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# Solvent Recovery System for a Co<sub>2</sub>-Mea Reactive Absorption-Stripping Plant

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The solvent recovery section from the exhaust gas represents an important auxiliary part for an industrial  $CO_2$  post-combustion capture plant by the reactive absorption-stripping process. In this work, a partial condenser and a water-wash section configuration were designed to reach 1 ppm of solvent in the exhaust gas, and compared using the Total Annual Cost (TAC) as economic index. Both the configurations ensured the required recovery performance. The results highlighted that the partial condenser alternative is more convenient in terms of capital annualized costs and water make-up, but at the same time it is strongly penalized by the high operating costs for the cooling water. Therefore, the configuration in which the absorber is equipped with the water-wash section resulted the option with the minimum TAC.

#### 1. Introduction

 $CO_2$  capture by reactive absorption-stripping is considered one of the most effective solutions for the mitigation of the industrial carbon dioxide emissions. A significant number of works related to the  $CO_2$  reactive absorption-stripping has been published in the literature, from the solvent selection (Lang et al., 2017) and the kinetic studies (Tristano et al., 2018) to the process modeling and simulation (Madeddu et al., 2017). In the recent years, the attention has been moved to the design and the economic assessment of the plant at an industrial scale (Madeddu et al., 2019).

One aspect that has not been systematically considered in the literature regards the solvent recovery from the exhaust gas after the absorption process. Depending on the operating conditions, a significant amount of solvent might be lost due to vaporization, leading to consequences either at an environmental and economic level. Up to now, the solvent recovery system has been overlooked in the works concerning the  $CO_2$  capture by reactive absorption-stripping plant design, though it might have a relevant role in the operation and economics of the system.

The aim of this work is to analyze two different configurations for an efficient solvent recovery in an industrial CO<sub>2</sub>-MEA reactive absorption-stripping plant: a partial condenser and a water-wash section represented by a packed column. In the first case the amine is recovered by condensation, while in the second case a physical absorption process is involved. The two configurations are firstly designed, reporting the results for the sizing and the most important parameters of the outlet streams. Then, the economic evaluation is performed and the different cost items are computed to obtain the total annual costs and choose the best configuration.

#### 2. Base Case Description

The CO<sub>2</sub> capture with MEA plant designed by Madeddu et al. (Madeddu et al., 2018), of which a simplified flowsheet is reported in Figure 1, was used as a base case to compare the alternatives considered.

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Figure 1: CO<sub>2</sub>-MEA system base case flowsheet

The process consists in a reactive absorption-stripping separation. The  $CO_2$  rich flue gas (FG-1) is sent to the bottom of the absorber where it flows countercurrent with the lean solvent (LS-3). From the top of the column the exhaust gas (FG-2) exits, while the rich solvent from the bottom (RS-1) is sent to the top of the stripping column after heating up in a cross heat-exchanger (RS-3). In the stripper the rich solvent flows countercurrent with the vapor stream generated in the reboiler (VAP-1). A gaseous mixture containing mainly  $CO_2$  and water (VAP-2) is sent to a partial condenser where the  $CO_2$  is concentrated in the gas phase ( $CO_2$ ) and sent to compression and storage, while the water (W-1) is recovered in the liquid phase. The regenerated solvent from the stripper bottom (LS-2) is cooled down in the cross heat-exchanger (LS-1) where it supplies its sensible heat to the rich solvent. Then, it is mixed with the water from the condenser and recycled in the absorber top.

### 3. Plant Configurations

During the absorption, part of the solvent is transferred to the gas phase, as a consequence of the vaporization induced by the exothermic reactions involving the  $CO_2$  and the solvent. This solvent must be recovered from the exhaust gas for two main reasons:

- 1. Environmental: MEA is a toxic compound that cannot be freely emitted in the atmosphere due to its harmful potential mostly related to solvent degradation compounds (Reynolds et al., 2012). Regulations exists on the maximum amount of MEA that can be released in the environment and this information is usually expressed as a threshold limit value. The TLV-TWA (*Threshold Limit Value Time Weighted Average*) for MEA is 3 ppm, according to the MSDS (*Material Safety Data Sheet*) produced by the Dow Chemical Company (The Dow Chemical Company, 2003). Then, the performance required in the solvent recovery section is to produce an exhaust gas with a MEA content below or equal to 1 ppm, in order to safely respect the TLV-TWA.
- 2. Economics: the cost of the amine is typically in the order of hundreds of dollars per tonne (Abu-Zahra et al., 2007), and the re-integration of fresh solvent to maintain the desired operating conditions can influence significantly the overall plant economics. The solvent recovery section is also useful to reduce the amount of make-up water to be re-integrated in the plant to close the water mass balance. In fact, a certain amount of water lost in the exhaust gas is transferred to the liquid phase together with the MEA. This function of the solvent recovery section is considered in the plant economics evaluation as a further cost item.

For these reasons, the solvent recovery becomes a mandatory task to be always included in the design of an industrial  $CO_2$  reactive absorption-stripping plant. In particular, the objective is to remove the MEA from the exhaust gas exiting the top of the absorber, for which the characterization is resumed in Table 1:

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Table 1: Absorber top exhaust gas characterization

Variable	Value
Temperature [K]	338
Pressure [bar]	1
Mass flow [kg/s]	137.48
CO <sub>2</sub> [mass frac]	0.0229
H2O [mass frac]	0.1603
MEA [mass frac]	0.0008
N <sub>2</sub> [mass frac]	0.816

The two configurations and their design are described separately in Sections 3.1 and 3.2. All the calculations were performed in Aspen Plus<sup>®</sup> v8.8 environment. In particular:

- the Elec-NRTL model and the Redlich-Kwong equation of state were used to describe the non-ideal thermodynamics of the liquid and the gas phase, respectively;
- the hybrid kinetic and equilibrium reactions set and corresponding parameters reported in the work of Errico et al. (Errico et al., 2016) was considered to evaluate the reaction rates in the system;
- the RadFrac<sup>™</sup> model was adopted for the material and energy balances.

#### 3.1 Configuration 1: Absorber + Partial Condenser (APC)

In this case, as reported in Figure 2, the exhaust gas exiting the top of the absorber (FG-2) is sent to a partial condenser, where the solvent is recovered in the liquid phase (W-PC). The exhaust gas is then sent to the stack (FG-3), while the solvent recovered is mixed with the lean solvent from the cross heat-exchanger (LS-1), the water make-up (W-MUP) and the water from the stripper condenser (W-1) and sent back to the top of the absorption column.



Figure 2: Absorber + Partial Condenser configuration flowsheet

Cooling water at 298.15 K is used as utility in the partial condenser. The cooling water outlet temperature should not exceed 313.15 K, in order to restrict fouling problems in the exchanger (Bott, 1995). Using the RadFrac<sup>TM</sup> model, it is possible to include the partial condenser within the absorber block. The software requires an input value for the reflux ratio, which was imposed to zero since no reflux is needed in this case. Then, the only design parameter is the outlet temperature of the exhaust gas. This value was found by means of *Model Analysis Tool – Sensitivity*, included in Aspen Plus<sup>®</sup>, varying the condenser temperature and checking the MEA mass fraction in the exhaust gas. Table 2 reports the design results for the partial condenser configuration.

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Table 2: Partial condenser design results

Variable	Value
Cooling water	
Mass flow [kg/s]	531.81
Exhaust gas	
Outlet temperature [K]	321.15
MEA [mass frac]	9.4·10 <sup>-7</sup>
Condenser	
Total exchange area [m <sup>2</sup> ]	1633.96
Number of exchangers	2
Duty [MW]	33.28
Water make-up	
Mass flow [kg/s]	3.558

#### 3.2 Configuration 2: Absorber + Water-Wash (AWW)

In this case the flue gas containing the MEA (FG-2) is sent to the bottom of a water-wash section, which is represented by a physical absorption packed section placed above the main absorber where the  $CO_2$  is chemically removed. The flowsheet of this configuration is reported in Figure 3.



Figure 3: Absorber + Water-Wash configuration flowsheet

The typical approach for the design of a physical absorption column would involve the evaluation of the minimum solvent flow rate with a theoretically infinite packing height and the evaluation of the effective solvent flow rate and column dimensions. In this case, the solvent used in the water-wash section is the water recovered in the stripper condenser (W-1). Furthermore, the water-wash section diameter was considered equal to that of the absorption one, since it was chosen to place the two sections within the same column. Therefore, the only design parameter to be determined is the water-wash packing height. For this purpose, a sensitivity analysis was performed, varying the packing height until the desired performance was achieved. The design results for the water-wash configuration are resumed in Table 3.

Table 3: Water-Wash design results

Variable	Value
Exhaust gas	-
MEA [mass frac]	9.7·10 <sup>-7</sup>
Water-wash	
Packing material	Mellapak Plus 252Y
Packing height [m]	4.1
Diameter [m]	9.3
Water make-up	
Mass flow [kg/s]	15.74

#### 4. Economic Evaluation

The Total Annual Cost (TAC) associated with the two configurations was evaluated by means of the Aspen Process Economic Analyzer<sup>®</sup> (APEA) in order to choose the most convenient one from an economic point of view. Furthermore, the cost associated with the MEA make-up for the plant without solvent recovery was also considered for comparison. The TAC is defined as the sum of the Capital Annualized Costs (CAC), i.e. the ratio between the Capital Costs (CC) and the payback period, and the Operating Costs (OC), according to Eq(1) (Sinnot, 2005):

$$TAC = CAC + OC = \frac{CC}{\text{payback period}} + OC$$
(1)

A payback period of 10 years was assumed for the evaluation of the CAC. Furthermore, the Installed Costs are considered as representative of the Capital Costs. Depending on the configuration, different costs are involved. In the case of the partial condenser, the Capital Costs are represented by the exchange area, while the Operating Costs are related to the consumption of cooling water. On the other hand, since the water-wash section is inside the absorber column, the Capital Costs associated are evaluated as the difference between the absorber Capital Costs before and after the addition of the water-wash section. No direct Operating Costs are associated with the second configuration. For both cases, the indirect cost for the water make-up, necessary to close the plant water mass balance, was considered. For what concerns the base, only the cost related to the MEA re-integration was taken into account for the comparison. It must be highlighted that the economic evaluations were performed considering specific costs for the cooling water and the make-up of water and MEA from the literature, as reported in Table 4.

Table 4: Specific of	costs for the co	oling and the i	make-up of wat	er and MEA

Variable	Value	Reference
Cooling water [\$/tonne]	0.082	(Rév et al., 2001)
Filtered and softened water [\$/tonne]	0.305	(Peters et al., 2003)
Fresh MEA [\$/tonne]	880	(Abu-Zahra et al., 2007)

Table 5 resumes the results for the economic evaluation of the two configurations.

Variable	Base case	APC	AWW
Total Capital Annualized Costs [k\$/y]	-	42.77	125.9
Total Operating Costs [k\$/y]	-	1376.18	-
Total water make-up cost [k\$/y]	155.11	32.52	151.53
Total MEA make-up cost [k\$/y]	3054.27	-	-
Total Annual Cost [k\$/y]	3209.38	1451.47	277.2

Table 5: Comparison between the total costs of the two configurations and the base case

From the results reported in Table 4 different conclusions can be made:

- In terms of Capital Annualized Costs, the partial condenser is the most convenient configuration compared to the water-wash, for which the CAC are almost three times higher. For what concerns the Total Annual Cost, the Capital Annualized Costs represent the 3 % and the 45 % of the Total Annual Cost for the partial condenser and the water-wash, respectively;
- In terms of Operating Costs, the water-wash has none, due to the fact that the solvent used is an
  internal plant stream. On the other hand, due to the high amount of cooling water needed for the
  partial condenser, the OC play a decisive role in this case, being them about 32 times higher than the
  CAC and representing the 95 % of the TAC;
- For what concerns the water make-up costs, the partial condenser ensures a high recovery of water from the exhaust gas, then a lower cost for the water re-integration compared to the water-wash. In fact, in the latter case the costs for the water make-up are almost five times higher and are responsible for more than 50 % of the total annual costs;

In terms of Total Annual Costs, the water-wash configuration is by far the most convenient one. The high amount of cooling water in the condenser penalizes this configuration, making it more than five times costlier then the water-wash one. Moreover, it can be noticed that the configuration without solvent recovery is the costliest among the three cases analysed. In fact, without the solvent recovery section, the costs would be more than two times higher than the configuration with partial condenser and more than eleven times higher than the configuration with water-washing. This demonstrates the necessity to include the solvent recovery section not only for environmental reasons, but also for the plant economics.

#### 5. Conclusions

In this work, two different configurations for the solvent recovery from the exhaust gas in an industrial CO<sub>2</sub>-MEA post-combustion capture plant were compared in Aspen Plus<sup>®</sup> v8.8: a partial condenser and a waterwash section. Both the configurations ensure the required performance on the mass fraction of MEA in the exhaust gas to the stack to be below or equal to 1 ppm. The comparison between the two configurations and the base case without solvent recovery was done based on the minimum TAC. The first important and general result is that the solvent recovery system makes the plant more economically convenient, avoiding the solvent make-up and reducing the water reintegration. Then, from the direct comparison between the two configurations, it was found that the absorber equipped with water-wash section has a TAC five times lower than the one equipped with partial condenser. This was explained by the penalization due to the high consumption of cooling water in the partial condenser.

The results obtained in this work demonstrate the importance of the solvent recovery in the  $CO_2$  capture process by reactive absorption-stripping and give an important indication on the best solution to be used for the solvent recovery section in the design of a complete industrial  $CO_2$  reactive absorption-stripping plant.

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