

1 **Operating the CO₂ absorption plant in a post-combustion unit in flexible**
2 **mode for cost reduction**

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Abstract

Carbon dioxide greatly contributes to climate change and its emissions must be limited. Combustion of fossil fuels in power plants to produce electricity generates the largest amount of CO₂ released into the atmosphere, therefore application of Carbon Capture and Storage (CCS) to this sector would help in reducing the emissions of this acid gas.

CO₂ absorption with aqueous amines is the most common capture technology for post-combustion CO₂ removal and is characterized by high energy requirements, mainly for CO₂ release from the solvent and compression of the obtained rich-CO₂ stream. For this reason operating the CCS system in a power plant significantly reduces the power output and, consequently, the revenues from selling electricity.

In order to deal with this issue while maintaining low carbon dioxide emissions, flexible operation may be applied.

In this work, a detailed analysis of the application of the Solvent Storage mode for flexible operation of the CO₂ removal section of a natural gas combined cycle power plant has been performed.

Simulations in ASPEN Plus[®], properly customized for the description of the system, and a techno-economic model created by the GASP group of Politecnico di Milano have been run to find the best solution. The variation of price of electricity from hour to hour for key days and for the overall year have been considered. Different values of carbon tax to be applied have been also taken into account.

Keywords

MEA solvent; energy requirement; electricity price; NGCC power plant; flexible operation; solvent storage.

46 **1. Introduction**

47 Most of the carbon dioxide emitted to the atmosphere is released by the combustion of fossil fuels to
48 produce electricity. This sector emits about 40% of the total CO₂ emissions (IEA, 2016), therefore
49 performing CO₂ removal would help in achieving the targets established by international treaties.
50 Indeed, after the United Nations Framework Convention on Climate Change of 1992 and the Kyoto
51 Protocol (UN, 1997), in order to strengthen the global response to climate change, the 2015 Paris
52 Agreement (UN, 2015) established to keep the global temperature rise below 2°C above the
53 temperature of the pre-industrial era.

54 One way to make the industrial sector perform Carbon Capture and Storage (CCS), then, is by setting
55 taxes on carbon dioxide emissions (carbon taxes), which have been implemented by many countries.
56 In this way, the cost of electricity production may be significantly increased if carbon dioxide is not
57 removed and is emitted to the atmosphere.

58 Recently new sources for energy and electricity production have started to be exploited to cope with
59 environmental issues, with biogas (Pellegrini et al., 2018) being considered a possible source because
60 of its being renewable and a carbon neutral fuel. However, to produce electricity in power plants
61 fossil fuels are still employed, because of the huge amounts needed.

62 Generally, electricity generation using natural gas emits a lower amount of carbon dioxide than the
63 one emitted from a coal-fired unit producing the same amount of electricity (Global CCS Institute,
64 2013), so, considering also the low prices of natural gas in recent years, there has been a shift towards
65 natural gas fed plants. The increasing demand has made also low quality natural gas reserves being
66 exploited for production of energy (De Guido et al., 2015). Despite the lower concentration of carbon
67 dioxide present in the flue gas streams of a NGCC plant, because of the huge flowrates of gas
68 circulating in the plant, a lot of carbon dioxide is still emitted to the atmosphere and CCS must be
69 applied also to power production in natural gas fed plants.

70 Amine scrubbing is one of the leading technologies for post-combustion CO₂ removal from flue
71 gases of power plants (Alhajaj et al., 2013). Amines are widely employed for the purification of
72 several gaseous streams including syngas for production of hydrogen and power production
73 (Giuffrida et al., 2016) and biogas for biomethane production (Pellegrini et al., 2015). For the
74 technology employing these solvents, however, the energy requirement for the regeneration of the
75 solvent and the compression of carbon dioxide is high. It has been estimated that it can reduce the
76 electrical output by 20-30% if compared to the one obtained in units without the CCS plant (Cohen
77 et al., 2012). Therefore, in order to reduce the losses of revenues due to losses of power outputs for
78 CCS, flexible operation must be taken into account.

79 Some modes of operation, as the one considered in this work, allow to avoid emitting carbon
80 dioxide while saving costs and to sell electricity at higher prices, and have been studied in the
81 literature for coal-fired power plants (Chalmers and Gibbins, 2007; Chalmers et al., 2009a; Chalmers
82 et al., 2009b; Lucquiaud et al., 2014; Mac Dowell and Shah, 2014; Zaman and Lee, 2015).

83 This paper deals with an in-depth analysis of a flexible operation for CO₂ removal to be applied
84 to a natural gas combined cycle power plant in Italy. A techno-economic estimation of the best
85 operation for key days during the year and for the overall year has been carried out. The study has
86 been performed also by considering the influence of the carbon tax.

87 ***1.1. The price of electricity***

88 Italian electricity is mostly produced by thermal power and heat generating plants (Terna Group,
89 2014), with 18 units producing more than 500 MW.

90 Data of the requested electric power in Italy for the year 2015 from Gestore Mercati Energetici
91 (GME, 2017), an institution of the Italian Ministry of Economy and Finance, have been used to
92 understand the variation of the requested power in Italy. In particular, a great difference depending
93 on the hour of the day and on the period of the year occurs (Moioli and Pellegrini, 2018b). It follows

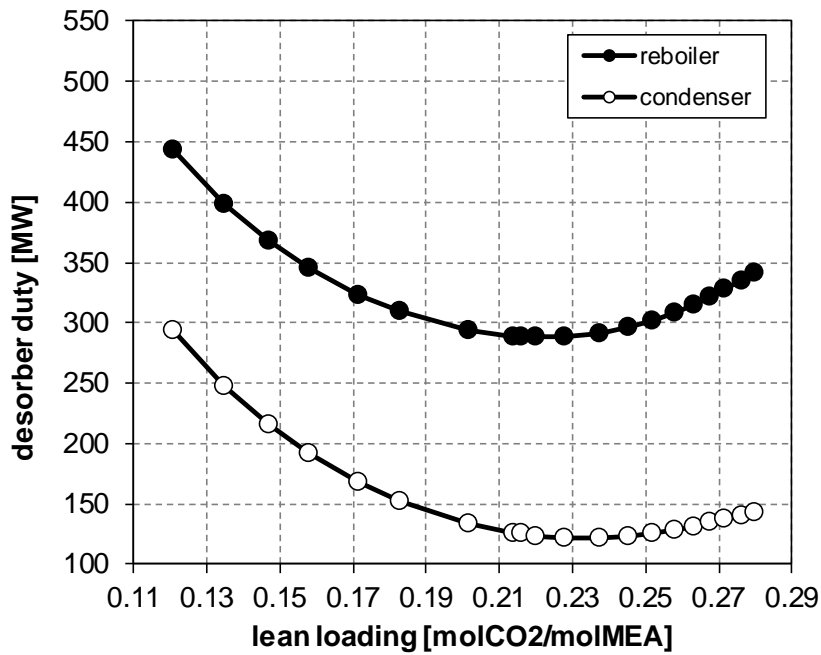
94 that also the price of electricity is different from time to time, ranging from very low values (as 18
95 €/MWh) to very high values (as 144.57 €/MWh), higher than 110 €/MWh in summer.

96 The operation of the CO₂ removal plant is related to power consumption in high amount due to
97 heat requirement (Moioli et al., 2017; Nagy et al., 2017) and, therefore, to lower electricity available
98 to the market. Its impact on the overall economics of the power plant may be reduced by running the
99 carbon dioxide removal plant in flexible mode. Indeed, adding the energy consumption of the
100 operation of a CO₂ removal plant when the price of electricity is lower may cause less economic
101 disadvantages than doing the same operation during the peak hours.

102 **2. The case study**

103 The flue gas stream of an advanced Natural Gas Combined Cycle (NGCC) plant (Fout et al.,
104 2015), with a power output of 630 MW, in the range of the big plants operating in the Italian territory,
105 has been considered. The gas, with a flowrate of 130538 kmol/h and a composition (mole fraction)
106 of carbon dioxide (0.0391), water (0.0841), nitrogen (0.7442), oxygen (0.1238) and argon (0.0089),
107 is available at 117°C and is cooled before being fed to the CO₂ removal plant.

108 The design of the plant has been performed in order to treat the very huge gas flowrate in suitable
109 and realizable columns while minimizing the energy consumption, which is located mainly at the
110 reboiler of the regenerating column and in the compression section. Therefore three packed
111 absorption columns with a diameter of 12.5 m each, similar to the size of columns built by Fluor
112 (Fluor, 2017) and Shell (Shell, 2017) have been considered. The solvent is an aqueous solution of
113 monoethanolamine (MEA) 30% wt., with lean loading and solvent flowrate chosen on the basis of a
114 minimum energy requirement analysis, resulting equal to 0.224 (Figure 1) and to 49.23 kmol/s
115 respectively.



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Figure 1. Requirements at the regeneration column vs. lean loading for the fixed configuration of the plant removing 95% of carbon dioxide.

Figure 2 shows the PFD of the plant designed for removing 95% of carbon dioxide present in the flue gas stream in fixed operation mode. Because of the very high flowrate, the flue gas (*HOTFLUEGAS*) is divided into three equal streams (*FLUEGAS 1*, *FLUEGAS 2* and *FLUEGAS 3*), cooled in a heat exchanger (*P-COOLER 1*, *P-COOLER 2* and *P-COOLER 3*). The cooled gaseous streams, which must be purified, flow upward through the absorbers (*ABSORBER 1*, *ABSORBER 2* and *ABSORBER 3*), counter-currently to the respective streams of aqueous amine solution (*LEANIN 1*, *LEANIN 2* and *LEANIN 3*) for achieving a 95% removal of the carbon dioxide present in the flue gas. The rich solution (*RICHOUT 1*, *RICHOUT 2* and *RICHOUT 3*) from the bottom of each absorber is mixed in *MIXRICH* forming a single stream (*RICH*). The *RICH* pressure is increased with a pump (*PUMP*) to the desired stripper pressure and then the solution (*RICHPUMP*) is heated in the heat exchanger *ECOHEAT* by the lean solution (*LEANOUT*) from the bottom of the stripping column (*DESORBER*). The rich solution (*RICHIN*) is then fed at the top of the stripping column. After partial

132 cooling in the lean-to-rich solution heat exchanger, the pressure of the lean solution from the stripper
 133 (*LEANOUT*) is lowered to 1 atm in an isenthalpic valve (*VALVE*) and furtherly cooled by heat
 134 exchange with cooling water (*COOLER*). After this step, the solvent is integrated with MEA and
 135 water and then *LEANIN* is split into three identical streams (*LEANIN 1*, *LEANIN 2* and *LEANIN 3*)
 136 and fed to the top of the absorbers. The acid gas removed from the solution in the stripping column
 137 (*CO2*) is cooled to condensate a major portion of the water vapor and is then sent to the CO₂
 138 compression station.

139 The main features of the columns are reported in Table 1.

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141 **Table 1.** Main features of the columns and of the compression train for the chosen configuration.

Parameter	Value
number of absorption columns	3
height [m]	7.92
diameter [m]	12.5
pressure [bar]	1.1
number of regeneration columns	1
height [m]	6
diameter [m]	9.5
pressure [bar]	2
maximum pressure in compressors [bar]	80
maximum pressure in pumps [bar]	150
intercooling temperature [K]	303.15
isentropic efficiency for compressors (Moioli et al., 2016)	0.85
mechanical-electric efficiency for compressors (Moioli et al., 2016)	0.94

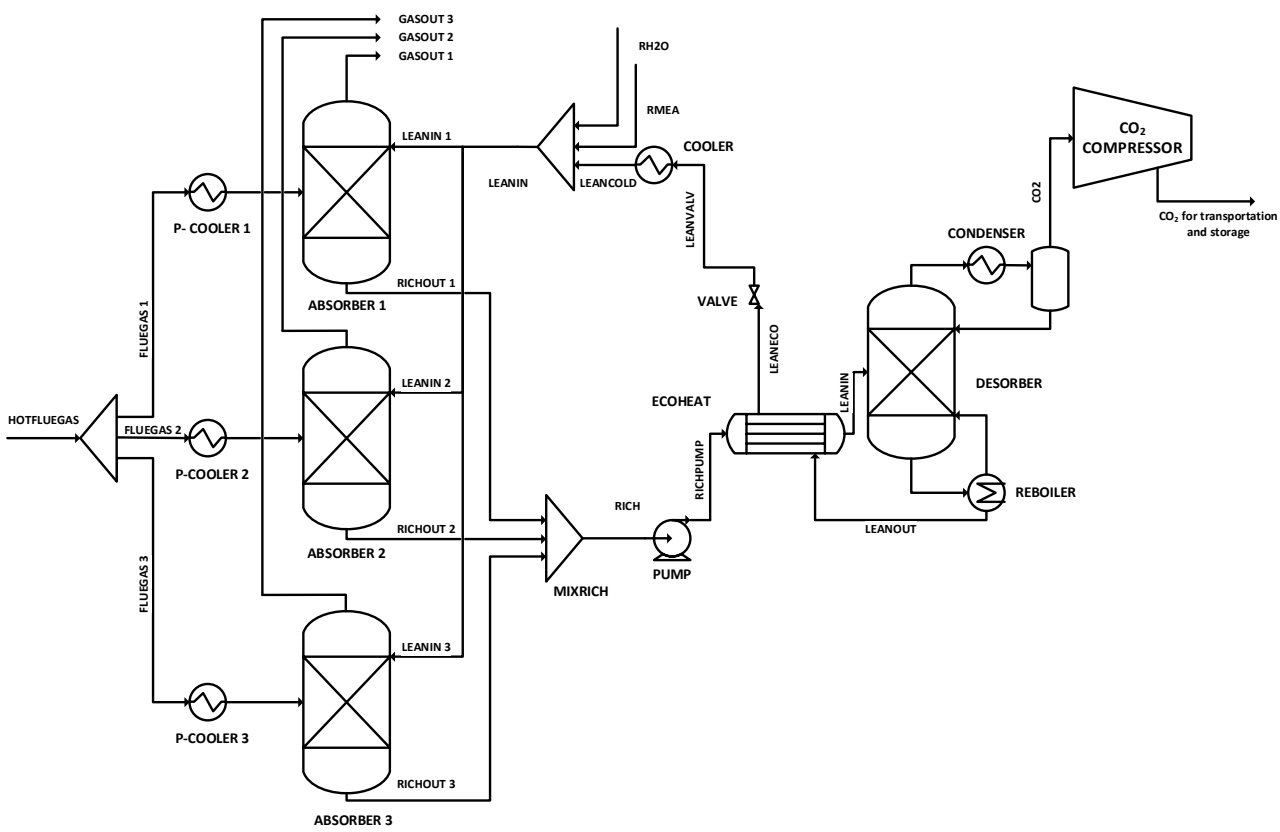
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143 In order to reduce the initial capital investment, the possibility of regenerating the total rich
 144 solvent flowrate in one single distillation column, with feasible dimensions, had been analyzed. One
 145 single column, with 9.5 m diameter, can be employed for regeneration.

146 The CO₂ intercooling compression (simplified in the scheme as *CO₂ COMPRESSOR*) has been
 147 designed considering that the stream coming from the top of the regeneration section is mainly
 148 composed of carbon dioxide, with an amount of water of about 5% mol. Most of the water is removed
 149 in a first section, where the gas is cooled down, then the gaseous stream is fed to the compression

150 train. The compression system is composed of several stages, with an additional unit for reduction of
 151 the water content at high pressure, based on absorption by triethylene glycol (TEG). In the final part
 152 of the process the stream is cooled and liquefied and a pump is used to increase the pressure of the
 153 carbon dioxide stream up to the final pressure (150 bar) (Fout et al., 2015). It is generally
 154 recommended an outlet pressure higher than 86 bar, in order to avoid dramatic changes in CO₂
 155 compressibility along the pipelines (McCoy and Rubin, 2008), with a pressure usually of 90-150 bar
 156 (Kohl and Nielsen, 1997), so the highest pressure (150 bar) has been chosen to perform a conservative
 157 study.

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160 **Figure 2.** PFD of the base plant.

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162 **3. Flexible configuration**

163 Several modes of operation are possible for the running of the carbon dioxide removal plant, with
164 both fixed operation or flexible operation being considered.

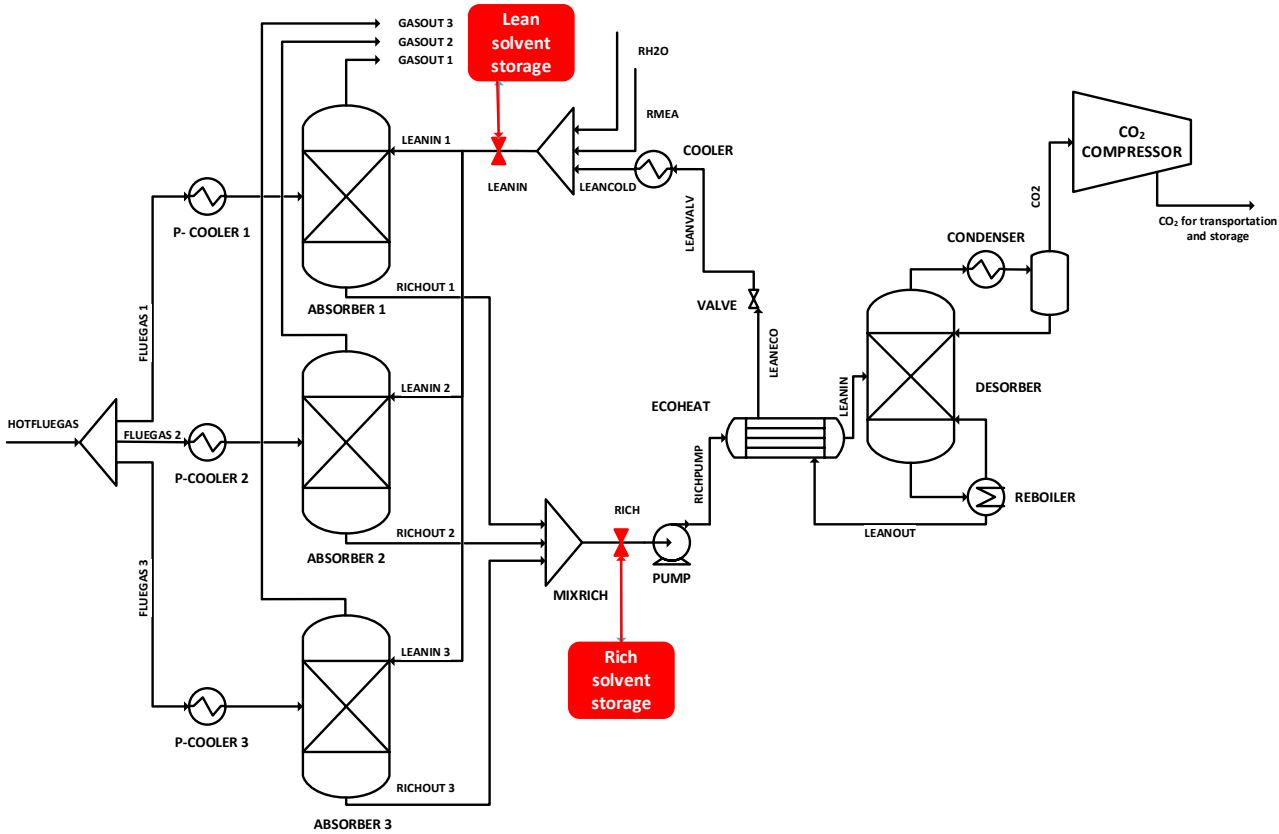
165 When running in fixed mode, the operation is steady-state with no variations of captured CO₂
166 with time. This allows an easy operation and management of the plant, for which all variables are set
167 to given values and the same conditions are constantly maintained. However, operating in flexible
168 mode would help in reducing the loss of revenues due to a lower amount of electricity sold, in
169 particular during peak hours.

170 Among the several modes of flexible operation, comprising also the options of venting part of the
171 carbon dioxide present in the flue gas stream to the atmosphere or of varying the time for solvent
172 regeneration so that a lower amount of solvent may be regenerated, in this work the Solvent Storage
173 mode has been selected. The time for regeneration can be varied, therefore globally providing a leaner
174 or richer solvent for carbon dioxide removal. All the options aim at reducing the energetic
175 requirements for purification of flue gases to increase the power output and therefore revenues (Oates
176 et al., 2014; Sanchez Fernandez et al., 2016; van der Wijk et al., 2014). Venting part of the CO₂ to
177 the atmosphere can be performed by diverting part of the flue gas towards the stack before it enters
178 the CO₂ removal system (Abdilahi et al., 2018) or by feeding the overall flue gas stream to the
179 absorber and redirecting part of the rich solvent directly to the absorption section without regenerating
180 it (Cohen et al., 2011). Differently from other methods, the Solvent Storage mode allows to maintain
181 a constant CO₂ removal while operating most of the regeneration when the price of electricity is low,
182 so presenting advantages also from an environmental point of view. When high revenues may be
183 obtained from selling electricity, the stripping and the compression systems operate at partial load
184 (Chalmers and Gibbins, 2007). To this aim, a lean and a rich solvent tanks are needed to store the rich
185 solution before feeding to the stripping column and the lean solvent exiting from the regeneration

186 section during periods of high electricity demands and/or prices. The stored lean solvent is employed
 187 to maintain a constant carbon dioxide removal in the absorption section, while the regeneration
 188 section works in flexible mode.

189 The scheme of the plant is therefore as in Figure 3.

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192 **Figure 3.** PFD of the base plant for Solvent Storage operation.

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194 The tank can be designed in order to store solvent for a given maximum period of time. In this
 195 work, several possible times for storage have been considered (1 h, 2 h, 3 h, 4 h), up to the maximum
 196 time which allows the regeneration of the solvent employed during the day, with no accumulation to
 197 the following day, equal to 5.54 h.

198 **4. Tanks for Solvent Storage**

199 For storing solvent at given times during the day in order to increase the power output of the plant,
200 additional tanks must be considered in the design of the plant and also a higher amount of solvent is
201 initially needed. These factors have an influence on the initial costs of the plant. Indeed, according to
202 the literature (Chalmers et al., 2009a; Chalmers et al., 2009b; Gibbins and Crane, 2004), about 10%
203 additional costs must be considered for storage tanks and pipework and 8000 \$/tonCO₂ for additional
204 solvent. Results from economic studies (Patiño-Echeverri and Hoppock, 2012) suggest that even if
205 additional investment costs have to be considered, amine storage systems offer an alternative to
206 potentially decrease the average cost of carbon dioxide capture, in particular when applied in
207 retrofitting already existing power plants.

208 In any case, the final decision on the type of operation must take into account the potential
209 additional profits obtained by operating in flexible mode and the total expenditure required to make
210 it available.

211 **5. Methodology**

212 **5.1. Choice of the day**

213 The analysis has been carried out considering the real price of the electricity applied in Italy.
214 Official data from 2015 were made available by the Italian Ministry of Economy and Finance and
215 used for the study (GME, 2017).

216 The work has focused on significant periods during the year, which have been selected according
217 to the following considerations:

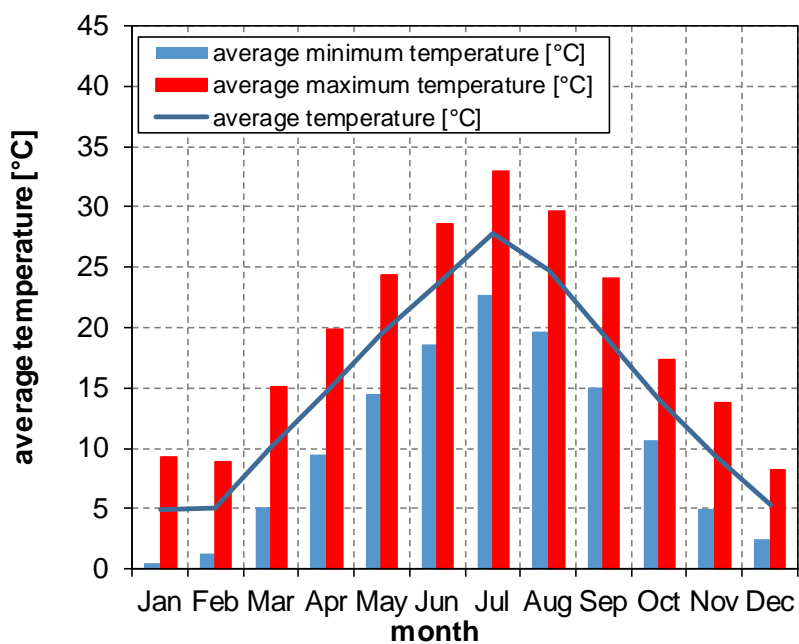
218 1) the profiles in winter and in summer differ significantly;

219 2) the difference between the values of the lowest and the highest energy prices during the day
220 may exert an influence on the flexible configuration of the plant. Literature works (Patiño-
221 Echeverri and Hoppock, 2012; Zaman and Lee, 2015), indeed, state that “*Savings from*
222 *adopting a flexible operation mode will be significant if the difference between low and high*
223 *market electricity prices is significant*”;

224 3) for winter the coldest month and for summer the hottest month have been considered.

225 The selection of the month to be taken into account has been made on the basis of temperature
226 data referring to the city of Milano, for which the maximum and the minimum temperature of
227 every day for each month were available.

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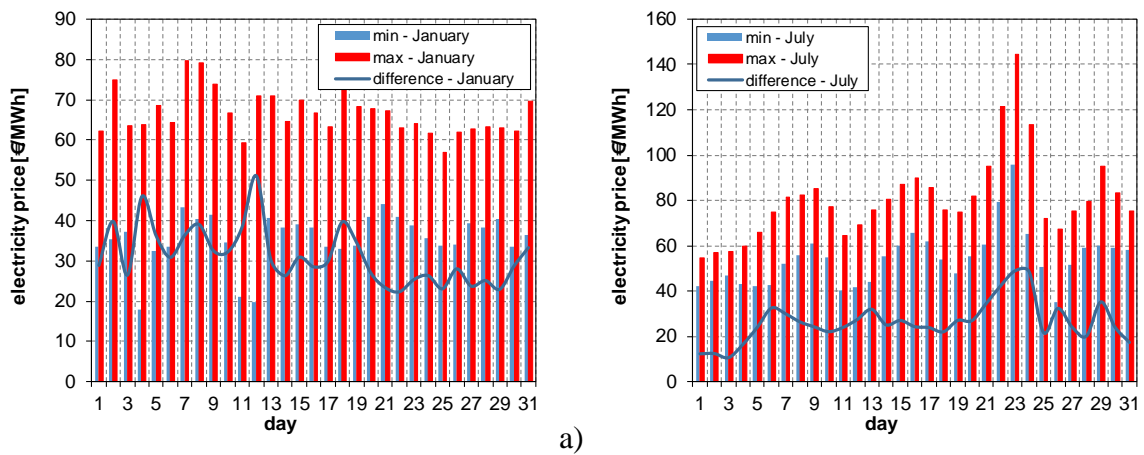
230 **Figure 4.** Average monthly temperature profile during the year 2015.

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232 Figure 4 shows the trend of temperatures, where the relevant temperature difference between
233 summer and winter in Italy can be outsourced. The coldest month is January, with a minimum average
234 temperature of 0.48°C and an average temperature of 4.85°C, while the hottest month is July, with a

235 maximum average temperature of 32.96°C and an average temperature of 27.86°C. The average
 236 temperatures also correspond to single values, with a minimum temperature in January of -3°C and a
 237 maximum one in July of 37°C.

238 The choice of the day for the analysis has been performed considering the daily trends of the price
 239 of electricity (Figure 5).



240
 241 **Figure 5.** Profile of average maximum and minimum price of electricity during the month of a)
 242 January 2015 and b) July 2015.

243
 244 The maximum price shows low deviations in January if compared to the month of July, for which
 245 the maximum price (144.57 €/MWh) occurs and significant differences (up to 90 €/MWh) occur from
 246 one day to the other. The minimum price in July follows a trend similar to the maximum price, though
 247 the difference with the maximum price can be as high as more than 45 €/MWh.

248 For this reason, the choice of the days in July has been based on:

- 249 - day with the highest energy price: resulting July 23rd, 2015;
- 250 - day with the highest difference between maximum and minimum energy prices: resulting July
 251 23rd, 2015 also in this case.

252 In order to perform an analysis which may take into account cases when low electricity prices are
 253 applied, the lowest price of electricity and the lowest difference between the highest and the lowest

254 electricity prices have been considered as parameters for the selection of the days to be studied for
255 the month of January.

256 Therefore, the chosen days in January are:

- 257 1) day with the lowest electricity price: resulting January 04th, 2015;
- 258 2) day with the lowest difference between maximum and minimum electricity prices: resulting
259 January 22nd, 2015.

260
261 Table 2 reports the characteristics of the chosen day.

262
263 **Table 2.** Days considered for the techno-economic analysis.

Parameter	Day	Maximum electricity price [€/KWh]	Minimum electricity price [€/KWh]
day with the highest energy price	July 23 rd , 2015	144.57	95.91
day with the highest difference between maximum and minimum energy prices	July 23 rd , 2015	144.57	95.91
day with the lowest electricity price	January 04 th , 2015	63.91	18.00
day with the lowest difference between maximum and minimum electricity prices	January 22 nd , 2015	63.13	40.88

264 265 **5.2. Model**

266 The present work employs both a process simulator for the simulations of the CO₂ removal and
267 compression plants, and a software environment for the development of the techno-economic
268 analysis. In detail, ASPEN Plus[®] has been used as a framework and linked to external subroutines
269 developed by the GASP group of Politecnico di Milano (Moioli and Pellegrini, 2015, 2016, 2018a)
270 to take into account the complexity of the chemical reacting system, by considering the influence of

271 thermodynamics, kinetics and mass transfer. Matlab has been employed for implementing the techno-
272 economic model and optimizing the flexible operation of the plant (Moioli and Pellegrini, 2018b).

273 The developed techno-economic model takes into account the effect on the power plant output
274 losses of the CO₂ capture and compression system and the influence of the carbon tax on the revenues
275 obtained by selling electricity. A profit objective function, considering also these terms, has been
276 created and the optimization for determining the flexible mode of operation which maximizes the
277 revenues has been performed.

278 The effect of carbon dioxide capture and compression system on power plant output losses, and
279 consequently on revenues, can be mitigated by operating the capture plant in flexible modes, using a
280 profit objective function for process optimization.

281 The net power W_{out} [MW] that can be effectively sold on the electricity market is the difference
282 between the full power plant capacity and the energy required for the CO₂ capture and compression
283 systems.

$$284 \quad W_{out} = W_{out}^{MAX} - (W_{reb} + W_{comp}) \quad (1)$$

285 where W_{out}^{MAX} [MW] is the power station net capacity without capture system; W_{reb} and W_{comp}
286 [MW] are respectively the reboiler and compression energy penalties. For the reboiler, the equivalent
287 work is calculated, considering that steam is withdrawn from the turbine.

288 The profit associated with the power station with CO₂ capture system can be expressed as:

$$289 \quad P = W_{out} C_{energy} - F_{CO_2} C_{CO_2Tax} - F_{fuel} C_{Fuel} - C_{b,O\&M} \quad (2)$$

290 where C_{energy} [€/MWh] is the price of energy and C_{CO_2Tax} [€/tonCO₂] is the carbon tax; F_{CO_2}
291 [tonCO₂] is the amount of carbon dioxide released in atmosphere in an hour; F_{fuel} [kg/h] and C_{fuel}
292 [€/kg] are the fuel consumption (Fout et al., 2015) and the fuel cost (EIA, 2019); $C_{b,O\&M}$ [€/h] is the
293 operation and maintenance cost of the plant, assumed constant.
294

295 The equipment start-up and shut-down costs have been neglected, considering that in the studied
296 system the maximum shut-down would be for 5.54 h and that for a CO₂ removal plant by amines hot
297 restart can be considered instead of cold restart if done within 16 h after shutdown (Ceccarelli et al.,
298 2014). As reported in the literature, for the overall CO₂ removal section of a Combined Cycle with
299 Gas Turbines (CCGT) power plant, the rate at which the setpoint is achieved is much faster than the
300 time for achieving steady-state operations (typically estimated as 60 minutes after steam is fed to the
301 reboiler). Moreover, considering that in Solvent Storage mode only regeneration is shut-down and
302 restarted, with all the remaining units continuously in operation, the assumption of neglecting
303 equipment start-up and shut-down costs can be reasonable for the purposes of the present work.

304 Also the solvent and water make-up, the costs for transport and storage of carbon dioxide and the
305 CO₂ capture transient costs associated with the efficiency losses during transient CO₂ capture
306 operation have not been accounted for.

307 The objective function (Eq. (2)) has been maximized by varying the stripper load, considering
308 also the constraints related to the storage capacity:

- 309 - the volume of stored solvent must be in the range from 0 to the maximum volume of storage;
- 310 - the stored volume at the beginning and at the end of the day must be the same, with no
311 accumulation during the day so that part of the solvent must be regenerated in following days.

312 The analysis has been performed considering a carbon tax from 5 to 100 €/tonCO₂, in order to
313 take into account a wide range of possible values for this tax (CTC, 2017).

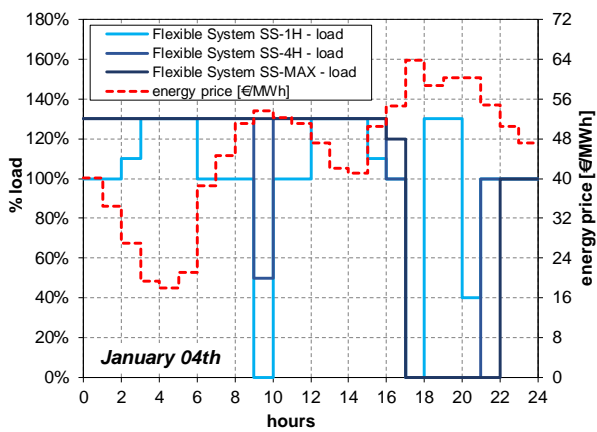
314 **6. Results and discussion**

315 The maximum capacity of the storage system has been varied considering five different values
316 that correspond to the volumes of the rich solvent storage tank for 1h, 2h, 3h, 4h and the maximum
317 allowable time of operation in one day. The amount of CO₂ vented to the atmosphere is constant,

318 since it is the same of the base plant configuration, when no flexible operation is applied,
319 characterized by a 95% removal of carbon dioxide.

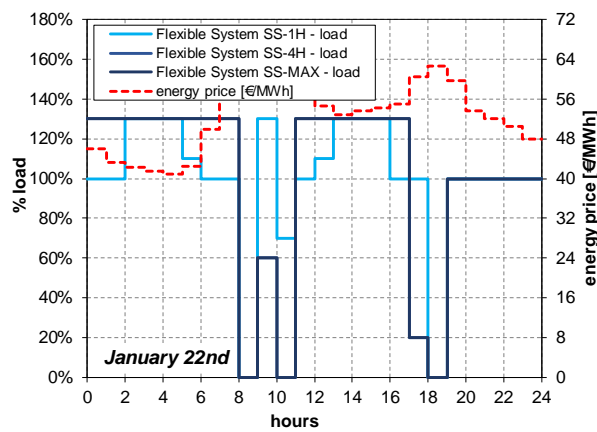
320 Results of the flexible analysis are reported in Figure 6, showing the trends for the considered
321 days of the stripper load at every hour for different solvent storage options as a result of the
322 optimization. The same figure reports the hourly electricity price which strongly influences the choice
323 of the stripper load. Results for storage times of 2 h and 3 h are not shown for reasons of space, and
324 are reported in Figure 7 and in Figure 8 with the volume of stored rich solvent for January 04th, 2015
325 and July 23rd, 2015.

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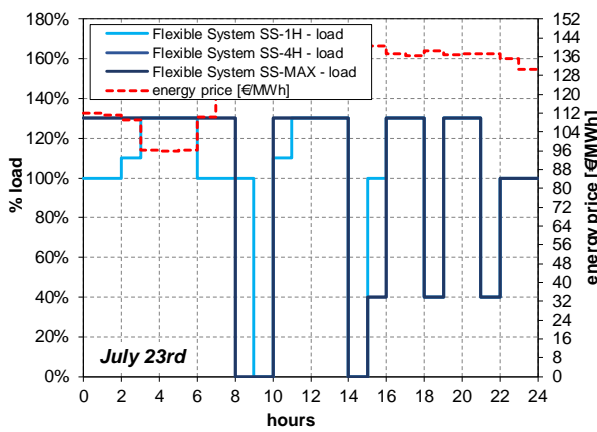


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a)



b)



328

c)

329 **Figure 6.** Energy price and stripper load for different operation modes (SS-1H = solvent storage for
330 maximum 1 h, SS-4H = solvent storage for maximum 4 h, SS-MAX = solvent storage for the
331 maximum time of the day) for a) January 04th, 2015, b) January 22nd, 2015 and c) July 23rd, 2015.
332

333 The best load profile varies a lot during the day and is strongly influenced by the storage of
334 solvent. For the case with storage of 1 h, indeed, most of time the regeneration column works at base
335 load, with only few hours working at different loads. These hours correspond to times during the day
336 when prices of electricity are high, so that regenerating the solvent would cause high losses of
337 revenues, or to times when the price of electricity is lower and more solvent can be regenerated. For
338 instance, at 09 am there is a local peak of price of electricity, which causes the non-regeneration of
339 the solvent and the subsequent regeneration periods (as between 2 am and 6 am or between 12 am
340 and 2 pm) when the price of electricity decreases. A similar operation can be found at 5 pm, when
341 the maximum price of electricity for January 04th occurs.

342 Moreover, also the fact that storage can be for 1 h results in regenerating when the tank is full
343 because no additional storage can be done. The solvent storage for 1 h occurs only in peak hours.

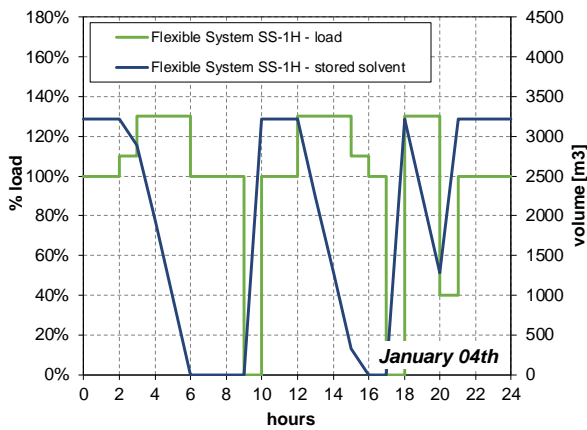
344 For solvent storage of 4 h or more, a very different stripper load profile is obtained. In particular,
345 for SS-MAX (storage with the maximum time, equal to 5.54 h) from 5 pm to 10 pm no regeneration
346 is performed and all the solvent circulating during the day is regenerated in the distillation column
347 running from 12 pm to 4 pm at the maximum stripper load (130%).

348 Generally, similar trends are obtained for January 22nd. For the solvent storage of 1 h regeneration
349 is preferred in the early morning (from 2 am to 5 am) and at noon time (from 12 am to 2 pm). The
350 profiles of SS-4H and SS-MAX show no differences each other and are characterized by a solvent
351 regeneration at high stripper loadings (equal to 130%) from 12 pm to 5 pm, with the exception of 8
352 am and 10 am. This difference in the profile, compared to the one of January 04th, is due to the fact

353 that the values of price of electricity are slightly different, though both of them being characterized
354 by a similar trend, typical of the winter period.

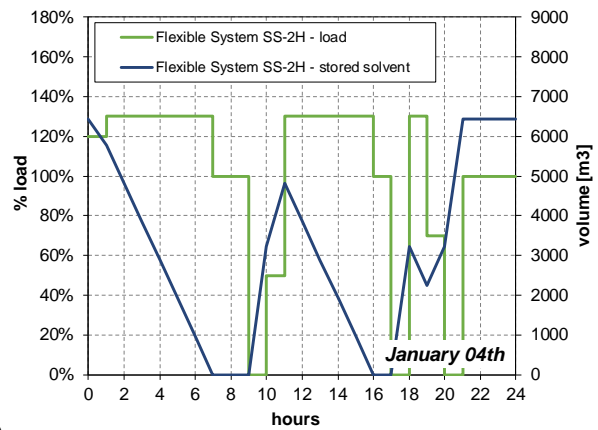
355 In summer time the price of electricity is characterized, overall, by a different profile during the
356 day and different values. In detail, the lowest price of electricity occurring on July 23rd, equal to 95.91
357 €/MWh, is higher than the highest price of January 04th and of January 22nd. This high difference
358 greatly affects the obtained best stripper load profiles, for all the solvent storage cases. When
359 considering storing solvent for 1 h, regeneration at high stripper loads occurs from 3 am to 6 am, from
360 11 am to 2 pm, from 4 pm to 6 pm and from 7 pm to 9 pm, in order to be able to limit regeneration in
361 peak hours, when it is decreased to stripper loads lower than 100%. Differently from the winter cases,
362 for July 23rd a very similar profile (with differences only for few hours) is obtained also when
363 considering storage for 4 h or more (maximum time), with no storage for the time for which the vessel
364 has been built. Similar trends are obtained also when considering storage times of 2 h and 3 h.

365

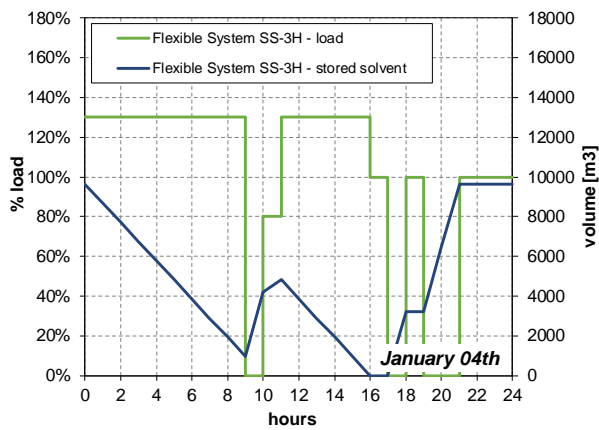


366

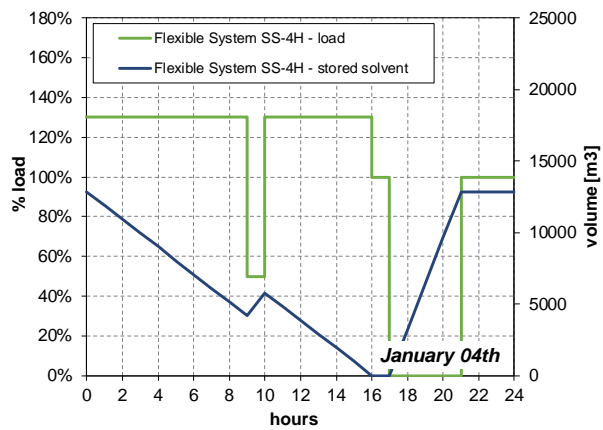
a)



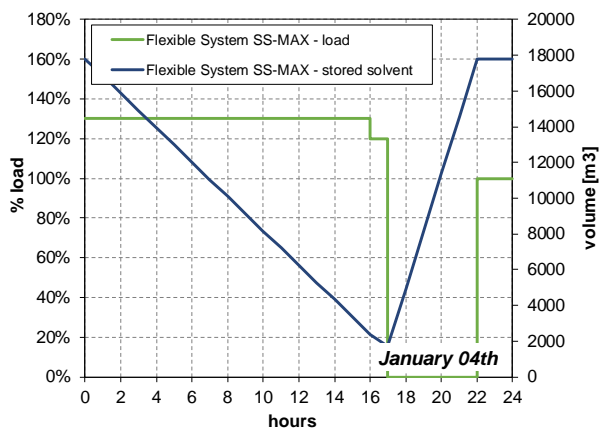
b)



c)



d)



e)

Figure 7. Volume of stored solvent and stripper load for January 04th, 2015 considering a) SS-1H = solvent storage for maximum 1 h, b) SS-2H = solvent storage for maximum 2 h, c) SS-3H = solvent storage for maximum 3 h, d) SS-4H = solvent storage for maximum 4 h and e) SS-MAX = solvent storage for the maximum time of the day.

Figure 7 reports the volume of rich solvent stored for being regenerated. Details of each considered storage option are reported because the obtained trends differ a lot one from the other, though all of them being characterized by the common feature of having the same volume at the beginning and at the end of the day with no accumulation at the end of the day (all the employed solvent is regenerated the same day of use). The volume of stored solvent remains constant when

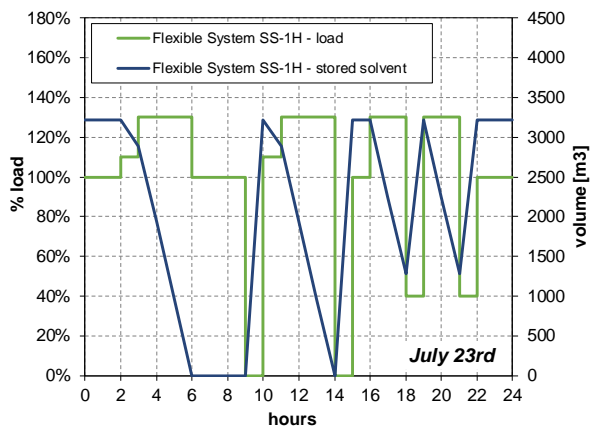
379 regeneration is at base stripper loads (100%), decreases for higher stripper loads and increases for
380 lower stripper loads.

381 For January 04th and SS-1H case, the volume of solvent starts decreasing at 2 am, when
382 regeneration is operated at stripper loadings higher than the base one, and after four hours, at 6 am,
383 all the rich solvent is completely regenerated. When the electricity price increases and the stripper
384 load decreases, a lower amount of rich solvent is regenerated, therefore the volume of rich stored
385 solvent increases (from 9 am to 10 am). The solvent is stored until times when the regeneration section
386 is operated at stripper loads higher than the base one, in this case from 12 am to 4 pm, and, later, from
387 6 pm to 8 pm.

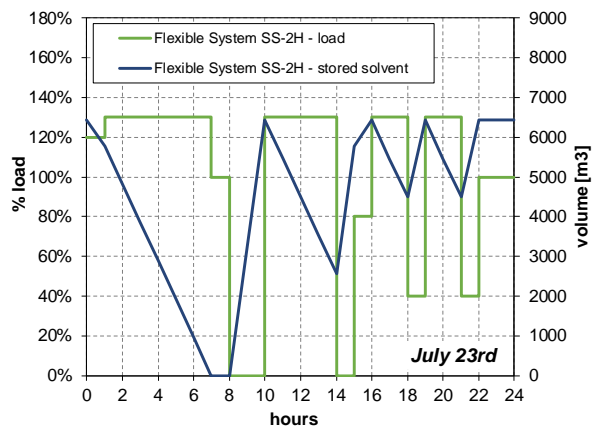
388 The maximum time considered for storing solvent (1 h, 2 h, 3 h, 4 h or maximum time) strongly
389 influences the profile of stored rich solvent, as shown in Figure 7. For SS-MAX on January 04th there
390 is only one emptying and one filling of the rich solvent storage, because of the obtained profile of
391 stripper load due to the price of electricity.

392 The trends obtained for January 22nd are similar to those obtained for January 04th (though taking
393 into account the differences in the stripper load as described before), while those of July 23rd are
394 strongly different and are reported in Figure 8. In particular, for this day several variations in emptying
395 and in filling the storage vessel occur for all the considered cases. For storage of more than three
396 hours the tank is never completely emptied, differently from the winter period.

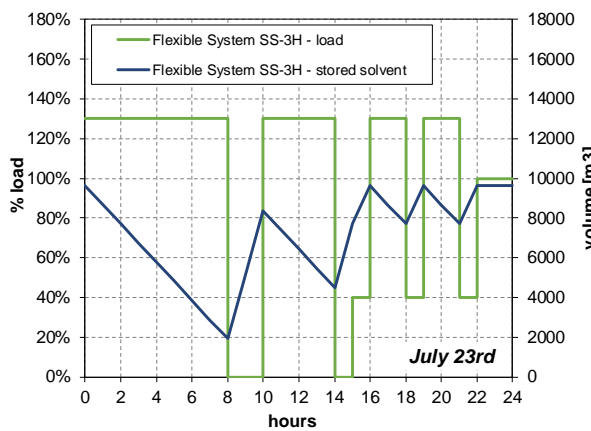
397



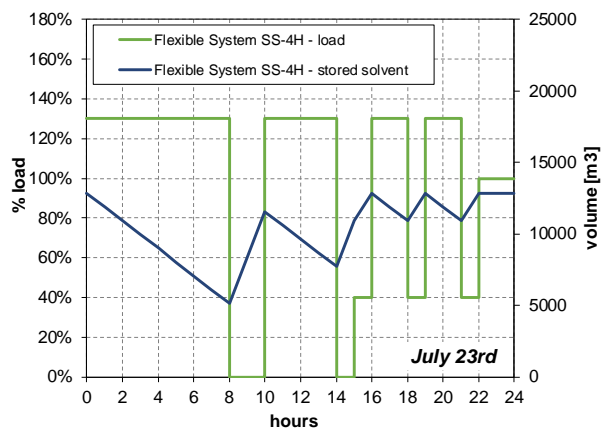
a)



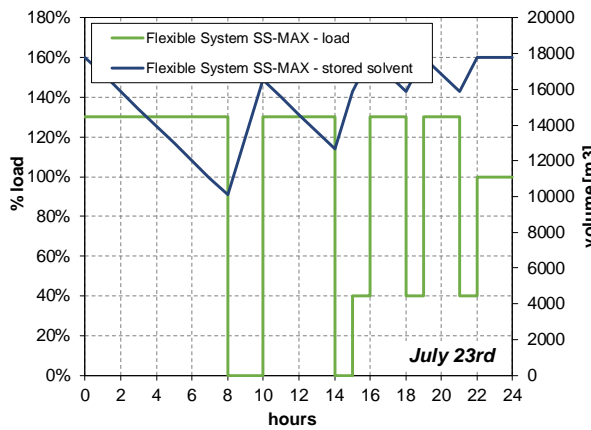
b)



c)



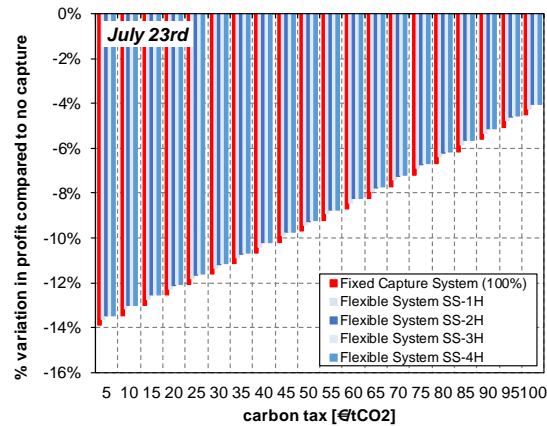
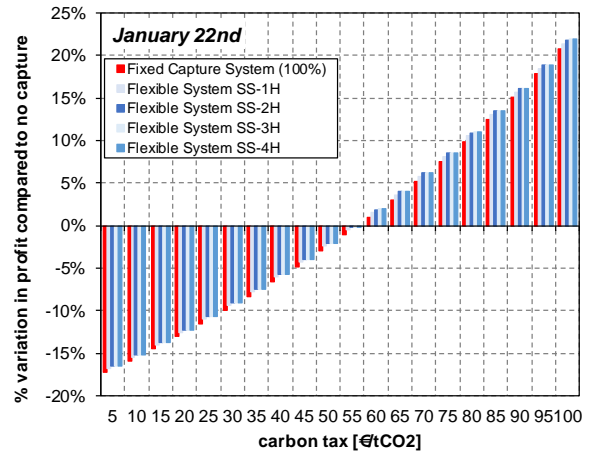
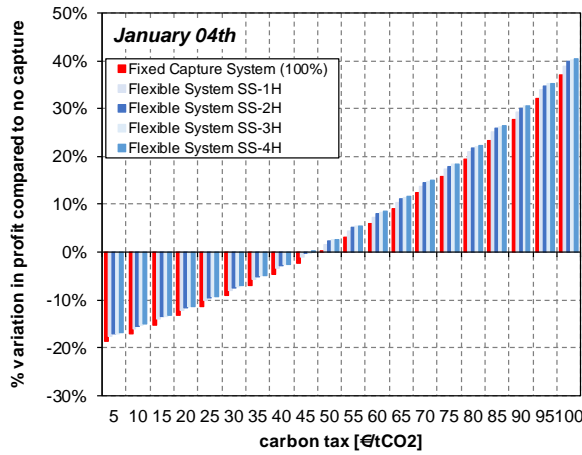
d)



e)

Figure 8. Volume of stored solvent and stripper load for July 23rd, 2015 considering a) SS-1H = solvent storage for maximum 1 h, b) SS-2H = solvent storage for maximum 2 h, c) SS-3H = solvent storage for maximum 3 h, d) SS-4H = solvent storage for maximum 4 h and e) SS-MAX = solvent storage for the maximum time of the day.

406 The influence on the carbon tax is shown in Figure 9, where the results of the techno-economic
 407 analysis performed are reported in terms of variation in the values of the profit function in comparison
 408 with those referring to a NGCC plant without the CO₂ removal and compression sections.
 409



410 a) b) c)

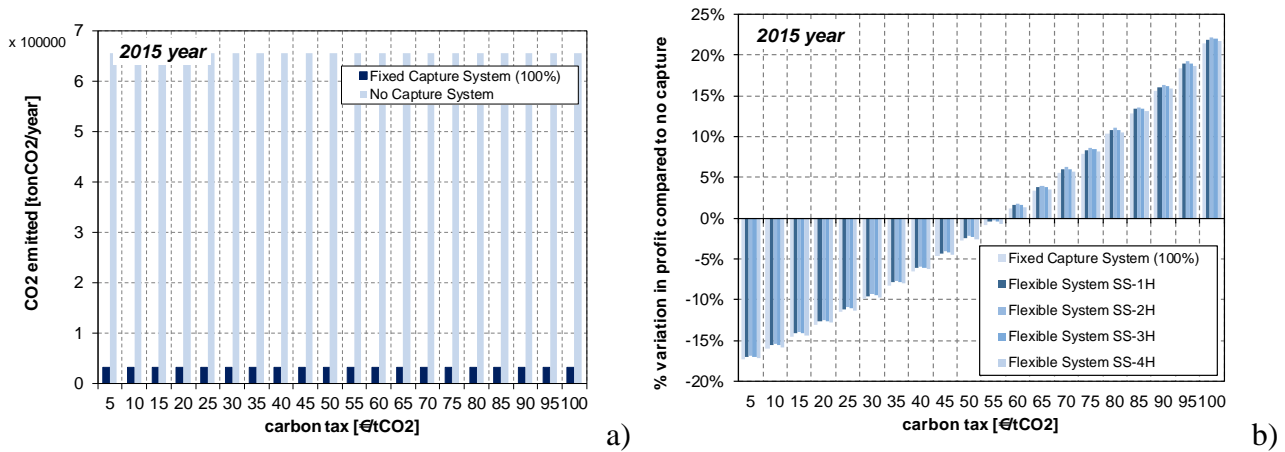
411

412 **Figure 9.** % variation in the value of the profit function compared to no capture for fixed capture
 413 and regeneration system (Fixed Capture System (100%)) and for different operation modes (SS-1H
 414 = solvent storage for maximum 1 h, SS-2H = solvent storage for maximum 2 h, SS-3H = solvent
 415 storage for maximum 3 h, SS-4H = solvent storage for maximum 4 h) for a) January 04th, 2015, b)
 416 January 22nd, 2015 and c) July 23rd, 2015 ($C_{b,O\&M}$ not considered).

417

418 As shown also in Eq. (2), the carbon tax represents a negative term in the economics of the power
 419 plant. Its value may determine whether removing carbon dioxide can be advantageous or not for the
 420 plant incomes. When dealing with the configuration of solvent storage, the CO₂ removal is kept
 421 constant, the absorption section is always run at 100% load. This favors a low amount of emissions
 422 of carbon dioxide, which does not depend on the carbon tax value (Figure 10a)) and which is the only
 423 variable in the term $F_{CO_2} C_{CO_2 Tax}$.

424



425

426 **Figure 10.** a) yearly emissions of carbon dioxide from the power plant with and without carbon
 427 dioxide capture and b) % variation in the value of the profit function compared to no capture for fixed
 428 capture and regeneration system (Fixed Capture System (100%)) and for different operation modes
 429 (SS-1H = solvent storage for maximum 1 h, SS-2H = solvent storage for maximum 2 h, SS-3H =
 430 solvent storage for maximum 3 h, SS-4H = solvent storage for maximum 4 h) for 2015 year.

431

432 For the winter period the obtained results show that there is a tradeoff between the amount of
 433 money lost due to a lower amount of energy sold to the market and the amount of money paid for
 434 emitting carbon dioxide (carbon tax). This occurs both for a configuration with fixed solvent
 435 regeneration and for the one with flexible operation by solvent storage. In case of January 04th, there
 436 is a change in the sign of the function for a carbon tax in the range 45-50 €/tonCO₂, with the options

437 for storage of three or more hours being advantageous at the lower value of 45 €/tonCO₂, while those
438 of storage of two hours or less being advantageous at 50 €/tonCO₂. A higher storage time provides
439 better performances because of higher flexibility in the operation of regeneration, which may be run
440 at stripper loads lower than the base one for a wider period of time.

441 Similar results are obtained also for January 22nd, though the value of carbon tax for which
442 removing carbon dioxide becomes advantageous is slightly higher (60 €/tonCO₂). This confirms the
443 influence of the electricity price on the objective function.

444 When considering the summer period, different results are obtained. In particular, since the price
445 of electricity is very high during the day, no values of carbon tax up to 100 €/tonCO₂ make CO₂
446 removal advantageous for any considered configuration, and paying the carbon tax for the emission
447 of all the carbon dioxide produced in the plant would give higher revenues than selling lower amounts
448 of electricity.

449 To deeply understand the economic viability of employing the CO₂ removal section in the NGCC
450 plant, therefore, an additional analysis taking into account the overall year 2015 has been performed.
451 In this way, the influence of the price of electricity for each hour of each day from January to
452 December can be considered. Results, reported in Figure 10b), highlight that globally removing
453 carbon dioxide can be advantageous for carbon tax values higher than 60 €/tonCO₂.

454 **7. Conclusions**

455 Carbon Capture and Storage (CCS) can be applied to power plants with the aim of mitigating CO₂
456 emissions, which must be reduced to achieve the goals of the Paris Agreement by removing the acid
457 gas from flue gases.

458 The operation, performed by commonly employed MEA solvent, is characterized by high energy
459 consumptions, which decrease the power output of the plant, and, therefore, the obtained revenues.

460 In this paper, the Solvent Storage flexible operation has been deeply analyzed to evaluate its
461 performances compared to the configuration with fixed carbon dioxide absorption and regeneration.
462 Moreover, the influence of the carbon tax has been considered. Results show that a carbon tax higher
463 than 55 €/MWh would make CCS economically viable and would help in significantly reducing the
464 amount of emitted CO₂.

465 **References**

- 466 Abdilahi, A.M., Mustafa, M.W., Abujarad, S.Y., Mustapha, M., 2018. Harnessing flexibility potential
467 of flexible carbon capture power plants for future low carbon power systems: Review. *Renewable
468 and Sustainable Energy Reviews* 81, 3101-3110.
- 469 Ceccarelli, N., van Leeuwen, M., Wolf, T., van Leeuwen, P., van der Vaart, R., Maas, W., Ramos,
470 A., 2014. Flexibility of Low-CO₂ Gas Power Plants: Integration of the CO₂ Capture Unit with CCGT
471 Operation. *Energy Procedia* 63, 1703-1726.
- 472 Chalmers, H., Gibbins, J., 2007. Initial evaluation of the impact of post-combustion capture of carbon
473 dioxide on supercritical pulverised coal power plant part load performance. *Fuel* 86, 2109-2123.
- 474 Chalmers, H., Leach, M., Lucquiaud, M., Gibbins, J., 2009a. Valuing flexible operation of power
475 plants with CO₂ capture. *Greenhouse Gas Control Technologies* 9 1, 4289-4296.
- 476 Chalmers, H., Lucquiaud, M., Gibbins, J., Leach, M., 2009b. Flexible Operation of Coal Fired Power
477 Plants with Postcombustion Capture of Carbon Dioxide. *J. Environ. Eng.-Asce* 135, 449-458.
- 478 Cohen, S.M., Rochelle, G.T., Webber, M.E., 2011. Optimal operation of flexible post-combustion
479 CO₂ capture in response to volatile electricity prices. *Energy Procedia* 4, 2604-2611.
- 480 Cohen, S.M., Rochelle, G.T., Webber, M.E., 2012. Optimizing post-combustion CO₂ capture in
481 response to volatile electricity prices. *Int. J. Greenh. Gas Control* 8, 180-195.
- 482 CTC, 2017. Carbon Tax Center. <https://www.carbontax.org/>.

483 Davis, J., 2009. Thermal degradation of aqueous amines used for carbon dioxide capture. PhD Thesis,
484 The University of Texas at Austin, Austin, TX, USA.

485 De Guido, G., Langè, S., Pellegrini, L.A., 2015. Refrigeration cycles in low-temperature distillation
486 processes for the purification of natural gas. *J. Natural Gas Sci. Eng.* 27, 887-900.

487 EIA, 2019. https://www.eia.gov/naturalgas/monthly/pdf/table_03.pdf.

488 Fluor, 2017. <http://www.fluor.com/econamine/pages/default.aspx>.

489 Fout, T., Zoelle, A., Keairns, D., Turner, M., Woods, M., Kuehn, N., Shah, V., Chou, V., Pinkerton,
490 L., 2015. Cost and Performance Baseline for Fossil Energy Plants. Volume 1a: Bituminous Coal (PC)
491 and Natural Gas to Electricity. Revision 3. DOE/NETL-2015/1723.

492 Freeman, S.A., Rochelle, G.T., 2011. Thermal degradation of piperazine and its structural analogs.
493 *Energy Procedia* 4, 43-50.

494 Gibbins, J.R., Crane, R.I., 2004. Scope for reductions in the cost of CO₂ capture using flue gas
495 scrubbing with amine solvents. *Proceedings of the Institution of Mechanical Engineers Part a-Journal*
496 *of Power and Energy* 218, 231-239.

497 Giuffrida, A., Moioli, S., Romano, M.C., Lozza, G., 2016. Lignite-fired air-blown IGCC systems
498 with pre-combustion CO₂ capture. *Int. J. Energ. Res.* 40, 831-845.

499 Global CCS Institute, 2013. Capturing CO₂ from gas or coal power generation - what's the
500 difference? [http://hub.globalccsinstitute.com/insights/capturing-co2-gas-or-coal-power-generation-
501 what%E2%80%99s-difference](http://hub.globalccsinstitute.com/insights/capturing-co2-gas-or-coal-power-generation-what%E2%80%99s-difference).

502 GME, 2017. Gestore Mercati Energetici. <http://www.mercatoelettrico.org/it/>.

503 IEA, 2016. World Energy Outlook 2016. Paris Cedex, France.

504 Kohl, A.L., Nielsen, R., 1997. Gas Purification, 5th ed. Gulf Publishing Company, Book Division,
505 Houston, Texas, USA.

506 Lucquiaud, M., Fernandez, E.S., Chalmers, H., Mac Dowell, N., Gibbins, J., 2014. Enhanced
507 operating flexibility and optimised off-design operation of coal plants with post-combustion capture.
508 12th International Conference on Greenhouse Gas Control Technologies, GHGT-12 63, 7494-7507.

509 Mac Dowell, N., Shah, N., 2014. Optimisation of Post-combustion CO₂ Capture for Flexible
510 Operation. *Energy Procedia* 63, 1525-1535.

511 McCoy, S.T., Rubin, E.S., 2008. An engineering-economic model of pipeline transport of CO₂ with
512 application to carbon capture and storage. *Int. J. Greenh. Gas Control* 2, 219-229.

513 Moioli, S., Giuffrida, A., Romano, M.C., Pellegrini, L.A., Lozza, G., 2016. Assessment of MDEA
514 absorption process for sequential H₂S removal and CO₂ capture in air-blown IGCC plants. *Appl.*
515 *Energy* 183, 1452-1470.

516 Moioli, S., Nagy, T., Langé, S., Pellegrini, L.A., Mizsey, P., 2017. Simulation Model Evaluation of
517 CO₂ Capture by Aqueous MEA Scrubbing for Heat Requirement Analyses. *Energy Procedia* 114,
518 1558-1566.

519 Moioli, S., Pellegrini, L.A., 2015. Physical properties of PZ solution used as a solvent for CO₂
520 removal. *Chem. Eng. Res. Des.* 93, 720-726.

521 Moioli, S., Pellegrini, L.A., 2016. Modeling the methyldiethanolamine-piperazine scrubbing system
522 for CO₂ removal: Thermodynamic analysis. *Front. Chem. Sci. Eng.* 10, 162-175.

523 Moioli, S., Pellegrini, L.A., 2018a. Describing physical properties of CO₂ unloaded and loaded
524 MDEA+PZ solutions. *Chem. Eng. Res. Des.* 138, 116-124.

525 Moioli, S., Pellegrini, L.A., 2018b. Optimal Operation of a CO₂ Absorption Plant in a Post-
526 Combustion Unit for Cost Reduction. *Chem. Eng. Trans.* 69, 151-156.

527 Nagy, T., Moioli, S., Langé, S., Pellegrini, L.A., Mizsey, P., 2017. Improvement of post-combustion
528 carbon capture process in retrofit case. *Energy Procedia* 114, 1567-1575.

529 Oates, D.L., Versteeg, P., Hittinger, E., Jaramillo, P., 2014. Profitability of CCS with flue gas bypass
530 and solvent storage. *Int. J. Greenh. Gas Control* 27, 279-288.

531 Patiño-Echeverri, D., Hoppock, D.C., 2012. Reducing the Energy Penalty Costs of Postcombustion
532 CCS Systems with Amine-Storage. *Environmental Science & Technology* 46, 1243-1252.

533 Pellegrini, L.A., De Guido, G., Consonni, S., Bortoluzzi, G., Gatti, M., 2015. From biogas to
534 biomethane: How the biogas source influences the purification costs. *Chem. Eng. Trans.* 43, 409-414.

535 Pellegrini, L.A., De Guido, G., Langé, S., 2018. Biogas to liquefied biomethane via cryogenic
536 upgrading technologies. *Ren. Energy* 124, 75-83.

537 Sanchez Fernandez, E., Sanchez del Rio, M., Chalmers, H., Khakharia, P., Goetheer, E.L.V., Gibbins,
538 J., Lucquiaud, M., 2016. Operational flexibility options in power plants with integrated post-
539 combustion capture. *Int. J. Greenh. Gas Control* 48, 275-289.

540 Shell, 2017. CANSOLV Carbon Dioxide (CO₂) Capture System. [http://www.shell.com/business-
541 customers/global-solutions/gas-processing-licensing/licensed-technologies/shell-cansolv-gas-
542 absorption-solutions/cansolv-co2-capture-system.html](http://www.shell.com/business-
541 customers/global-solutions/gas-processing-licensing/licensed-technologies/shell-cansolv-gas-
542 absorption-solutions/cansolv-co2-capture-system.html).

543 Terna Group, 2014. Power Plants.

544 UN, 1997. Kyoto Protocol to the United Nations Framework Convention on Climate Change.
545 <http://unfccc.int/2860.php>.

546 UN, 2015. The Paris Agreement. http://unfccc.int/paris_agreement/items/9485.php.

547 van der Wijk, P.C., Brouwer, A.S., van den Broek, M., Slot, T., Stienstra, G., van der Veen, W., Faaij,
548 A.P.C., 2014. Benefits of coal-fired power generation with flexible CCS in a future northwest
549 European power system with large scale wind power. *Int. J. Greenh. Gas Control* 28, 216-233.

550 Veawab, A., Tontiwachwuthikul, P., Chakma, A., 1999. Corrosion Behavior of Carbon Steel in the
551 CO₂ Absorption Process Using Aqueous Amine Solutions. *Ind. Eng. Chem. Res.* 38, 3917-3924.

552 Zaman, M., Lee, J.H., 2015. Optimization of the various modes of flexible operation for post-
553 combustion CO₂ capture plant. *Comp. Chem. Eng.* 75, 14-27.

554