

Design of the CO₂ removal section for PSA tail gas treatment in hydrogen production plant

1 **Laura A. Pellegrini¹, Giorgia De Guido¹, Stefania Moioli^{1*}**

2 ¹Dipartimento di Chimica, Materiali e Ingegneria Chimica “G. Natta”, Politecnico di Milano, Piazza
3 Leonardo da Vinci 32, I-20133 Milano, Italy

4 *** Correspondence:**

5 Stefania Moioli

6 stefania.moioli@polimi.it

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8 **Abstract**

9 CO₂ Capture, Storage and, recently, Utilization (CCSU) is considered effective for achieving the
10 target of 2°C established to reduce the gradual increase in global warming. In the literature, most of
11 research has focused on the removal of carbon dioxide from power plants, particularly those fed by
12 coal, which account for higher amounts of CO₂ emissions if compared to those fed by natural gas.
13 CCSU in other non-power sectors is still not fully considered, while its importance in mitigating the
14 environmental impact of industrial activities is equivalent to the one of power plants.

15 In the field of hydrogen production, treatment of gaseous streams to remove carbon dioxide is
16 performed for producing a stream of almost pure H₂ starting from syngas and for reducing the carbon
17 dioxide emissions, so that CO₂ removal units can be part of different sections of the plant.

18 In this work, a state-of-the-art Steam Methane Reforming (SMR) plant for production of 100 000
19 Nm³/h of hydrogen has been considered. Hydrogen is produced from syngas by employing the
20 Pressure Swing Adsorption (PSA) technology and the exiting tail gas is fed to the burners of the
21 SMR unit, after removal of carbon dioxide.

22 This work focuses on the design of the units for the treatment of the PSA tail gas by employing an
23 aqueous solution of MethylDiEthanolAmine (MDEA). Simulations have been performed with the
24 commercial process simulator ASPEN Plus[®], customized by the GASP group of Politecnico di
25 Milano for best representing both the thermodynamics of the system and the mass transfer with
26 reaction. For the scheme composed of the absorber and the regenerator, several column
27 configurations have been considered and the optimal solution, which minimizes the operating costs
28 of the plant, has been selected.

29 **1 Introduction**

30 The Carbon Capture and Storage (CCS) technology has recently received a great attention as a
31 mitigation action for decreasing the environmental impact of energy conversion processes based on
32 the use of fossil fuels. Another example of mitigation action includes the switch from a fossil fuel-
33 based economy to an economy that relies on the use of renewable energy sources as biomass, solar
34 and wind energies (Jäger-Waldau, 2007;Blanco, 2009;Nema et al., 2012;Schaber et al.,

Design of the CO₂ removal section for PSA tail gas treatment in hydrogen production plant

2012;Timilsina et al., 2012;Corsatea, 2014). However, given the current state of development of the latter ones, fossil fuels will continue to play an important role in the future and, as a result, actions like CCS are worth being investigated. In recent years, attention has also been paid to CO₂ utilization, promoting the use of the expression “Carbon Capture, Storage and Utilization” (CCSU) (Hasan et al., 2015).

In order to capture CO₂, a number of processes is currently available, which can be categorized as follows: pre-combustion, post-combustion, and oxy-fuel combustion. A pre-combustion system consists in CO₂ capture before the combustion step. On the contrary, a post-combustion system consists in removing CO₂ from flue gases after the combustion of fossil fuels in air has taken place (Alie et al., 2005;Rochelle, 2009;Moioli et al., 2019a;Moioli et al., 2019b). In oxy-fuel combustion, nearly pure oxygen is used for combustion instead of air, resulting in a flue gas that mainly consists of CO₂ and H₂O, which would allow using simpler post-combustion separation techniques (*e.g.*, condensation) with significantly lower energy and capital costs. To cope with the demerits of other CCS technologies, the chemical looping combustion (CLC) process has also been recently considered as a solution for CO₂ separation (De Guido et al., 2018).

Another possible integration of CCS is in a steam methane reforming (SMR) based hydrogen plant. On a large industrial scale, the SMR is the leading technology for H₂ production from natural gas or light hydrocarbons, which involves a concurrent production of CO₂ as by-product (Rostrup-Nielsen and Rostrup-Nielsen, 2002;Riis et al., 2005). In particular, in this plant, CO₂ can be captured from three possible locations: the shifted syngas, the PSA tail gas, and the SMR flue gas. Using aqueous solutions of MethylDiEthanolAmine (MDEA) can be a possible method to remove carbon dioxide from these streams.

MDEA washing is certainly a well-established technology, but it is well-known that the main drawback related to CO₂ capture by amine absorption is due to the energy consumption for solvent regeneration (Pellegrini et al., 2019). This also applies when CO₂ separation from natural gas is considered for producing either a pipeline-quality natural gas (De Guido et al., 2015) or liquefied natural gas (LNG) (Pellegrini et al., 2015b). Indeed, when the CO₂ content exceeds 8-9 mol% (Langè et al., 2015), separation by means of chemical absorption into aqueous amines solutions becomes energy-intensive and other types of technologies (*e.g.*, low-temperature/cryogenic ones) can be considered as valuable alternatives. This also applies when CO₂ separation from biogas is considered for producing liquefied biomethane (Pellegrini et al., 2017), since biogas can be seen as a particular natural gas stream, characterized by a fixed composition (*i.e.*, about 40 mol% CO₂). Indeed, also for biogas upgrading, even if MDEA washing is more profitable than water scrubbing considering the same feedstock (Pellegrini et al., 2015a), it involves higher energy consumptions (due to the heat needed for solvent regeneration and for CO₂ pressurization, if considered) with respect to low-temperature technologies (Pellegrini et al., 2017).

Considering the integration of CCS in a SMR based hydrogen plant and the energy-consumption related issues associated with MDEA washing for CO₂ capture, this work investigates the CO₂ removal section for the treatment of the PSA tail gas, which can achieve a CO₂ avoidance of 52% (IEAGHG, 2017) with additional energy consumptions. The reference plant is the one presented in the IEAGHG Technical Report, which produces 100 000 Nm³/h of H₂ using natural gas as feedstock and fuel. It includes the hydrogen plant, the cogeneration plant, the demi-water plant and utilities and balance of plant (BOP) consisting of other systems (cooling water system, *etc.*).

Design of the CO₂ removal section for PSA tail gas treatment in hydrogen production plant

78 The capture step, based on chemical absorption of CO₂ into a MDEA aqueous solution, consists of an
79 absorber, a flash unit and a distillation column for solvent regeneration. Several column
80 configurations have been taken into account. For each of them, a sensitivity analysis has been
81 performed varying the CO₂ lean loading, in order to determine the optimal configuration from an
82 energy point of view, namely the one that minimizes the energy required for solvent regeneration.

83 **2 Methods**

84 In the following, the model used in the simulations and the analysis procedure are outlined.

85 **2.1 Model used for simulation**

86 The analysis of the system has been carried out by using the commercial process simulator ASPEN
87 Plus[®] V9.0 (AspenTech, 2016), which had been previously user-customized.

88 In particular, vapor-liquid equilibrium with chemical reactions generating ions in the liquid phase
89 occurs and the system is strongly non-ideal. Its description can be well accomplished by a γ / ϕ
90 method, based on the Electrolyte-NRTL (Chen et al., 1979; Chen et al., 1982; Chen and Evans,
91 1986; Mock et al., 1986) for the calculation of the activity coefficient in the liquid phase and on the
92 Redlich-Kwong Equation of State (Redlich and Kwong, 1949) for the calculation of the fugacity
93 coefficient in the vapor phase.

94 The kinetics and mass transfer with reactions have also been considered in the simulation, and the
95 performance of the columns has been determined on the basis of a rate-based approach. To this
96 purpose, ASPEN Plus[®] V9.0 has been integrated with a home-made routine developed by the GASP
97 group of Politecnico di Milano (Moioli et al., 2013).

98 **2.2 Procedure employed in this study**

99 The analysis, the results of which are presented in this work, involved the simulation of the CO₂
100 capture section from the PSA tail gas for the reference plant previously reported. The following
101 seven alternatives have been taken into account, which differ because of the internal configuration of
102 the absorption column:

103 - *Case A*: tray column with 51 four-pass valve trays;

104 - *Case B*: tray column with 51 two-pass valve trays;

105 - *Case C*: tray column with 21 four-pass valve trays;

106 - *Case D*: tray column with 21 two-pass valve trays;

107 - *Case E*: packed column with structured packing (*Sulzer Mellapak Standard 250X*);

108 - *Case F*: tray column with 24 four-pass valve trays;

109 - *Case G*: tray column with 24 two-pass valve trays.

110 *Case E* is the only one involving a packed column: for it, the structured *Sulzer Mellapak Standard*
111 *250X* packing has been chosen because of its excellence performance in columns with diameter up to
112 15 m as reported industrially (Mellapak, 2015), and because of its choice also in previous literature

Design of the CO₂ removal section for PSA tail gas treatment in hydrogen production plant

113 studies (Zhang and Rochelle, 2014;Moioli and Pellegrini, 2019). Indeed, it offers a low pressure drop
114 and it can be used for a quite wide range of liquid loads. For the simulation of this case, 51 stages
115 have been considered for the discretization of the column height.

116 As far as the other cases, which involve a tray column, are concerned, the choice of the tray type has
117 been made on the basis of a previous work (Cassiano, 2015). The standard tray spacing of 0.60 m and
118 0.76 m has been considered and the column dimensions have been selected taking into account the
119 sizes provided in the report (IEAGHG, 2017). According to the available data, the internal diameter
120 and the total height of the absorption column are, respectively, 3.399 m and 20 m. The value of the
121 column diameter has been checked in the simulations by means of the tool *Tray Sizing* available in
122 ASPEN Plus® V9.0 (AspenTech, 2016): the result has been found to be in accordance with the one
123 provided in the IEAGHG report.

124 *Case A* and *Case B* refer to an absorber with a different height, selected on the basis of a previous
125 work concerning CO₂ removal by MDEA scrubbing applied to pre-combustion syngas purification
126 (Cassiano, 2015).

127 A sensitivity analysis on the CO₂ lean loading has been performed, varying it in a suitable range
128 depending on the case study under investigation, with the aim of determining the value that
129 minimizes the reboiler duty. For each value of the CO₂ lean loading, the solvent flow rate has been
130 varied in order to meet the design specification on the CO₂ capture rate (*i.e.*, 96.49%), which can be
131 calculated on the basis of the data available in the report (IEAGHG, 2017), as explained in the next
132 section.

133 In the following, the reference case and the data available for it and relevant to the analysis are
134 described for the sake of clarity (section 2.3). Then, more details are given about the simulations
135 (section 2.4).

136 **2.3 Reference case**

137 The flowsheet of the simulated CO₂ capture section on the basis of the reference case study is shown
138 in Figure 1 and the data for the main streams are reported in Table 1.

140 [Figure 1]

141 [Table 1]

144 The “*TAIL GAS*” stream, with a CO₂ content of about 51 mol% on a wet molar basis, is initially
145 compressed to 1.1 MPa, before being fed into the bottom of the absorption column (*ABSORBER*).
146 Here, the CO₂ in the gas stream is absorbed by contacting it counter-currently with the lean solvent
147 fed at the top. The purified tail gas (“*GASOUT*”) that exits from the top of the absorber is
148 characterized by a CO₂ content of nearly 3.5 mol% on a wet molar basis. At the bottom of the
149 absorption tower, the rich solvent is recovered and sent to the *FLASH*: the vapour outlet stream is
150 sent to the burners to be employed as additional fuel in the steam reformer. On the contrary, the
151 liquid outlet stream, which is the rich solvent, is sent to the lean/rich heat exchanger, where it is
152 heated up by the hot lean solvent coming from the reboiler of the solvent regeneration column
153 (*REGOCO21*).

Design of the CO₂ removal section for PSA tail gas treatment in hydrogen production plant

154 After being heated in the lean/rich heat exchanger, the hot rich solvent is fed into the top of the
155 *REGOCO21* for regeneration. This is accomplished by a counter-current contact with the vapor
156 stream travelling upwards, which is generated at the bottom reboiler, where low-pressure steam from
157 the back pressure steam turbine of the cogeneration plant is used as heating medium.

158 The gas stream leaving the top of the distillation column is sent to the condenser, where the steam
159 present in the overhead gas is condensed, collected and returned as reflux to the column. As for the
160 CO₂-rich gas exiting from the top condenser, it is delivered to the CO₂ compression and dehydration
161 unit.

162 From the data reported in Table 1, it is possible to calculate the CO₂ capture rate according to Eq. (1),
163 where $F_{\text{CO}_2,\text{GASIN}}$ and $F_{\text{CO}_2,\text{GASOUT}}$ denote, respectively, the molar flow rate of CO₂ in the gas streams
164 entering and leaving the absorption column. Thus, the CO₂ capture rate is 96.49%. It represents the
165 target to be met in all the simulations described in the following section.

$$166 \quad \text{CO}_2 \text{ capture rate} = 100 \cdot \frac{F_{\text{CO}_2,\text{GASIN}} - F_{\text{CO}_2,\text{GASOUT}}}{F_{\text{CO}_2,\text{GASIN}}} \quad (1)$$

167 2.4 Simulations

168 Figure 1 illustrates the flowsheet of the CO₂ capture section that has been simulated in ASPEN Plus®
169 V9.0 (AspenTech, 2016).

170 The PSA tail gas (“*TAILGAS*”) is compressed from 0.13 MPa to 1.1 MPa before being fed into the
171 bottom of the absorption column (*ABSORBER*). This value is different from the one reported in the
172 IEAGHG report (*i.e.*, 1 MPa), and this is due to the definition of the pressure profile in the absorber
173 in the simulations: the pressure at the first stage from the top has been set equal to the pressure of the
174 gas stream exiting the top of the absorber (*i.e.*, 0.98 MPa, as reported in Table 1). When varying the
175 solvent flow rate in the simulations in order to obtain the target CO₂ absorption rate of 96.49% for
176 each value of CO₂ lean loading, for high values of the solvent flow rate a high pressure was reached
177 at the bottom of the absorber, higher than 1 MPa (*i.e.*, the pressure of the PSA tail gas entering the
178 bottom of the absorption column, according to the IEAGHG report). By setting the outlet pressure
179 from the compression train at 1.1 MPa (rather than at 1 MPa), this has been avoided.

180 The data for the two streams entering the absorber are reported in Table 2. The conditions of the lean
181 amine solvent stream (“*LEANIN*”) in terms of temperature, pressure and composition of the free
182 MDEA solvent (only composed of MDEA and water) have been kept constant in this study in order
183 to ensure comparison consistency. Obviously, its molar composition and flow rate vary in the
184 sensitivity analysis on the CO₂ lean loading, so that the target CO₂ capture rate is always met. The
185 composition of the lean solvent reported in Table 2 corresponds to a MDEA weight fraction of 0.5
186 and to a CO₂ lean loading of 0.0203 mol CO₂/mol MDEA.

187
188 [Table 2]

190 The absorption tower has been simulated defining its internals depending on which of the seven case
191 studies previously reported (see section 2.2) is considered.

192 The rich-solvent from the bottom of the absorption tower is sent to the separator (*FLASH*), which is
193 operated at 74 °C and 0.45 MPa. The liquid outlet stream (*TOREGI*) is sent to the lean/rich heat

Design of the CO₂ removal section for PSA tail gas treatment in hydrogen production plant

194 exchanger (*CROSSI*), in which the temperature approach between the hot outlet stream and the cold
195 inlet stream has been set equal to 10 °C, with the minimum temperature approach set equal to 5 °C.
196 The pre-heated rich-solvent (*HOTREGI*) is, then, fed at the top of the regeneration column
197 (*REGOCO2I*). It has been designed on the basis of the internal diameter and total height available in
198 the IEAGHG report (IEAGHG, 2017), and making reference to a previous work (Cassiano, 2015) for
199 what concerns the number of stages and internals type. The specifications and design parameters for
200 the stripping column are reported in Table 3.

201 Taking into account the availability of cooling water at 25 °C, it is assumed that the condenser works
202 at 49 °C (temperature of the stream “*CO₂ TO COMPRESSOR*” in Table 1, named as stream
203 *CO2REGI* in Figure 1). This specification ensures a CO₂ concentration in the gas stream exiting the
204 distillation column of 96 mol%.

205 The other specification required to simulate the stripping column refers to the CO₂ apparent molar
206 fraction in the regenerated solvent stream, which is equal to the CO₂ apparent molar fraction in the
207 lean solvent stream fed to the CO₂ capture plant (namely, stream “*LEANIN*” in Figure 1).

208 The operating pressure has been set equal to 0.29 MPa, considering the available datum for the CO₂
209 stream exiting from the top of the column (as reported in Table 1). A sensitivity analysis was actually
210 performed also on this operating condition, by varying it in the range 0.1-0.3 MPa. However, the
211 reboiler and condenser duties of the stripping column were found to vary only slightly with the
212 regeneration pressure.

213

214 [Table 3]

215

216 With reference to Figure 1, it is possible to define the CO₂ lean loading (*LL*) and the CO₂ rich loading
217 (*RL*) according to Eqs. (2)-(3), respectively.

$$218 \quad LL = \frac{\text{moles of CO}_2 \text{ in the lean solvent}}{\text{moles of MDEA in the lean solvent}} = \frac{F_{\text{CO}_2, \text{LEANIN}}}{F_{\text{MDEA, LEANIN}}} \quad (2)$$

$$219 \quad RL = \frac{\text{moles of CO}_2 \text{ in the rich solvent}}{\text{moles of MDEA in the rich solvent}} = \frac{F_{\text{CO}_2, \text{RICHOUT}}}{F_{\text{MDEA, RICHOUT}}} \quad (3)$$

220 3 Results and discussion

221 The results of the sensitivity analysis performed on the CO₂ lean loading are illustrated in Figure 2-
222 Figure 4 for *Case B*, *Case-E* and *Case-G*, respectively (they are representatives of the trends
223 observed in the considered case studies), showing the effect on the most important process
224 parameters, namely the solvent flow rate, the CO₂ rich loading, the energy requirements. It is
225 important to point out that, while performing such analysis, also the operating constraint on the CO₂
226 rich loading should be taken into account, considering that the maximum allowable value is in the
227 range 0.7-0.8 [mol/mol] in case of MDEA to avoid corrosion problems. Nevertheless, for all the
228 examined cases, the investigated values of the CO₂ lean loading have led to values of the CO₂ rich
229 loading that are significantly lower than the upper operational limit (as shown in Figure 2b, in Figure
230 3b and in Figure 4b). Therefore, for each of the examined configurations, the optimum CO₂ lean
231 loading can be identified on the basis of the minimization of the energy requirements only.

232 [Figure 2]

Design of the CO₂ removal section for PSA tail gas treatment in hydrogen production plant

233 [Figure 3]

234 [Figure 4]

235 Considering the influence of the CO₂ lean loading on the solvent flow rate (as shown in Figure 2a, in
236 Figure 3a and in Figure 4a), obviously by increasing the CO₂ lean loading, larger solvent flow rates
237 are required to guarantee the same CO₂ removal efficiency. Indeed, an increase in the *LL* results in a
238 lower purity of the solvent, thus penalizing its absorption capacity. As a result, more solvent is
239 required in order to capture the same amount of CO₂.

240 If accounting for the influence of the CO₂ lean loading on the CO₂ rich loading, different trends result
241 from the sensitivity analysis. The functional dependence of the *RL* on the *LL* is expressed by Eq. (4).

$$242 \quad RL = LL + CO_2 \text{ capture rate} \cdot \frac{F_{CO_2, ABSIN}}{F_{MDEA, LEANIN}} \quad (4)$$

243 Since the CO₂ capture rate and the molar flow rate of CO₂ in the inlet gas do not change in the
244 sensitivity analysis and in all the considered case studies, the specific trend observed in Figure 2b, in
245 Figure 3b and in Figure 4b depends on the relative increase of the MDEA flow rate in the lean
246 solvent with respect to the increase of the *LL* as the *LL* increases. This increase can be more or less
247 relevant, thus providing different trends in Figure 2b, in Figure 3b and in Figure 4b, on the type of
248 the characteristics of the column considered, also because of the kinetics occurring in the system.

249 In particular, for *Case B* the rich loading presents a minimum (Figure 2b), for *Case E* it decreases
250 though remaining within a small range (Figure 3b) and for *Case G* it monotonically increases as the
251 lean loading increases (Figure 4b). These trends can be fully understood by considering Figure 5 and
252 Figure 6. Indeed, as previously reported, the total flowrate generally increases as the lean loading
253 increases. However, as can be outsourced from Figure 5, the mole fraction of MDEA in the solvent
254 decreases (due to the higher amount of carbon dioxide), so, at different values of *LL*, the trend of the
255 flowrate of MDEA may be different from the one of the total amine flowrate. Considering that all the
256 analyses are carried out with the same gaseous stream to be treated (so with fixed amount of carbon
257 dioxide entering the absorber) and with a constant % removal of carbon dioxide, it follows that only
258 $F_{MDEA, LEANIN}$ varies in the second term of Eq. (4) (named “adding group” in Figure 6). Therefore,
259 since at different values of the lean loading different values of $F_{MDEA, LEANIN}$ occur, also different
260 values of the “adding group” result. The rich loading, obtained as the sum of this term and the related
261 lean loading, is then characterized by a specific trend depending on the considered case (Figure 6).

262

263 [Figure 5]

264

265 [Figure 6]

266

267 Finally, the dependence of the reboiler duty on the CO₂ lean loading is discussed. Two factors affect
268 this, namely the sensible heat that has to be supplied to bring the solvent temperature to the reboiler

269 temperature and the latent heat that must be supplied in order to vaporize the needed amount of
270 stripping agent in the regeneration column, provided that the heat needed to reverse the chemical
271 reaction occurred in the absorber is the same. At low values of the lean loading, a lower solvent flow
272 rate is sufficient to reach the target CO₂ capture rate, but a higher amount of stripping agent is
273 necessary in the regeneration column to strip more CO₂ off. Therefore, the latent heat of vaporization
274 plays a more important role. On the contrary, at high values of the lean loading, as it increases also
275 the solvent flow rate needed to reach the target CO₂ capture rate increases and more energy is
276 required to heat it up to the desired temperature in the regeneration column, even if less stripping
277 agent can be produced because less CO₂ has to be stripped off. Therefore, the sensible heat plays a
278 more important role in this case. For these reasons, a minimum in the reboiler duty as a function of
279 the CO₂ lean loading is observed (as shown in Figure 2c, Figure 3c, and Figure 4c).

280 For each of the examined configurations, the optimum CO₂ lean loading, which guarantees the
281 minimum energy requirement, is reported in Table 4. It is possible to observe that the optimum CO₂
282 lean loading obtained for *Case E* is much higher than the one involved in all the other cases. This is a
283 direct consequence of the fact that, in this case, the absorber is a packed column, with different fluid
284 dynamics (also influenced by the type of considered packing) and mass transfer occurring inside the
285 unit. In addition, the number of theoretical stages is different than the one of the other cases with tray
286 columns, thus exerting an influence on the total solvent flowrate needed to perform the CO₂ removal
287 and, thus, also on the optimal lean loading.

288 [Table 4]

289 Another important observation concerns the extremely high solvent flow rates required to reach the
290 desired CO₂ capture rate for *Case C*, *Case D*, *Case F* and *Case G*. This is due to the fact that in these
291 cases the absorption column has been modelled as a tray column with a number of stages
292 (respectively, 21 and 24) that is considerably lower than the one involved in *Case A* and in *Case B*
293 (*i.e.*, 51). For this reason, it has been necessary to significantly increase the solvent flow rate in order
294 to push the CO₂ removal from the gaseous stream to the target value.

295 Comparing all the investigated case studies, *Case E* turns out to be the most convenient one from an
296 energy point of view: indeed, the use of a packed absorption column rather than a tray column allows
297 to reach the target CO₂ capture rate using less solvent and requiring lower energy consumptions at
298 the reboiler of the solvent regeneration column.

299 4 Conclusions

300 This work has been focused on the study of a purification process for the CO₂ removal from PSA tail
301 gas within an SMR-based hydrogen plant, for which data are available in the literature. To this
302 purpose, an aqueous solution of MDEA has been employed. Despite the advantages associated with
303 this technology, it is fundamental to account for the fact that amine-based CO₂ capture processes are
304 generally quite energy-intensive. Therefore, the application of this technology at large-scale is mainly
305 subject to the optimization of the process energy performances, with the aim of specifically reducing
306 the energy requirement at the reboiler of the regeneration column for the solvent purification.

307 To this aim, different configurations have been taken into account for the absorber, performing the
308 simulations in ASPEN Plus[®] V9.0, integrated with a home-made routine developed by the GASP
309 group of Politecnico di Milano. The different configurations differ for the type of column internals. A
310 sensitivity analysis has been performed to investigate the effect of the lean loading on the reboiler

Design of the CO₂ removal section for PSA tail gas treatment in hydrogen production plant

311 duty, as well as on the rich loading and on the solvent flow rate required to meet the target CO₂
312 capture rate of 96.49%. The lean loading, which provides the minimum reboiler duty, varies from
313 0.05 to 0.17 depending on the considered case. Kinetics and mass transfer influence the needed
314 solvent flowrate, that, in turn, has an effect on the value of the rich loading for which different trends
315 result as the lean loading varies, each one specific for each configuration.

316 Comparing all the investigated case studies, the one which has turned out to be the most convenient
317 one from an energy point of view is the case in which the absorber has been modelled as a packed
318 column. Indeed, in such a case, because of the characteristics of the considered column, a lower
319 solvent flow rate can be used to reach the target CO₂ capture rate, requiring lower energy
320 consumptions at the reboiler of the solvent regeneration column.

321 **5 Nomenclature**

322 *Acronyms*

323	<i>BOP</i>	Balance of plant
324	<i>CCS</i>	CO ₂ Capture and Storage
325	<i>CCSU</i>	CO ₂ Capture, Storage and Utilization
326	<i>CLC</i>	Chemical Looping Combustion
327	<i>IEAGHG</i>	International Energy Agency Greenhouse Gas R&D Programme
328	<i>LL</i>	CO ₂ lean loading
329	<i>LNG</i>	Liquefied Natural Gas
330	<i>MDEA</i>	MethylDiEthanolAmine
331	<i>PSA</i>	Pressure Swing Adsorption
332	<i>RL</i>	CO ₂ rich loading
333	<i>SMR</i>	Steam Methane Reforming

334 *Symbols*

335	<i>F</i>	Molar flow rate [kmol/h]
336	<i>P</i>	Pressure [MPa]
337	<i>Q_{reb}</i>	Reboiler duty, [MW]
338	<i>T</i>	Temperature [°C]
339	<i>x_{MDEA}</i>	Molar fraction of MDEA in the solvent [-]

340 **6 Conflict of Interest**

Design of the CO₂ removal section for PSA tail gas treatment in hydrogen production plant

341 *The authors declare that the research was conducted in the absence of any commercial or financial*
342 *relationships that could be construed as a potential conflict of interest.*

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Table 1. Data for the main streams involved in CO₂ capture section studied in this work (IEAGHG, 2017).

<i>Variable</i>	<i>Unit</i>	<i>Streams</i>		
		<i>TAIL GAS FROM PSA</i>	<i>SWEET TAIL GAS TO BURNERS</i>	<i>CO₂ TO COMPRESSOR</i>
T	[°C]	28	44	49
P	[MPa]	0.13	0.98	0.29
Molar Flow	[kmol/h]	2106.3	1062.9	1080.0
Mass Flow	[kg/h]	60658	14939	46362
<i>Composition</i>				
CO₂	[mol/mol]	0.5095	0.0354	0.9585
CO	[mol/mol]	0.1454	0.2878	0.0001
Hydrogen	[mol/mol]	0.2369	0.4694	0.0001
Nitrogen	[mol/mol]	0.0062	0.0122	0.0002
Oxygen	[mol/mol]	0.0000	0.0000	0.0000
Methane	[mol/mol]	0.0945	0.1870	0.0000
Ethane	[mol/mol]	0.0000	0.0000	0.0002
H₂O	[mol/mol]	0.0076	0.0080	0.0409

Table 2. Data for the PSA tail gas stream entering the absorber after compression (“*ABSIN*” in Figure 1) and for the lean amine solvent stream (“*LEANIN*” in Figure 1) (the composition of the lean solvent corresponds to a MDEA weight fraction of 0.5 and to a CO₂ lean loading of 0.0203 mol CO₂/mol MDEA).

<i>Variable</i>	<i>Unit</i>	<i>Stream</i>	
		<i>ABSIN</i>	<i>LEANIN</i>
T	[°C]	28	40
P	[MPa]	1.1	1.0
Molar Flow	[kmol/h]	2106.3	(*)
Mass Flow	[kg/h]	60658	(*)
<i>Composition</i>			
CO₂	[mol/mol]	0.5095	0.0026914
CO	[mol/mol]	0.1454	0.0000
Hydrogen	[mol/mol]	0.2369	0.0000
Nitrogen	[mol/mol]	0.0062	0.0000
Methane	[mol/mol]	0.0945	0.0000
H₂O	[mol/mol]	0.0076	0.86499
MDEA	[mol/mol]	0.0000	0.1323

(*) Varied in the sensitivity analysis on the CO₂ lean loading, in order to meet the target CO₂ capture rate of 96.49%.

Table 3. Design parameters and specifications for the stripping column.

Variable	Value
Internal diameter [m]	5.155
Number of trays	8
Tray type	Valve
Condenser temperature [°C]	49
CO ₂ loading [mol CO ₂ /mol MDEA]	CO ₂ lean loading “ <i>LEANIN</i> ”

Table 4. Optimal operating conditions resulting from the lean loading sensitivity analysis.

Case	CO₂ lean loading [mol CO ₂ /mol MDEA]	CO₂ rich loading [mol CO ₂ /mol MDEA]	Solvent Flow Rate [kg/s]	Reboiler Duty [MW]	Condenser Duty [MW]
<i>A</i>	0.070	0.254	377.7	29.13	3.98
<i>B</i>	0.050	0.390	203.4	22.03	3.89
<i>C</i>	0.076	0.089	5484.2	216.18	5.76
<i>D</i>	0.074	0.096	3155.6	131.91	5.73
<i>E</i>	0.168	0.661	143.2	10.63	0.67
<i>F</i>	0.082	0.101	3705.7	151.04	5.10
<i>G</i>	0.080	0.109	2395.9	103.70	5.12

425 **Figure Captions**

426 **Figure 1.** Flowsheet of the simulated CO₂ capture system.

427 **Figure 2.** Effect of the CO₂ lean loading on: a) the solvent flow rate; b) the rich loading; c) the
428 reboiler duty (*Case B*).

429 **Figure 3.** Effect of the CO₂ lean loading on: a) the solvent flow rate; b) the rich loading; c) the
430 reboiler duty (*Case E*).

431 **Figure 4.** Effect of the CO₂ lean loading on: a) the solvent flow rate; b) the rich loading; c) the
432 reboiler duty (*Case G*).

433 **Figure 5.** Effect of the CO₂ lean loading on the mole fraction of MDEA in the solvent.

434 **Figure 6.** Effect of the CO₂ lean loading on the second term (“adding group”) of Eq. (4) for: a) *Case*
435 *B*; b) *Case E*; c) *Case G*.