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A comparative analysis of the efficiency penalty in power plants of different amine-based solvents for CO₂ capture.

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ABSTRACT

Amine solvents are one of the main options for post-combustion CO2 capture applications. The main drawback of the carbon capture processes is the required energy to regenerate the solvent once it has reacted with the carbon dioxide. When applied to a power plant, the energy requirement has an important impact on the net efficiency of the overall system. Several solvents i.e. MEA, DEA, MDEA and many others have been proposed to overcome this drawback. Regeneration temperature and heat duty reduction are considered as the significant objectives. Moreover, enhancement on the amine's concentration and its working capacity without the impact on the other variables are of importance.

In this work, different types of amines with a wide range of heat duty and regeneration temperatures under the same set of assumptions are calculated and compared. The effect of both variables on the energy penalty caused by carbon capture is measured. A review of amines and their effects on the net efficiency of the overall system (power plant, chemical absorption, CO₂ compression) are conducted and analysed. As it is expected, the impact of heat duty is higher than the modification of regeneration temperature. The effect of reducing 1 GJ/ton CO₂ in the heat duty is similar to the effect of reducing between 25 and 40°C in the regeneration temperature.

Keywords: CCS, CO₂ emissions, CO₂ capture, power plants, amine, energy requirements.

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1. INTRODUCTION

The global climate policy is focused on the deployment of renewable technologies to fight against climate change caused by CO₂ emissions. Nevertheless, some heavy industries are still dependent on the consumption of fossil fuels rather than the electricity for their operation. Moreover, renewables are generally capital-intensive and, in some scenarios, their availability and accessibility reduce their competitiveness with the fossil fuels [1]. As a result, fossil fuels seemingly would still play an important role in the future energy mix of the world; therefore, the nations should reconsider their climate policies and turn their attention towards CO₂ Capture and Storage (CCS) technologies if inclined to attain a carbon-free, and more importantly, reliable energy system.

Chemical absorption based on amine solvents is the main technology for post-combustion CO_2 capture [2]. The technology has some drawbacks such as the giant energy consumption for regeneration of the CO_2 -loaded amine solution, the amine solvent degradation and the equipment corrosion [3]. But the energy consumption of regeneration is considered as the major challenge, because it consumes more than 70% of the total operating costs of a CO_2 capture plant. Consequently, the reduction in heat duty of regeneration should be the main priority for further development in amine-based CO_2 capture technology [4].

Several works in the literature have demonstrated through techno-economic analysis the improvement or advantages of using one specific solvent instead of, mainly, MEA. Nevertheless, MEA is the most common, developed and demonstrated solvent for carbon capture. For example, an optimization and economic analysis for an amine-based acid gas capture unit using monoethanolamine (MEA) and methyl diethanolamine (MDEA) [5]. They utilized Aspen Plus software to demonstrate that using of MEA/MDEA mixture in lieu of MEA leads to surging in CO₂ removal rate and reduction in energy penalty. For industrial applications, it has been highlighted for a cement plant, that the total equipment cost and capital expenditure and the energy penalty of the AMP-PZ-MEA blend is lower compared to the MEA [6]. Furthermore, it was shown the effect of reduction in percentage of CO₂ captured in an industrial CCS plant integrated to the natural gas fired power plant. The influence of the CCS plant on the efficiency of the power plant was analysed. The efficiency of power plants declined from 33.22 to 32.86 by capturing of 5% of the flue gas [7].

It is more common in literature to present comparison between several solvents to prove the improvement is some specific variables. For energy regeneration, it has been shown that DEA had superiority over MEA for several configurations studied in terms of total equivalent work and reboiler duty [8]; amine-carbonate blend with 30 wt% (MEA) experimentally needed 10% lower energy regeneration than MEA [9]; or the use of tri-blend amines (MEA-MDEA-PZ) was an excellent approach for increasing CO₂ desorption activity and extremely declining the energy penalty of amine-based CO₂ capture systems [10]. CO₂ absorption rate [10] [11] and high absorption and desorption efficiencies [12] are other variables that have been used for comparison.

In spite of all literatures, there is a lack of literature to compare energetically, the performance of different solvents under common assumptions. Some relevant attempts have been made using Aspen and multi-objective genetic algorithm optimization to select the best process design and operating conditions for monoethanolamine (MEA), diethanolamine(DEA), and 2-amino-2-methyl-1-propanol (AMP) [13]. In general, most of the studies are specific for pilot plants and using ASPEN software for simulations. MEA with heat consumption around 3.6-3.7 GJ/tCO₂ is the most popular option used in these works [8][14][15][16]. Different capture rates were reported in these studies, from 79.9% [8] to 86% [14][15]. Studies also shows that there is room for improvements and the previous value of 3.6 GJ/tCO₂ could be reduced to 3.1 GJ/tCO₂ [16]. They did not show any effect of this reduction on hypothetical power plant efficiency. The use of other solvents is not as numerous as MEA, for example, blended amines with combination of mixtures of AMP and MDEA using DEA and MEA as activating agents has been also simulated for a 600 MWe conventional coal-fired power plant [17] or monoethanolamine (MEA), piperazine (PZ) and piperazine-methyldiethanolamine (MDEA) blends for the flue gas from the Norcem Brevik cement plant [18]. Results showed that the mixture of 5%wt DEA and 25%wt AMP was performed better than the other mixtures by obtaining heat consumptions of 3.03 GJ/tCO₂. Likewise, ammonia as a carbon dioxide solvent has been compared and evaluate under optimum operating conditions that minimizes the impact on the thermal performance of the regeneration depending on the CO2-loading of the lean solution and the ammonia concentration [19].

In this work, a comparative analysis in terms of the efficiency penalty in power plants is conducted for different amine-based solvents aiming at capturing of CO₂. Firstly, a sensitivity analysis of the efficiency penalty depending on regeneration temperature and stripper heat duty is presented. Then, a comparison of several amines' impact with different energy requirements on the efficiency of the power plants based on literature data is presented. It should be noted that, apart from the significance of energetic requirement, it is not the only variable to be considered when the amine is selected for CO₂ capture. Operability, cost, maintenance, corrosive risk and etc. should be also considered.

2. AMINE-BASED SOLVENTS FOR CO₂ CAPTURE

Several types of amines have been chosen for simulations. Amines are organic compounds that can act as bases by protonation of the lone pair of electrons in the nitrogen atom. In the case of CO_2 capture, a molecule of H_2O is involved in the reaction leading to the formation of substituted ammonium bicarbonates:

$$R_1R_2R_3N + H_2O + CO_2 \rightarrow R_1R_2R_3NH^+ HCO_3^-$$

Besides this general mechanism of reaction, ammonia and amines containing a hydrogen atom bonded to the nitrogen one, that is, primary and secondary amines, can react with CO₂ forming substituted ammonium carbamates. The reaction proceeds in two steps:

$$R_1R_2NH + CO_2 \rightarrow R_1R_2NH^+HCOO^-$$

$$R_1R_2NH^+HCOO^- + R_1R_2NH \rightarrow R_1R_2NCOO^- + R_1R_2NH_2^+$$

The first reaction involves a molecule of amine plus a molecule of CO₂ to form a Zwitterion that, subsequently, forms the substituted ammonium carbamate.

It can be seen from the reaction equations that absorption as bicarbonate requires one molecule of amine per molecule of CO_2 , while the formation of ammonium carbamate requires two molecules of amine per molecule of CO_2 . In spite of the different loading of amine required, primary and secondary amines are mainly used due to the different kinetics of the reactions, with bicarbonate formation being much slower that carbamate formation. Work done in the capture of CO_2 by different amines show that the reaction constants can vary from 7500 m³/s/kmol for MEA [20], to 1200 m³/s/kmol for DEA [21] and to 3.5 for MDEA [22]. A mixed primary-secondary amine like DETA has a reaction constant of 47740

m³/s/kmol [23]. Other amines not used in this work like piperazine have been proposed [24][25]. The use of other amines can be found in a review [26].

Table 1 shows the amines used in this work. Apart from ammonia, there are three primary amines (MEA, DGA and AMP), a secondary amine (DEA), a tertiary amine (MDEA) and a mixed primary-secondary amine (DETA). Thermodynamic data for used in the calculations are shown in Table 2.

Primary amines seem to be more capable to capture CO₂, while they have the highest reaction enthalpies, meaning that the regeneration operation will be conducted in strong operating conditions. Several options for MEA are summarized in table 2. Heat duty is ranged between 3.1 and 16 GJ/ton CO₂, but it is usual not exceed 5 GJ/ton CO₂ [27]. Efforts to reduce this inconvenient have led to the use of other types of amines as DEA with heat duty between 2.8 and 4.2 GJ/ton CO₂ and regeneration temperatures of 70-130°C. MDEA and DGA have also show low regeneration energy requirements with values of 2.8 2 GJ/ton CO₂ with usual stripper temperatures of 120-130°C. Furthermore, DETA and AMP, that is a sterically-hindered primary amine that produces unstable carbamates leading to easier regeneration than other primary amine carbamates even though with reduced speed capture [28], exhibit low regeneration temperatures with heat duties in the range of 3.2-4.9 GJ/ton CO₂.

Acronym	Name	Chemical formula
MEA	Monoethanolamine 2-aminoethanol	HONH ₂
DEA	Diethanolamine bis(2-Hydroxyethyl)amine	HO NOH
MDEA	Methyldietanolamine Bis(2-hydroxyethyl) methyl amine	CH ₃
DGA	Diglycolamine 2-(2-aminoethoxy)ethanol	HO NH ₂
AMP	Aminomethylpropanol 2-amino-2-methyl-1- propanol	HO NH ₂
DETA	Diethyelenetriamine 2,2'-Diaminodiethylamine	H_2N N NH_2
NH3	Ammonia	NH ₃

Table 1. Amines used in this work

116.1 4.0 30%wt, 0.25 lean loading, 0.478 rich loading, 1.5 bar [8] 116.3 3.9 30%wt, 0.25 lean loading, 0.481 rich loading, 1.5 bar [10] 115.2 4.0 30%wt, 0.25 lean loading, 0.487 rich loading, 1.5 bar [10] 115.0 8.7 0.30 rich loading [29] 115.0 4.5 0.45 rich loading [29] 130.0 12.0 0.21 lean loading, 0.5 rich loading, (4kmol/m³), 1 atm [30] 130.0 5.4 0.22 rich loading, 0.5 rich loading, (4kmol/m³), 1 atm [30] 130.0 3.8 0.26 rich loading, 0.5 rich loading, (4kmol/m³), 1 atm [30] 130.0 3.8 0.32 lean loading, 0.5 rich loading, (5kmol/m³), 1 atm [30] 130.0 3.8 0.32 lean loading, 0.5 rich loading, (5kmol/m³), 1 atm [30] 130.0 3.8 0.32 lean loading, 0.5 rich loading, 2 bar [31] 112.0 3.56 30%wt, 0.16 lean loading, 0.47 rich loading, 2 bar [31] 112.0 3.98 30.3wt [32] 112.0 3.98 30.3wt [33] 126.7 4.01 0.414 lean loading, 29.3%wt MEA, 2.23 bar [16] 115.0 3.75 150kPa [16] 114.0 3.09 0.30 lean loading, 0.47 rich loading, 7 mol/kg MEA (30%wt), 1.7 bar [34] 114.0 3.09 0.30 lean loading, 0.47 rich loading, 7 mol/kg MEA (30%wt), 1.7 bar [34] 114.1 6.75 20%wt, 30kPa [27] 123.0 5.1 20%wt, 50kPa [27] 123.0 5.1 20%wt, 50kPa [27] 136.0 4.4 20%wt, 200kPa [27] 136.0 4.4 20%wt, 200kPa [27] 136.0 4.4 20%wt, 200kPa [27] 136.0 4.4 20%wt, 300kPa [27] 14.9 3.3 40%wt, 150kPa [27] 114.9 3.5 3.5 30%wt [35] 117.1 3.2 40%wt, 30kPa [27] 118.5 3.55 30%wt [35] 2.8 0.447 rich loading (molCO ₂ /molDeA) [35]	Amine	Temperature (ºC)	Heat duty (MJ/kg CO₂)	Details				
115.2		116.1	4.0	30%wt, 0.25 lean loading, 0.478 rich loading, 1.5 bar [8]				
115.0		116.3	3.9	30%wt, 0.25 lean loading, 0.481 rich loading, 1.5 bar [10]				
115.0 6.5 0.35 rich loading [29] 115.0 4.5 0.45 rich loading [29] 130.0 12.0 0.21 lean loading, 0.5 rich loading, (4kmol/m³), 1 atm [30] 130.0 5.4 0.22 rich loading, 0.5 rich loading, (4kmol/m³), 1 atm [30] 130.0 4.8 0.26 rich loading, 0.5 rich loading, (4kmol/m³), 1 atm [30] 130.0 3.8 0.32 lean loading, 0.5 rich loading, (5kmol/m³), 1 atm [30] 120.0 4.3 30%wt, 0.16 lean loading, 0.42 rich loading, 2 bar [31] 112.0 4.55 30%wt [32] 112.0 3.36 30%wt, process improvement [32] 120.0 3.98 30.3%wt [33] 126.7 4.01 0.414 lean loading, 29.3%wt MEA, 2.23 bar [16] 115.0 3.75 150kPa [16] 115.0 3.75 150kPa [16] 114.0 3.09 0.30 lean loading, 0.477 rich loading, 7 mol/kg MEA (30%wt), 1.7 bar [34] 71.6 16.0 20%wt, 30kPa [27] 83.8 11.0 20%wt, 50kPa [27] 14.1 6.75 20%wt, 150kPa [27] 123.0 5.1 20%wt, 250kPa [27] 130.0 4.7 20%wt, 250kPa [27] 136.0 4.4 20%wt, 300kPa [27] 136.0 4.4 20%wt, 300kPa [27] 82.3 4.0 40%wt, 30kPa [27] 82.3 4.0 40%wt, 30kPa [27] 114.9 3.3 40%wt, 75kPa [27] 114.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 150kPa [27] 114.9 3.3 40%wt, 150kPa [27] 114.9 3.5 3.5 30%wt [35] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] 3.55 30%wt [35]		115.2	4.0	30%wt, 0.25 lean loading, 0.477 rich loading, 1.5 bar [10]				
115.0		115.0	8.7	0.30 rich loading [29]				
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133.0 3.45 275kPa [16] 114.0 3.09 0.30 lean loading, 0.477 rich loading, 7 mol/kg MEA (30%wt), 1.7 bar [34] 71.6 16.0 20%wt, 30kPa [27] 83.8 11.0 20%wt, 50kPa [27] 94.3 9.0 20%wt, 75kPa [27] 114.1 6.75 20%wt, 150kPa [27] 123.0 5.1 20%wt, 200kPa [27] 130.0 4.7 20%wt, 250kPa [27] 136.0 4.4 20%wt, 30kPa [27] 70.4 4.2 40%wt, 30kPa [27] 82.3 4.0 40%wt, 50kPa [27] 92.0 3.8 40%wt, 75kPa [27] 110.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 114.9 3.3 40%wt, 175kPa [27] 117.1 3.2 40%wt, 200kPa [27] 3.55 30%wt [35] 3.15 40%wt [35]		126.7	4.01	0.414 lean loading, 29.3%wt MEA, 2.23 bar [16]				
114.0 3.09 0.30 lean loading, 0.477 rich loading, 7 mol/kg MEA (30%wt), 1.7 bar [34] 71.6 16.0 20%wt, 30kPa [27] 83.8 11.0 20%wt, 50kPa [27] 94.3 9.0 20%wt, 75kPa [27] 114.1 6.75 20%wt, 150kPa [27] 123.0 5.1 20%wt, 200kPa [27] 130.0 4.7 20%wt, 250kPa [27] 136.0 4.4 20%wt, 300kPa [27] 82.3 4.0 40%wt, 30kPa [27] 82.3 4.0 40%wt, 50kPa [27] 92.0 3.8 40%wt, 75kPa [27] 110.9 3.4 40%wt, 175kPa [27] 114.9 3.3 40%wt, 200kPa [27] 117.1 3.2 40%wt, 300kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.15 40%wt [35] 2.9 50%wt [35]		115.0	3.75					
114.0 3.09 (30%wt), 1.7 bar [34] 71.6		133.0	3.45	275kPa [16]				
83.8 11.0 20%wt, 50kPa [27] 94.3 9.0 20%wt, 75kPa [27] 114.1 6.75 20%wt, 150kPa [27] 123.0 5.1 20%wt, 200kPa [27] 130.0 4.7 20%wt, 250kPa [27] 136.0 4.4 20%wt, 30kPa [27] 82.3 4.0 40%wt, 30kPa [27] 92.0 3.8 40%wt, 75kPa [27] 110.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 127.6 3.05 40%wt, 30kPa [27] 3.55 30%wt [35] 12.9 50%wt [35]		114.0	3.09					
94.3 9.0 20%wt, 75kPa [27] 114.1 6.75 20%wt, 150kPa [27] 123.0 5.1 20%wt, 200kPa [27] 130.0 4.7 20%wt, 250kPa [27] 136.0 4.4 20%wt, 300kPa [27] 82.3 4.0 40%wt, 50kPa [27] 92.0 3.8 40%wt, 75kPa [27] 110.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 114.9 3.3 40%wt, 175kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] - 40%wt [35] 50%wt [35]		71.6	16.0	20%wt, 30kPa [27]				
114.1 6.75 20%wt, 150kPa [27] 123.0 5.1 20%wt, 200kPa [27] 130.0 4.7 20%wt, 250kPa [27] 136.0 4.4 20%wt, 300kPa [27] 82.3 4.0 40%wt, 50kPa [27] 92.0 3.8 40%wt, 75kPa [27] 114.9 3.3 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 117.1 3.2 40%wt, 200kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] 3.15 40%wt [35]		83.8	11.0	20%wt, 50kPa [27]				
123.0 5.1 20%wt, 200kPa [27] 130.0 4.7 20%wt, 250kPa [27] 136.0 4.4 20%wt, 300kPa [27] 70.4 4.2 40%wt, 30kPa [27] 82.3 4.0 40%wt, 50kPa [27] 92.0 3.8 40%wt, 75kPa [27] 110.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 114.9 3.3 40%wt, 175kPa [27] 127.6 3.05 40%wt, 200kPa [27] 3.55 30%wt [35] 3.15 40%wt [35] 2.9 50%wt [35]		94.3	9.0	20%wt, 75kPa [27]				
130.0 4.7 20%wt, 250kPa [27] 136.0 4.4 20%wt, 300kPa [27] 70.4 4.2 40%wt, 30kPa [27] 82.3 4.0 40%wt, 50kPa [27] 92.0 3.8 40%wt, 75kPa [27] 110.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 114.9 3.3 40%wt, 175kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] 3.15 40%wt [35]		114.1	6.75	20%wt, 150kPa [27]				
136.0 4.4 20%wt, 300kPa [27] 70.4 4.2 40%wt, 30kPa [27] 82.3 4.0 40%wt, 50kPa [27] 92.0 3.8 40%wt, 75kPa [27] 110.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 117.1 3.2 40%wt, 200kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] - 40%wt [35]		123.0	5.1	20%wt, 200kPa [27]				
70.4 4.2 40%wt, 30kPa [27] 82.3 4.0 40%wt, 50kPa [27] 92.0 3.8 40%wt, 75kPa [27] 110.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 117.1 3.2 40%wt, 200kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] 3.15 40%wt [35] 50%wt [35]		130.0	4.7	20%wt, 250kPa [27]				
82.3 4.0 40%wt, 50kPa [27] 92.0 3.8 40%wt, 75kPa [27] 110.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 117.1 3.2 40%wt, 200kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] 3.15 40%wt [35] 50%wt [35]		136.0	4.4	20%wt, 300kPa [27]				
92.0 3.8 40%wt, 75kPa [27] 110.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 117.1 3.2 40%wt, 200kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] 3.15 40%wt [35] 2.9 50%wt [35]		70.4	4.2	40%wt, 30kPa [27]				
110.9 3.4 40%wt, 150kPa [27] 114.9 3.3 40%wt, 175kPa [27] 117.1 3.2 40%wt, 200kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] 3.15 40%wt [35] 2.9 50%wt [35]		82.3	4.0	40%wt, 50kPa [27]				
DEA 114.9 3.3 40%wt, 175kPa [27] 117.1 3.2 40%wt, 200kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] 3.15 40%wt [35] 2.9 50%wt [35]		92.0	3.8	40%wt, 75kPa [27]				
DEA 117.1 3.2 40%wt, 200kPa [27] 127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] 3.15 40%wt [35] 2.9 50%wt [35]		110.9	3.4	<u> </u>				
127.6 3.05 40%wt, 300kPa [27] 3.55 30%wt [35] 3.15 40%wt [35] 2.9 50%wt [35]		114.9	3.3	1 1				
3.55 30%wt [35] 3.15 40%wt [35] 2.9 50%wt [35]	DEA	117.1	3.2	1				
3.15 40%wt [35] 2.9 50%wt [35]		127.6	3.05	40%wt, 300kPa [27]				
2.9 50%wt [35]			3.55	30%wt [35]				
2.9 50%wt [35]			3.15					
		-	2.9					
			2.8					

Table 2. Review of regeneration temperature and heat duties of MEA and DEA

Amine	Temperature (ºC)	Heat duty (MJ/kg CO₂)	Details				
	130.0	1.2	0.06 lean loading, 0.5 rich loading, (4kmol/m³ solvent), 1				
	150.0	1.2	atm [30]				
	130.0	2.8	0.04 lean loading, 0.5 rich loading, (4kmol/m³ solvent), 1				
MDEA			atm [30] 0.03 lean loading, 0.5 rich loading, (4kmol/m³ solvent), 1				
	130.0	7.5	atm [30]				
	120.0	4.36	3/27%wt DEA/MDEA [36]				
	112.9	3.82	30%wt [36]				
	85.8	4.5	60%wt, 50kPa [37]				
	96.5	4.1	60%wt, 75kPa [37]				
DCA	110.9	3.2	60%wt, 150kPa [27]				
DGA	116.0	2.9	60%wt, 200kPa [27]				
	120.7	2.8	60%wt, 250kPa [27]				
	124.1	2.7	60%wt, 300kPa [27]				
	115.9	3.18	30%wt [36]				
	95.2	3.6	5/25%wt DEA/AMP 0.41 lean loading 0.54 rich loading [17]				
	114.7	3.05	5/25%wt DEA/AMP 0.07 lean loading 0.545 rich loading [17]				
	95.7	3.6	10/20%wt DEA/AMP 0.43 lean loading 0.575 rich loading [17]				
A N A D	112.3	3.05	10/20%wt DEA/AMP 0.11 lean loading 0.548 rich loading [17]				
AMP	95.2	3.8	15/15%wt DEA/AMP 0.44 lean loading 0.568 rich loading [17]				
	114.6	3.1	15/15%wt DEA/AMP 0.07 lean loading 0.541 rich loading [17]				
	115.0	9.2	5/25%wt PZ/AMP 0.04 lean loading 0.26 rich loading [38]				
	112.0	4.9	5/25%wt PZ/AMP 0.14 lean loading 0.28 rich loading [38				
	110.0	4.6	5/25%wt PZ/AMP 0.14 lean loading 0.28 rich loading [38]				
DETA	100.0	4.8	2 kmol DETA/m³, 0.4 cyclic loading [39]				
DETA	100.0	2.2	2 kmol DETA/m³, 0.56 cyclic loading [39]				
	90.0	5.75	0.23 lean loading [40]				
	131.0	2.53	0.33 lean loading, 0.66 rich loading 7.3%wt NH ₃ , 10 bar [41]				
	149.7	1.86	10.2%wt NH ₃ , 0.236 lean loading, 0.41 rich loading, 12 bar [42]				
NH ₃	145.5	3.27	0.225 lean loading, 0.41 rich loading, 10 bar [43]				
	145.5	2.46	0.225 lean loading, 0.41 rich loading, process improvement, 10 bar [43]				
	110.0-139.0	4-4.2	1.9-5.8%wt NH ₃ , 0.21-0.41 lean loading [44]				

Table 3. Review of regeneration temperature and heat duties of MDEA, DGA, AMP, DETA and NH_3 .

3. MODELLING AND SIMULATION

Simulations have been carried out considering a Rankine cycle power plant that generates gross 500 MW_e with a net efficiency of 43.42%. The boiler of the case-study power plant produces 353.0 kg/s of steam at 300 bar and 600 °C. There is a single reheat at 620 °C. At nominal load, boiler steam output is 1073 MW_{th}. Boiler efficiency is assumed as 92 %. Overall cycle data, electricity output and efficiency estimations are summarized in Table 4. Figure 1 shows the flow diagram of the power cycle. Live steam is expanded through nine turbine stages to a condenser pressure of 0.05 bar. Two HP turbine stages operate between 600°C and 300 bars at inlet, and 320°C and 50 bars at outlet. Three MP turbine stages works between 620°C and 45 bars at inlet, and 386°C and 10 bars at outlet. And finally, five LP turbine stages operate up to the condenser pressure. There are four high-pressure (HP) heaters, deaerator and five low-pressure (LP) heaters. Table 5 shows the m-P-T data corresponding to the flows of Fig. 1.

Coal consumption and CO_2 emissions have been calculated through a governmental report [45] with the average of coal low heating value (LHV) for Spain (22.40 GJ/t coal) and its emission factor 99.40 kg CO_2 /GJ_{PCI}. This represents a CO_2 emission of 384.5 kg CO_2 /h (106.8 kg/s) at nominal power. This value is fixed for the comparative analysis and do not influence in the solvent comparison.

Simulation of the power cycle is accomplished by means of EES (Engineering Equation Solver) and the following simplifying assumptions have been used:

• For the different stages of the HP, MP and LP turbines: Constant isentropic efficiency, equal to 0.90 for HP stages, 0.92 for MP stages and 0.90 for low pressure turbine have been assumed. As not partial load operation is evaluated, constant pressure bleeding in HP and IP turbines are considered. For the LP turbine, as the steam bleeding is influenced by the regeneration temperatures in stripper, small pressure variations are allowed as it is explained.

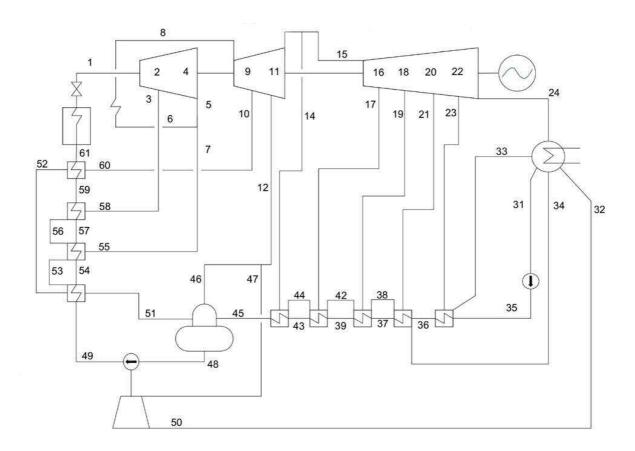


Figure 1. Layout of the Rankine steam cycle considered for simulations.

- Pressure drop in feedwater heaters: 2% inlet pressure at both steam and water sides. When amine scrubbing is considered, the extraction pressure is set by the steam temperature required in the stripper. The pressure is set whose saturation temperature is that of regeneration and a pressure drop of 2% is taken into account.
- Terminal Temperature Difference (TTD) and Temperature Drain Cooler Approach (TDCA) have been chosen for modelling HP and LP heaters. They remain constant for the simulations, TTD are ranged between 3 and 4°C and the values for TDCA are between 5 and 6°C, excepting in the LPH2 that is set to 10°C.

Boiler energy input	1073 MW _{th}	CO ₂ produced	106.6 kg/s
Gross power output	500.9 MW _e	Gross power plant efficiency	46.70 %
Net power output	$465.8~\text{MW}_{\text{e}}$	Net power plant efficiency	43.42 %
Thermal energy LPH	$169.9~\mathrm{MW_{th}}$	Thermal energy LPH	121.9 MW _{th}

Table 4. Overall cycle data, electricity output and efficiency estimations.

Absorber pressure is assumed at 1 bar for all cases. To supply the energy for the rich CO₂ solvent regeneration, one LP steam bleeding is used. There are two main variables that determine the analysis. The required regeneration temperature fixes the pressure of the steam bleeding, and the required regeneration energy fixes the amount of steam mass flow needed in the steam turbine extraction. Steam bleeding pressures range from 0.3 bar of the last LP extraction before the condenser, to 10 bars of input to the LP turbine. Then, regeneration temperature, which is the steam saturation temperature at these pressures, could range from 68.9°C to 179.5°C. These values agree with regeneration requirements of the selected amines. Higher regeneration temperatures require an increase in steam bleeding pressure; consequently, a reduction in the power produced by turbine.

In this study, it is assumed that the third steam bleeding changes the pressure to adapt the stripper necessities. The fourth steam bleeding is not considered, it is a close bleeding. This due to the thermal energy of the CO₂ compression intercooler is used to preheat the water after the condenser. Temperature of the water after these heat exchangers is usually in the range 89-132°C that is well below the maximum temperature of the CO₂ after compressors (143-160°C). It makes technically feasible the heat exchange with enough temperature difference. A new mixing heat exchanger is located instead of the second low-pressure heater (LPH2) as shown in figure 2. Water from condenser, after being heated in CO₂ compression intercoolers, are injected in this heat exchanger with the condensed water from the stripper and the condensed water from the third low-pressure heater (LPH3). When the regeneration temperature increases, the stripper pressure has to be higher than the second low-pressure steam bleeding. In order to avoid any potential problem or unfair result comparison for all cases, the pressure of the second low-pressure steam bleeding is calculated as the average of the first (10 bar) and stripper (depending on the regeneration temperature) low-pressure steam bleeding.

Stream	m (kg/s)	p (bar)	t (ºC)	Stream	m (kg/s)	p (bar)	t (ºC)
1	353,00	300,00	600,0	33	16,02	0,29	39,4
2	328,56	75,00	375,2	34	49,17	1,18	76,1
3	24,44	75,00	375,2	35	281,48	20,91	33,4
4	328,56	50,00	320,7	36	281,48	20,49	66,1

328,56	50,00	320,7	37	281,48	20,08	101,3
304,01	50,00	320,7	38	34,08	3,43	107,3
24,56	50,00	320,7	39	281,48	19,68	135,9
304,01	45,00	620,0	41	281,48	19,68	135,9
296,44	29,00	545,7	42	18,85	5,88	140,9
7,57	29,00	545,7	43	281,48	19,29	154,8
266,30	18,00	470,7	44	10,08	9,90	160,8
30,14	18,00	470,7	45	281,48	18,90	175,9
266,30	10,00	386,1	46	14,96	18,00	470,7
10,08	10,00	386,1	47	15,18	18,00	470,7
256,22	10,00	386,1	48	353,00	18,52	208,5
247,44	6,00	320,5	49	353,00	330,00	215,3
8,77	6,00	320,5	50	15,18	0,05	32,1
232,22	3,50	257,4	51	56,56	27,85	221,3
15,23	3,50	257,4	52	7,57	28,42	293,5
217,12	1,20	150,0	53	48,99	49,00	232,9
15,09	1,20	150,0	54	353,00	326,70	226,9
201,10	0,30	69,1	55	24,56	50,00	320,7
16,02	0,30	69,1	56	24,44	73,50	265,7
201,10	0,05	32,9	57	353,00	323,43	259,7
			58	24,44	75,00	375,2
281,48	0,05	32,9	59	353,00	320,20	287,5
15,18	0,05	32,1	60	7,57	29,00	545,7
	304,01 24,56 304,01 296,44 7,57 266,30 30,14 266,30 10,08 256,22 247,44 8,77 232,22 15,23 217,12 15,09 201,10 16,02 201,10 281,48	304,01 50,00 24,56 50,00 304,01 45,00 296,44 29,00 7,57 29,00 266,30 18,00 30,14 18,00 266,30 10,00 10,08 10,00 256,22 10,00 247,44 6,00 8,77 6,00 232,22 3,50 15,23 3,50 217,12 1,20 15,09 1,20 201,10 0,30 16,02 0,30 201,10 0,05	304,01 50,00 320,7 24,56 50,00 320,7 304,01 45,00 620,0 296,44 29,00 545,7 7,57 29,00 545,7 266,30 18,00 470,7 30,14 18,00 470,7 266,30 10,00 386,1 10,08 10,00 386,1 256,22 10,00 386,1 247,44 6,00 320,5 8,77 6,00 320,5 232,22 3,50 257,4 15,23 3,50 257,4 217,12 1,20 150,0 15,09 1,20 150,0 201,10 0,30 69,1 201,10 0,05 32,9 281,48 0,05 32,9	304,01 50,00 320,7 38 24,56 50,00 320,7 39 304,01 45,00 620,0 41 296,44 29,00 545,7 42 7,57 29,00 545,7 43 266,30 18,00 470,7 44 30,14 18,00 470,7 45 266,30 10,00 386,1 46 10,08 10,00 386,1 47 256,22 10,00 386,1 48 247,44 6,00 320,5 50 8,77 6,00 320,5 50 232,22 3,50 257,4 51 15,23 3,50 257,4 52 217,12 1,20 150,0 53 15,09 1,20 150,0 54 201,10 0,30 69,1 56 201,10 0,05 32,9 57 58 281,48 0,05 32,9 59	304,01 50,00 320,7 38 34,08 24,56 50,00 320,7 39 281,48 304,01 45,00 620,0 41 281,48 296,44 29,00 545,7 42 18,85 7,57 29,00 545,7 43 281,48 266,30 18,00 470,7 44 10,08 30,14 18,00 470,7 45 281,48 266,30 10,00 386,1 46 14,96 10,08 10,00 386,1 47 15,18 256,22 10,00 386,1 48 353,00 247,44 6,00 320,5 49 353,00 8,77 6,00 320,5 50 15,18 232,22 3,50 257,4 51 56,56 15,23 3,50 257,4 52 7,57 217,12 1,20 150,0 54 353,00 201,10 0,30 69,1	304,01 50,00 320,7 38 34,08 3,43 24,56 50,00 320,7 39 281,48 19,68 304,01 45,00 620,0 41 281,48 19,68 296,44 29,00 545,7 42 18,85 5,88 7,57 29,00 545,7 43 281,48 19,29 266,30 18,00 470,7 44 10,08 9,90 30,14 18,00 470,7 45 281,48 18,90 266,30 10,00 386,1 46 14,96 18,00 10,08 10,00 386,1 47 15,18 18,00 256,22 10,00 386,1 48 353,00 18,52 247,44 6,00 320,5 49 353,00 330,00 8,77 6,00 320,5 50 15,18 0,05 232,22 3,50 257,4 51 56,56 27,85 15,23

Table 5. m-P-T data corresponding to the Rankine steam cycle shown in Fig. 1

Figure 2 illustrates the original low-pressure heaters layout and two modified layouts to take into account the carbon capture installation and its integration in the power plant. In some cases where the CO₂ intercooling heat exceeds the capacity of the water to be heated, the remaining energy is integrated into the mixing heat exchanger after checking of any temperature limitation. This criterion is assumed to compare under the same assumptions (maximum heat recovery form CO₂ intercooling) the different alternatives. For most of the cases, the first layout is analyzed when the required heat duty is below 3.5 MJ/kgCO₂. For higher heat requirements than 3.5 MJ/kgCO₂ and high temperatures, both the pressure of the bleeding and the water through the low-pressure heaters limit the temperature difference in heat exchangers and the steam bleeding two has to be also closed.

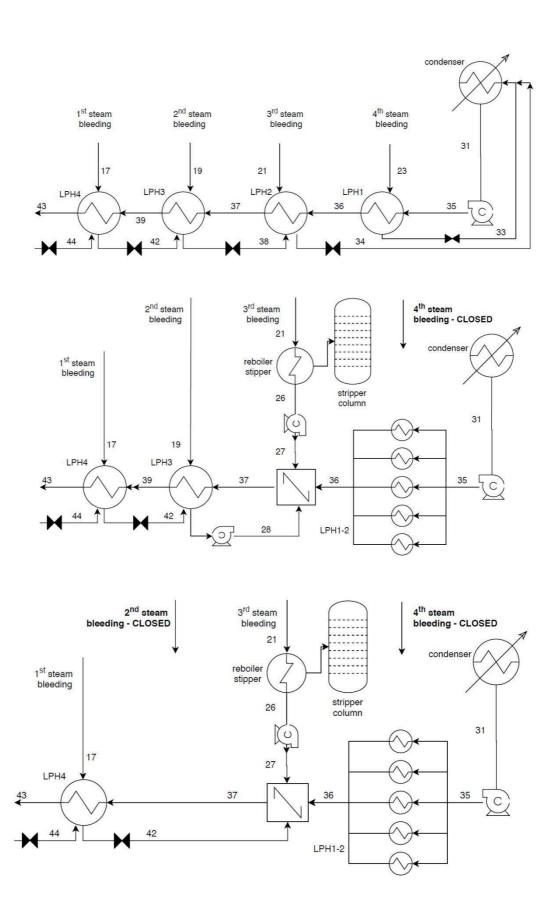


Figure 2. Original low-pressure heaters layout and modified layout with the carbon capture installation

CO₂ compression scheme is simulated after [46]. Four CO₂ compressor stages with intermediate intercooling and a pressure ratio of 3.23 are used to raise the pressure up to 120 bar. Each intercooler is divided into two heat exchangers. The first one reduce the CO₂ temperature from the compressor outlet, in the range of 143-160°C to 60°C. This is a useful heat stream that is integrated in the low pressure part of the steam cycle as showed in Figure 2. The second stage heat exchanger reduces the CO₂ temperature from 60°C to 30°C to diminish the CO₂ compressor power requirements. This heat stream is discarded and is released to the ambient. Isentropic efficiency of each CO₂ compressor is assumed in 0.8.

4. RESULTS AND DISCUSSION

4.1. Effect of the regeneration temperature and stripper heat duty.

First, a sensitivity analysis of the impact of regeneration temperature and heat duty shows how both variables influence on the net global efficiency of the CCS power plant. Regeneration temperature and heat duty are varied from 90 to 160°C and 1.5 to 5.5 GJ/ton CO₂, respectively. Figure 3 illustrates the influence of the regeneration temperature for different heat duties, and Figure 4 shows the influence of the heat duty for different regeneration temperatures.

With high regeneration temperatures, the steam bleeding pressure increases and, consequently, reduces the steam turbine power and net efficiency. It may also effect on the design of the low-pressure heaters. The condensed steam from stripper recycled to the steam cycle has high temperatures and influences on the layout of the low-pressure heaters.

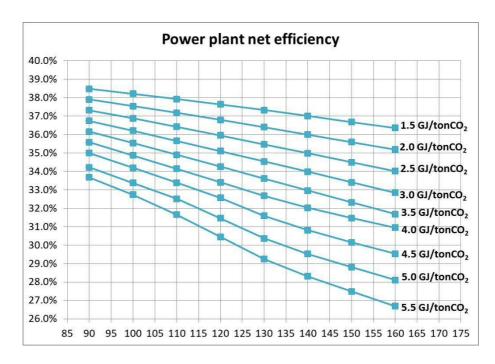


Figure 3. Influence of the regeneration temperature for different heat duties in the power plant net efficiency.

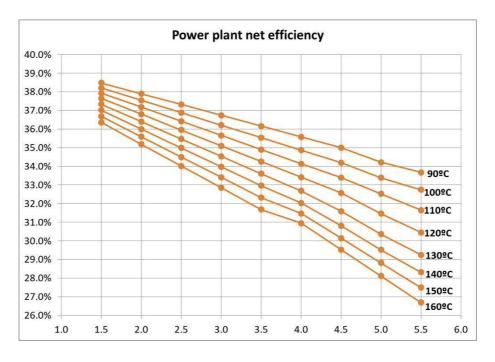


Figure 4. Influence of the heat duty for different regeneration temperatures in the power plant net efficiency.

For illustration purposes, when the heat duty and regeneration temperature are 3.0 MJ/kgCO₂ and 130°C, the heat required in the stripper ascends to 287.8 MW_{th} that is fulfilled with 123.16 kg/s of steam at 2.7 bar. Steam bleedings (1st, 2nd and 3rd) are completely open. If heat duty increases up to 5.5 MJ/kgCO₂ and 150°C, the heat required in the stripper increases to 479.7 MW_{th} that is fulfilled with 203.68 kg/s of steam at 4.8 bar. For this reason the second steam bleeding is not necessary and the contribution of the first steam bleeding is near negligible. In this case the temperature of stream 27 is high enough to make unnecessary the heating of the condensate before deaerator.

For the heat duty of 2.0 GJ/ton CO_2 , the net efficiency ranges are between 35.19 and 37.90%, and the values for regeneration temperatures are between 160 and 90°C. For the heat duty of 5.0 GJ/ton CO_2 , the ranges of net efficiency are slightly higher between 28.11 and 34.22%. The difference in efficiency penalty is close to 10 points, from 7 to approximately 17 points, when the heat duty to the stripper changes from 1.5 to 5.5 GJ/ton CO_2 for high regeneration temperatures (160°C). Moreover, the value is about 5 points for regeneration temperatures of 90°C. Taking into consideration stripper temperatures, the efficiency range for 90°C is 33.68 and 38.48%, and for 160°C is 26.69-36.36%. The difference in efficiency is 9.7 points for the highest heat duty (5.5 GJ/ton CO_2) and 4.8 points for the lowest heat duty of 1.5 GJ/ton CO_2 . It is clear that the heat duty has more influence on the efficiency penalty in the power plants than the regeneration temperature, but this last influence is also remarkable. The effect on the net efficiency of increasing 1 GJ/ton CO_2 is similar to the reduction between 40°C (for 1.5 GJ/ton CO_2) and 20°C (for 4.5 GJ/ton CO_2) of the regeneration temperature.

As Figure 5 shows, for a heat duty of 3.0 GJ/tonCO₂ at 130°C regeneration temperature, the penalty into the power plant is 8.9 efficiency points. A similar penalty is also caused by a solvent with a heat duty of 3.5 GJ/ton CO₂ and a regeneration temperature about 115°C, and with a solvent of a heat duty of 2.5 GJ/ton CO₂ and a regeneration temperature of more than 150°C. In this last case, even with lower heat duty, if regeneration temperature is high the integration possibilities decreases, and a part of the low-grade heat has to be discarded to condensers in some cases.

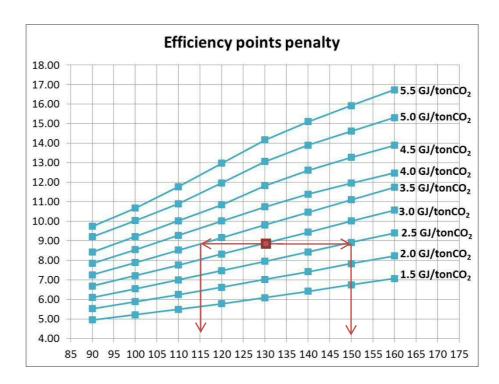


Figure 5. Net power plant efficiency as a function of the regeneration temperature and heat duty in the amine regeneration.

The effect of high regeneration temperatures is more critical when combines with high heat duties. When regeneration requirements are high, the steam bleeding to stripper enlarges, and a small fraction of the steam drives the LP turbine and goes into the condenser. As the condenser stream is small, the most of the CO₂ intercooler heat has to be used together with the mixing heat exchanger as the temperature of stream 36 is limited by the CO₂ maximum temperature after compressors. This causes that the temperature of stream 37 would be high enough to make the steam bleeding (19) and even (17) useless (see figure 1) due to the high condensate temperature. This effect is observed with heat duty of higher than 4.0 GJ/ton CO₂ when temperatures are higher than 150°C. When heat duty increases more than 5.0 the steam bleeding is closed for the all temperature ranges.

When regeneration temperature is high, the temperature of steam (37) should be limited to maintain a suitable temperature difference in CO₂ intercoolers and mixing heat exchangers. Then, part of the intercooling heat has to be thrown away. In these cases, efficiency decreases due to the discarded energy. It happens for heat duty of 5.5 GJ/ton CO₂ and temperature above 120°C, for heat duty of 5.0 and temperatures above 130°C and for heat duties of 4.0-4.5 for temperature above 140°C. It is illustrated in Figure 5 as the slope of the high heat duties increases more than the case of low heat duties.

4.2 Energy comparison of different solvents for CO₂ capture.

Table 6 illustrated the comparison of the selected solvents showed in bold in tables 2 and 3. There are 5 solvents based on MEA, 1 on DEA and MDEA, 2 on DGA, 2 on AMP and one DETA. Different regeneration energy requirements and temperatures have been selected. Ammonia has not been taken into consideration. It requires different energy integration and additional assumptions should be made to perform the comparison.

Simulations have been run with taking the following parameters as inputs: the stripper heat duty, regeneration temperature, amine concentration in the dissolution and lean and rich amine loading. Results include the impact on the steam cycle streams, as a consequence, the calculation of the power plant net efficiency and efficiency point losses. The general trend of the results is in agreement with the previous figures. In this case, the quantification of the impact in efficiency is the most important outcome.

Amine		Temperature (ºC)	Heat duty (MJ/kg CO₂)	Details		
	MEA1	116.3	3.9	30%wt, 0.25 lean loading, 0,481 rich loading, 1.5 bar [10]		
	MEA2	130.0	5.4	0.22 rich loading, 0.5 rich loading, (4kmol/m³), 1 atm [30]		
MEA	MEA3	130.0	3.8	0.32 lean loading, 0.5 rich loading, (5kmol/m³), 1 atm [30]		
	MEA4	120.0	4.3	30%wt, 0.16 lean loading, 0.42 rich loading, 2 bar [31]		
	MEA5	114.0	3.1	0.30 lean loading, 0.477 rich loading, 7 mol/kg MEA (30%wt) [34]		
DEA	DEA	110.9	3.4	40%wt, 150kPa [27]		
MDEA	MDEA1	130.0	2.8	0.04 lean loading, 0.5 rich loading, (4kmol/m³ solvent), 1 atm [30]		
DGA	DGA1	96.5	4.1	60%wt, 75kPa [37]		
DGA	DGA2	120.7	2.8	60%wt, 250kPa [27]		
AMD	AMP1	95.2	3.8	15/15%wt DEA/AMP 0.44 lean loading 0.568 rich loading [17]		
AMP	AMP2	112.0	4.9	5/25%wt PZ/AMP 0.14 lean loading 0.28 rich loading [38]		
DETA	DETA	100.0	4.8	2 kmol DETA/m³, 0,4 cyclic loading [39]		

Table 6. Solvent selected to do the energetic comparison

For MEA, regeneration temperatures are between 110-130°C and heat duty are from 3.1 to 5.4 GJ/ton CO₂. Results are in agreement with some references [47][48] [49] [50]. In this solvent, as Figure 6 illustrates, the effect on efficiency loss varies between 7.7 and 13.82 points. Differences between MEA1 and MEA3 are mainly caused by temperature and the effect on efficiency is relatively small (10.36 for 130°C and 9.57 for 116°C). However, for MEA2 and MEA3 the deviation is caused by the difference on heat duty and a gap of 3.46 efficiency points is observed.

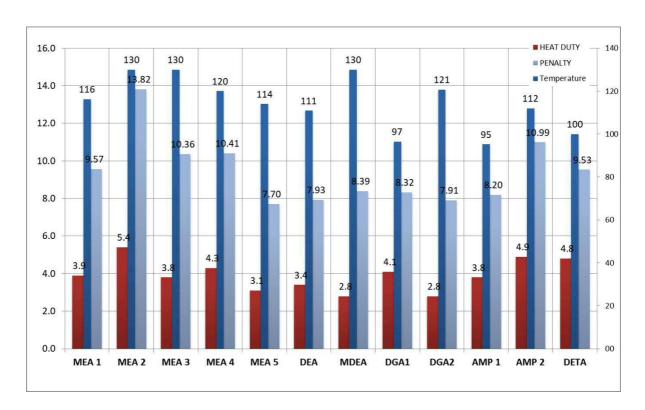


Figure 6. Net power plant efficiency as a function of the regeneration temperature and heat duty in the amine regeneration.

In the case of DEA, the results are significantly good with low efficiency penalty similar to MEA with lowest heat duty and temperature. The cases of MDEA and DGA also show good results with efficiency losses around 8 points. In these cases, the heat duty is low compared with MEA, 2.8 GJ/ton CO₂, and in the case of comparable requirements the regeneration temperature, 96.5°C, is much lower than 130°C for MEA.

The cases selected for AMP that are blended with DEA and PZ in different proportions [17][38] do not have evidence of improved results, even if a low stripper temperature is

necessary for AMP1. Finally, the case of DETA is in agreement with the general trend and shows better results than AMP2 (similar heat duty) caused by a lower temperature required.

5. CONCLUSIONS.

There are a lot of possible solvents for CO_2 capture based on amine scrubbing. A common feature is the high energy requirements in the regeneration step. Two main variables define the energy necessities, the heat duty and the regeneration temperature. A literature review shows different values for these variables, and it is difficult to know and isolate the independent effect of each variable in the net effect of energy requirements of the carbon capture.

A comparison under the same set of assumptions of the effect in net power plant efficiency of heat duty and regenerations temperatures in the stripper of amine scrubbing for CO₂ capture has been presented. Results shows that efficiency points penalty ranges between 7 for heat duty of 1.5 GJ/ton CO₂, and 90°C regeneration temperature to near 17 points for 5.5 GJ/ton CO₂ and 160°C. The effect on efficiency is more important for higher heat duties, and steam cycle modification should be done in order to use as much waste energy form CO₂ intercooling and steam turbine bleeding as possible. The effect on net efficiency of increasing 1 GJ/ton CO₂ the heat duty is similar to the reduction in the regeneration temperature between 40°C (for 1.5 GJ/ton CO₂) and 20°C (for 4.5 GJ/ton CO₂).

For the amines, the impact in efficiency points varies between 7-70, for DEA and 13.82 for MEA2. This is mainly caused by the difference in heat duty (3.1 vs 5.4 GJ/ton CO_2) and regeneration temperatures (114 vs 130 $^{\circ}$ C) as well. There are several options, MEA5, MDEA, DGA1, DGA2, AMD1, that show achieving a reduction in efficiency around 8 points is possible. It is important to highlight that these conclusions only show the results of an energy analysis. It is evident that in the utilization of these amines for carbon capture there are other limitations that can affect a complete techno-economic feasibility study.

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