1°C. The design parameters of this island are detailed in section 2.6.

## 2.5. Carbon dioxide compression

The compression island includes a two-stage intercooled compressor followed by an aftercooler and by a condensed water separator to dehydrate the flow; subsequently, a single-stage compressor followed by another aftercooler to bring the flow to a slightly supercritical liquid state; finally, a pump to reach the delivery pressure. The inlet pressure varies accordingly to the regeneration pressure. The three compressors have the same pressure ratio. This island is modeled in Aspen Plus using the Peng-Robinson EOS. The assumed parameters are in Table 5.

#### 2.6. Design parameters

The design parameters identified are: (i) ammonia initial concentration in the aqueous solution, (ii) ammonia-tocarbon dioxide ratio in the absorber, (iii) regeneration pressure, (iv) regeneration temperature, (v) absorber chiller evaporation temperature. The considered values are in Table 6. 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 evaporation temperature values apply to the three chillers processing: (i) the exhaust gas, (ii) the lean solution and (iii) the solution recycle, prior to entering into the absorber. The total number of simulated combinations is 129.

#### 2.7. Performance indexes

The carbon capture efficiency,  $\eta_{CO2}$  [%] 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 exhaust chilling island, is one performance index. Commonly, the specific heat duty,  $q_{CO2}$  [MJ<sub>th</sub>/kg<sub>CO2</sub>] defined as the ratio of the reboiler heat duty [MW<sub>th</sub>] and the mass flow rate [kg/s] of effectively captured carbon dioxide, is utilized as another performance index. However, such index does not include the information on the capture efficiency nor on the temperature at which the heat duty is required (or in equivalent terms the loss of electrical power from the steam turbine). Therefore, here is adopted another index, introduced by Campanari et al. [22] and now in use by the EBTF, that solves the issues while sharing the same units. It allows so to compare plants characterized by different capture efficiencies, regeneration temperatures and electric efficiency penalties. The Specific Primary Energy Consumption for Carbon Avoided (*SPECCA*) [MJ<sub>th</sub>/kg<sub>CO2</sub>] is defined as:

$$SPECCA \stackrel{\text{def}}{=} \frac{HR - HR_{REF}}{E_{REF} - E} \equiv \frac{3600 \left(\frac{1}{\eta_e} - \frac{1}{\eta_{e,REF}}\right)}{E_{REF} - E}$$
(1)

where all parameters refer to either the power plant equipped with the carbon capture or the reference power plant without it: HR is the heat rate [MJ<sub>th</sub>/MWh<sub>e</sub>], E the specific CO<sub>2</sub> emission [kg<sub>CO2</sub>/MWh<sub>e</sub>],  $\eta_e$  [nondimensional] the net electrical efficiency and REF stays for reference. Table 3. Assumptions for the exhausts entering the capture block.

Lastly, the ammonia slip is definitely an important parameter. Nevertheless, given the uncertainty on the thermodynamic modeling and the much lower order of magnitude of its values compared to other concentrations, the numerical results are not here reported explicitly. A targeted study, numerical or more likely experimental, shall be conducted.

Table 1. General assumptions (unless otherwise stated).

Parameter	Unit	Value			
Ambient	t				
Temperature	°C	15			
Air-coole:	rs				
End temperature	°C	25			
Specific electric consumption	$MW_{e}/MW_{th}$	0.0159			
Chillers					
Evap. minimum temp. difference	°C	3			
Condensation temperature	°C	30			
COP / COP of Carnot cycle	%	65			
Pumps					
Hydraulic efficiency	%	75			
Electro-mechanical efficiency	%	95			

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Parameter	Unit	Value		
Low Pressure turbin	e-generator			
Isentropic efficiency	%	88		
End pressure	bar	0.05		
End vapor title	%	93		
Exit velocity	m/s	250		
Electrical efficiency	%	98		
Reboiler	•			
Minimum temperature difference	°C	10		
Steam superheated temperature	°C	5		
Steam subcooled temperature	°C	0		
Reference power plant				
Net electrical efficiency	%	45.0		
Specific CO <sub>2</sub> emission	$kg_{\rm CO2}/kWh$	0.83		

Parameter	Unit	Value

Unit	Value
bar	1.04
°C	49
% (vol. dry)	
	14.5
	82.3
	3.2
	Saturated
	Unit bar °C % (vol. dry)

Table 4. Assumptions for the absorption/regeneration/washing island.

Parameter	Unit	Value
Recupera	ator	
Minimum temperature difference	°C	5

Table 5. Assumptions for the compression island.

Parameter	Unit	Value			
Compress	ors				
Isentropic efficiency	%	85			
Electro-mechanical efficiency	%	95			
Last compressor end pressure	bar	80			
Air-coolers					
Intercooler end temperature	°C	35			
1 <sup>st</sup> aftercooler end temperature	°C	35			
Pump					
Delivery pressure	bar	110			

Table 6. Assumptions for the design parameters.

Parameter and values	Unit
Ammonia initial concentration: 0.095 <sup>a,b</sup> , 0.10, 0.15, 0.20 <sup>c</sup>	kg/kg
NH3-to- CO2 ratio: 2.0 <sup>a,b</sup> , 2.5 <sup>b</sup> , 3.0, 3.5 <sup>c</sup> , 4.0 <sup>b</sup>	kmol/kmol
Regeneration pressure: 20, 30°, 40 <sup>a</sup>	bar
Regeneration temperature: 100 <sup>b</sup> , 115 <sup>c</sup> , 120 <sup>a,b</sup> , 125, 135	°C
Chiller evaporation temperature: -1 <sup>a</sup> , 4 <sup>c</sup> , 9 <sup>b</sup>	°C

<sup>a</sup> value adopted also in the previous work [1]

<sup>b</sup> not all possible combinations with other parameters are run

<sup>c</sup> value adopted in the base case of the present work

## 3. Results and discussion

Before presenting the parametric and base case investigation results, some preliminary considerations are introduced that, despite approximate, may be of use in the critical review of results of any study on CAP.

## 3.1. Preliminary considerations

The enthalpy flux of the chilled exhausts entering the abs/reg/wash island is roughly equal to the sum of the

enthalpy fluxes of all exiting streams (treated gases, regenerated carbon dioxide and purges). Consequently, the sum of the mechanical and thermal powers into the system shall be roughly equal to the sum of those from the system. Neglecting the power to pumps, the main input is the reboiler heat duty. The main output is the chilling load. Thus, in approximate terms, the chilling load is equal to the heat duty. Moreover, as it will be shown, the electrical power loss from the power block is between one fifth and a quarter of the heat duty. The electrical power consumed by the chillers is about one fifth - a quarter of the chilling load, assuming a Coefficient Of Performance (COP) of 4-5. So, the electrical power loss equals approximately the chiller electrical consumption. Any increase of the reboiler heat duty has a "two-times" effect on the electricity penalty through both the power loss from the power block and the power consumption by the chillers.

#### 3.2. Parametric investigation

The electric loss due to steam extraction referred to the heat duty is in Table 7. The estimation of the electrical cost of chilling the exhausts at the considered evaporation temperatures and of compressing the carbon dioxide from the considered regeneration pressures are in Table 8.

The influence of all five design parameters is well defined, as seen in Figure 2. The increase of NH<sub>3</sub> concentration in the initial solution has remarkable benefits over the SPECCA and the capture efficiency, however its upper value is limited by the ammonia slip. As mentioned above, the ammonia slip is not reported here numerically, but the ammonia content in the treated flue gas is monitored in this study. The ammonia-to-carbon dioxide ratio has an optimum value from the SPECCA perspective, despite an increase leads to higher capture efficiencies. Regeneration pressure has a modest effect on SPECCA but a negative influence on the capture. In contrast, the lower the regeneration temperature the lower the SPECCA, but at the cost of a reduced capture that may reach inacceptable levels. Finally, higher evaporation temperatures of those chillers serving the absorber yield better values of SPECCA, but again at the cost of lower capture efficiency and higher ammonia slip.

Table 7. Results for the approximated power block.

Electrical loss	Unit	Value
Regenerating at:	MWe/MWth	
100°C		0.1179 <sup>a</sup>
115°C		0.2119 <sup>a</sup>
125°C		$0.2340^{a}$
135°C		$0.2556^{a}$

<sup>a</sup> referred to boiler heat duty

Table 8. Results for exhaust chilling and compression islands.

Electrical loss	Unit	Value
Exhaust	chilling	
Chiller evaporation at:	kWhe/kg <sub>CO2</sub>	
-1°C		$0.0186^{a}$
+4°C		$0.0160^{a}$
+9°C		$0.0138^{a}$
Carbon dioxid	e compression	
Compressor starting from:	kWh <sub>e</sub> /kg <sub>CO2</sub>	
20 bar		0.265 <sup>b</sup>
30 bar		0.183 <sup>b</sup>
40 bar		0.127 <sup>b</sup>

<sup>a</sup> referred to CO<sub>2</sub> entering the chilling island

<sup>b</sup> referred to CO<sub>2</sub> entering the compression island

Table 9. Results for the reference and base case plants.

Unit	Reference	Base case
MW <sub>e</sub>	757.7	615.5
%	45.17	36.65
kg <sub>CO2</sub> /kWh <sub>e</sub>	0.6788	0.1084
MJ/kg <sub>CO2</sub>	NA	3.18
	Unit MWe % kg <sub>CO2</sub> /kWh <sub>e</sub> MJ/kg <sub>CO2</sub>	Unit Reference   MWe 757.7   % 45.17   kg <sub>CO2</sub> /kWhe 0.6788   MJ/kg <sub>CO2</sub> NA

Table 10. Comparison of the previous and the present works.

Parameter	Unit	GHGT-9	Base case
Reboiler heat duty	MJ/kg <sub>CO2</sub>	1.53	2.46
Electrical loss due to:	$kWh_e/kg_{CO2}$		
steam extraction		0.0959	0.1645
gas chilling		0.0207	0.0181
abs/reg/wash		0.0657	0.1152
compression		0.0134	0.0183
Total loss		0.1957	0.3161
Net electrical efficiency	%	39.2	36.65
SPECCA	$MJ/kg_{\rm CO2}$	1.84	3.18

## 3.3. Base case investigation

The results of the investigation with the detailed power model are shown by Table 9, in absolute terms, and by Table 10, in specific terms. For comparison, Table 10 recalls the previous work [1]. However, the two cases are not directly comparable because the design parameters differ, as indicated by Table 6, and the thermodynamic models also differ. Globally, carbon capture reduces the net electrical power by 19% and the electrical efficiency by 8.5 percent points. With respect to the past results, the reboiler heat duty is 60% higher, leading to losses greater by about 60%, which is in agreement with the reasoning in section 3.1, and to SPECCA greater by 73%.

## 3.4. Net electrical efficiency and SPECCA dependence on the heat duty

Due to the uncertainty on the heat of reaction calculated by the Aspen Plus modeling, the influence of the heat duty, which is strictly related to the heat of reaction, on both the net electrical power plant and SPECCA is here analyzed. The numerical results for the base case are taken as starting point. In particular, the ratio of the chilling load in the abs/reg/wash island and the heat duty (which is roughly unity, as reasoned in section 3.1) is employed.

Assuming the power consumption for exhausts chilling, pumping and carbon dioxide compression are constant, a variation of the heat duty influences only the electrical power loss from the power block, which can be computed as illustrated in section 2.1, and the electrical consumption for the chillers in the abs/reg/wash island, which can be computed from the mentioned chilling load-to-heat duty ratio. The net electrical power and, thus, the net electrical



Figure 1. Validation of the Aspen Plus built-in electrolyte model and library against experimental data from the open literature and against calculated data via the code Refprop.

efficiency as linear functions of the heat duty can be determined. Being the specific emission inversely proportional to the net electrical power at a fixed capture efficiency, SPECCA as function of the heat duty is calculated.

Figure 3 illustrates the yielded net electrical efficiency and SPECCA for the base case with a variable heat duty. Reasonably, it proves that the thermodynamic uncertainty has a marked effect on the overall performances. Moreover, it confirms the results of Table 10. As an indication, the SPECCA of a conventional MEA plant is about 4.2 MJ/kg<sub>CO2</sub>, therefore there is still an appreciable margin within which the Chilled Ammonia is competitive, at least energy wise. No economic comparison is performed in this paper.



Figure 2. Influence of the design parameters on the performance indexes.



Figure 3. SPECCA and efficiency as function of heat duty.

## 4. Conclusions

The integration of USC plants with CAP is assessed by way of a parametric investigation to determine the optimal design parameters and by a more detailed base case investigation. SPECCA is used as performance index. With respect to a reference power plant, carbon capture reduces the net electrical power by 19% and the net electrical efficiency by 8.5 percent points. SPECCA is  $3.18 \text{ MJ/kg}_{CO2}$ . The results are though influenced by the thermodynamic model that is still not fully validated.

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