

Multi-objective optimization of a hybrid carbon capture plant combining a Vacuum Pressure Swing Adsorption (VPSA) process with a Carbon Purification Unit (CPU)

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Abstract

The imperative challenge posed by climate change requires urgent actions to counteract the harmful effects of greenhouse gas emissions, particularly CO₂, which contributes to approximately 80% of emissions responsible for global warming. A hybrid system combining Vacuum Pressure Swing Adsorption (VPSA) unit with a Cryogenic Carbon Purification Unit (CPU) is evaluated to enhance recovery and purity of CO₂ captured from flue gas containing CO₂ concentration ranging from 5% to 20%. VPSA preconcentrates the CO₂ and CPU completes the separation and purifies the CO₂. The study uses surrogate models for multi-objective optimization, considering energy consumption, cost, and CO₂ recovery, providing a time-efficient approach for investigating computationally demanding processes. Results from the study indicate that the hybrid system achieves over 90% recovery for flue gas concentration range considered, while ensuring the production of high-purity CO₂ (> 99.99%) suitable for transportation. A trade-off analysis reveals the balance between recovery, electricity consumption, and economic viability. A sensitivity analysis identifies parameters influencing recovery and energy consumption, providing guidance for future optimization efforts. The techno-economic analysis highlights the impact of electricity prices and carbon taxes on total costs, identifying an optimum towards higher recovery values under rising carbon taxes. Furthermore, the research underscores concentration-dependent economic feasibility, emphasizing the attractiveness of concentrations above 10% compared other technologies, which require higher concentrations. For an electricity price of 75 €/MWh⁻¹, the total cost of the CO₂ capture hydride system considering CO₂ emissions with carbon tax of 100 €/t_{CO2}⁻¹ for concentrations ranging from 10% to 20% is from 123 to 80 €/t_{CO2}⁻¹, respectively. The analysis of the electricity source shows the importance of a low-carbon emission energy mix for optimal carbon emissions reduction.

Keywords

Carbon capture process, hybrid process, vacuum pressure swing adsorption, carbon purification unit, optimization, techno-economic analysis

1 Introduction

The imperative challenge of climate change needs urgent and impactful actions to limit the harmful effects of greenhouse gas emissions. Among these emissions, carbon dioxide is a major driver of global warming, accounting for approximately 80% of the greenhouse gas emissions responsible for climate change and the main contributor to the greenhouse effect with over 50% compared with other gases [1]. At the COP 21 in Paris, on 12th of December 2015, the Paris Agreement, adopted by 196 Parties, aims to limit global warming to a level well below 2°C, and for the best scenario to 1.5°C, compared to the pre-industrial period [2]. To reach the goal of net-zero emissions, proposed scenarios advocate for a

43 widespread adoption of renewable energies, steering clear of fossil fuels and prioritizing electrification
44 whenever feasible [1,3].

45 Nevertheless, a significant percentage of emissions originates from chemical reactions, such as the
46 decarbonation process in cement or lime production (65% of the CO₂ cement plant emissions come from
47 the decarbonation). These CO₂ emissions are unavoidable, regardless of the energy processes employed.
48 Consequently, this underscores the crucial need to develop robust Carbon Capture Utilization and/or
49 Storage (CCUS) systems as one of the solutions to address this issue. Furthermore, the transition to
50 renewable energies will not be instantaneous, necessitating, in transition, the addition of carbon capture
51 systems to functional units to gradually reduce CO₂ emissions. By capturing, utilizing, and storing
52 carbon dioxide emissions, a significant step forward in curbing the impact of industrial processes on the
53 planet's climate can be taken [3].

54 The CO₂ storage involves transporting it from capture sites to storage locations, whether onshore or
55 offshore. In Europe, offshore storage is currently favored and requires sea-based conveyance. Pipelines
56 or ships are the only two viable options for CO₂ transport. As the distance increases, a tipping point
57 emerges where the cost-effectiveness of shipping surpasses that of pipelines, dependent on specific
58 assumptions [4].

59 Ensuring safe and efficient maritime transport of CO₂ requires stringent specifications. For instance,
60 maintaining O₂ levels below 10 ppm and H₂O content below 30 ppm becomes imperative to mitigate
61 the risks of corrosion [5]. These conditions remain relatively consistent for pipeline transport, with
62 values that may vary based on the source, akin to the variation in water vapor levels (40 to 650 ppm)
63 [5,6]. Moreover, when catalysts are involved in CO₂ conversion field, the utilization aspect necessitates
64 specific high CO₂ purity to prevent catalyst deactivation or the formation of undesirable by-products
65 [7]. This aspect assumes great significance when analyzing the entire CCUS process chain, aiding in the
66 determination of the required purity level for CO₂. Comprehensive consideration of these factors
67 enhances the efficacy and sustainability of carbon capture initiatives.

68 Various adaptations of existing industrial processes have been developed to incorporate carbon capture
69 technologies, including pre-combustion, oxy-combustion, and post-combustion techniques [8].

70 Post-combustion technologies focus on extracting CO₂ from a flue gas at the end of the process chain,
71 necessitating minimal modifications to the industrial plant. However, a disadvantage is that the flue gas
72 is more diluted, which results in increased energy consumption associated with the capture processes.
73 Typical CO₂ contents of flue gases coming from: gas power plant: ±5%, waste burner: ±10%, coal power
74 plant: ±15% and lime or cement plant: ±20% [9]. Each approach offers unique advantages and
75 challenges, and selecting the most suitable method depends on the specific characteristics of the
76 industrial process and the desired level of CO₂ capture [10].

77 Various technologies are available for carbon capture, such as absorption, adsorption, membrane
78 technologies and cryogenics [11]. Chemical or physical absorption involves using a solvent with a high
79 affinity for CO₂ to capture it in an absorber, which can then be regenerated in a stripper through the
80 application of thermal energy [12]. Amines-based solvents currently serve as the benchmark due to their
81 maximum Technology Readiness Level (TRL) thanks its development in the 1930s to extract CO₂ from
82 natural gas [13]. The generated CO₂ is relatively pure with classic target of 98 mol% CO₂, requiring
83 only a drying unit for transportation. However, they come with several drawbacks, such as thermal or
84 oxidative degradation into toxic chemicals which can have health impacts or such as volatility, which
85 can have significant environmental and health impacts. Another concern is the thermal consumption
86 required for the solvent regeneration, necessitating steam generation, which introduces new emissions
87 if no fatal excess heat is available at the industrial site [14].

88 Adsorption uses solid materials like active carbon, zeolite, Metal Organic Frameworks (MOFs) with a
89 strong affinity for CO₂, allowing it to be retained within the material's pores during the adsorption phase

90 and released when a Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA) or
91 Temperature Swing Adsorption (TSA) differential is applied during the regeneration phase of the
92 adsorbent [15]. There is an optimum trade-off between two performance indicators, namely CO₂ purity
93 and recovery, necessitating to define a compromise between them or requiring two units to achieve both
94 performances. In addition, this process can be sensitive to water reducing the adsorption performances
95 depending on the adsorbent used.

96 Membrane technologies, primarily polymer-based, enable CO₂ separation from other molecules by
97 applying pressure differentials across the membrane, allowing molecules to permeate [16]. However,
98 achieving recovery higher than 90% with 95-99 mol% CO₂ purity requires also duplicating units, leading
99 to increased capital expenditure (CAPEX) and site footprint.

100 Cryogenics involves manipulating temperature conditions to liquefy or sublimate flue gas, separating
101 CO₂ from other processes. Carbon Purification Unit (CPU) works well for high concentrated flue gas
102 from oxy-combustion by partially liquefying the stream [17]. Cryogenic Carbon Capture (CCC) can
103 treat post-combustion flue gas by sublimate the CO₂ [18]. Cryogenics offers highly pure CO₂ at the
104 process output, yet energy consumption and operational expenditure (OPEX) are significant for flue gas
105 in post-combustion conditions due to the low CO₂ concentration in the inlet flue gas [19].

106 All capture techniques present efficiency, scalability, and cost-effectiveness advantages and challenges.
107 Ongoing research aims to optimize these methods for broad application in industries such as power
108 generation, cement production, and natural gas processing. Considering the necessary specifications for
109 gas transport or post-capture utilization, it is crucial to explore wider boundaries in capture unit design
110 to take into account for final CO₂ purification requirements. Based on these considerations, the present
111 study's objective is to investigate a hybrid system capable of producing CO₂ reaching required CO₂
112 specification for transportation or utilization with catalyst while minimizing energy consumption.

113 Numerous investigations have explored hybrid post-combustion systems, as described by Song et al.
114 [20], employing processes commonly organized in a sequential manner. For instance, by combining
115 membrane-absorption [21], membrane-adsorption [22], adsorption-membrane [22], cold membrane
116 integrated into a cryogenic unit [23–26], or adsorption-cryogenics [27] approaches. In the present work,
117 a hybrid system that combines a Vacuum Pressure Swing Adsorption (VPSA) process with a high purity
118 cryogenic carbon purification unit is considered, following the concept outlined by Rodrigues et al.
119 [28,29]. The combination of these two technologies makes it possible to mix high CO₂-recoveries of
120 VPSAs and high CO₂-purities of CPUs, resulting in an optimized capture process that combines both
121 qualities.

122 Adsorption has already demonstrated its effectiveness in gas treatment, whether in refineries to purify
123 hydrogen produced by Steam Methane Reforming (SMR), or in natural gas extraction to purify methane
124 from carbon dioxide. PSA allows to perform rapid cycle compared to TSA which limits the investment
125 costs. The main drawback of PSA process is the electrical energy required. Therefore, the optimization
126 of energy consumption is an essential point to design an efficient separation unit [30,31]. In the
127 literature, numerous PSA processes have been developed for CO₂ capture. Since the flue gas is already
128 at atmospheric pressure, VPSA processes are preferred due to the better selectivity at low adsorbent
129 loading [30,32]. Several adsorbent and cycle configurations have been studied for CO₂ capture with
130 VPSA process. Among the numerous materials available (active carbon, zeolite, MOF, etc.), zeolite 13X
131 is one of the most interesting materials, exhibiting high CO₂ adsorption capacity and selectivity at low
132 and moderate partial pressure of CO₂ (0.05-0.5 bar) and ambient temperature. For a 15/85% CO₂/N₂
133 mixture at 1 bar and 25 °C, the CO₂ adsorption capacity is around 2.5 to 3.5 mmol.g⁻¹ with a selectivity
134 between 150 and 850 [33–35] and for 5% CO₂ at 1 bar et 25°C, the selectivity remains higher than 100
135 with a capacity higher than 1 mmol.g⁻¹ [34]. Nevertheless, zeolite 13X is sensitive to contaminants such
136 as NO_x or SO_x reducing the CO₂ adsorption capacity of the material. Water is also a concern for this
137 material since zeolite is a hydrophilic material, making the adsorption of water preferential instead of

138 CO₂. Presence of water vapor in flue gas leads to a drastic reduction of the CO₂ adsorption capacity of
139 the zeolite, and a reduction of performance in VPSA cycle. Therefore, a pretreatment line is required to
140 remove contaminants and water before the VPSA unit [32,34,36,37].

141 VPSA processes can be operated with different cycle configurations depending on the number of
142 adsorption beds used, and the sequence of steps performed. Skarstrom cycle is the first (V)PSA cycle
143 developed and consists of an adsorption, blowdown, purge, and pressurization step [38]. A pressure
144 equalization step can be used between adsorption and blowdown to improve the performance of the
145 cycle [30,31,38]. This cycle was already tested for CO₂ capture with activated carbon on a laboratory
146 pilot allowing to reach a CO₂ recovery of 96.16% and a CO₂ purity of 63.04% for a flue gas containing
147 15% of CO₂. This result was obtained with a vacuum pressure of 0.1 bar and an adsorption pressure of
148 3.25 bar [39]. Jiang et al. [40] studied this cycle through simulation works with zeolite 13X showing
149 CO₂ recovery higher than 95% and purity higher than 50% for a desorption pressure of 0.06 bar and an
150 adsorption pressure of 1.5 bar. Skarstrom cycle with pressure equalization was also simulated by Liu et
151 al. [41] obtaining 93% of CO₂ recovery and 58% of purity for 15/85 CO₂/N₂ mixture, a blowdown
152 pressure of 0.15 bar and adsorption pressure of 1.5 bar. Other 2-column configurations have been
153 developed to capture CO₂ in post-combustion. Zeolite 13X was tested by simulation and experimentally
154 on a 4-step cycle including adsorption, co-current blowdown, counter-current blowdown, and
155 pressurization from the gas coming from the adsorption step. Results obtained from this cycle give a
156 high CO₂ recovery (86.4%) and purity (95.9%) with a single unit [42–44]. Nevertheless, the vacuum
157 pressure used is very low (0.011 bar), which significantly increases the energy consumption of the
158 vacuum pump and leads to unrealistic conditions for an industrial process. Moreover, the cycle includes
159 idle step where the flue gas is not treated requiring more units or a gas tank to process the flue gas in a
160 continuous way. More adsorption beds can be used to increase the performance of a VPSA unit. 3-bed
161 5-step cycle including rinse step was studied with 13X by simulation in order to reach higher CO₂ purity
162 than Skarstrom cycle with the same pressure level (adsorption = 1.5 bar and blowdown 0.1 bar). The
163 unit is able to reach almost 99% of CO₂ recovery with a purity of 65% [45]. 3-bed with 6-step, 9-step
164 and 12-step were studied to reach purity higher than 90% in a single unit. This purity can be achieved
165 by the mean of low vacuum pressure (0.03 bar), and recovery between 60 and 70% [46,47]. Even if the
166 3-bed configuration allows to increase the performance of the VPSA unit, the amount of adsorbent
167 required by kg of CO₂ captured and the capital investment are generally higher than 2-bed configuration.

168 Several studies [19,48–55] have addressed their interest on CPU technology, examining its adaptability
169 to different oxy-combustion flue gas compositions with CO₂ concentrations ranging from 75 to 95 mol%
170 (dry basis). Remarkably, CPU can achieve CO₂ recovery rates as high as 90%, although the potential
171 exists for even higher recoveries, depending on the initial CO₂ concentration at the system inlet.
172 Achieving the desired purity levels depends largely on the inclusion of unitary operations in the CPU
173 process, such as a distillation column or a desorber.

174 Two main types of CPUs: medium purity CPU and high purity CPU. The medium purity CPU, often
175 equipped with 1 or 2 flash separators, can deliver CO₂ with a purity of 95 mol%. The high purity CPU,
176 on the other hand, is equipped with a column system that allows it to consistently exceed the coveted 99
177 mol% purity level and even achieve food-grade CO₂ quality [56]. In terms of energy consumption, it
178 should be noted that the high purity CPU typically consumes 10 to 15% more electrical energy compared
179 to its medium purity counterpart [48,52,55]. This discrepancy in energy consumption results from the
180 more complex separation processes required to achieve high CO₂ purity.

181 Consistent with the general principles of carbon capture, it's also important to recognize that the energy
182 required for CO₂ capture decreases as the initial CO₂ concentration in the flue gases increases. Values
183 range from about 164 kWh.tCO₂⁻¹ captured for flue gases containing 75 mol% CO₂ [51] to a more efficient
184 112 kWh.tCO₂⁻¹ for flue gases containing 94 mol% CO₂ [52]. This progressive reduction in energy
185 demand highlights the potential energy saving benefits of CPU systems, particularly when used in

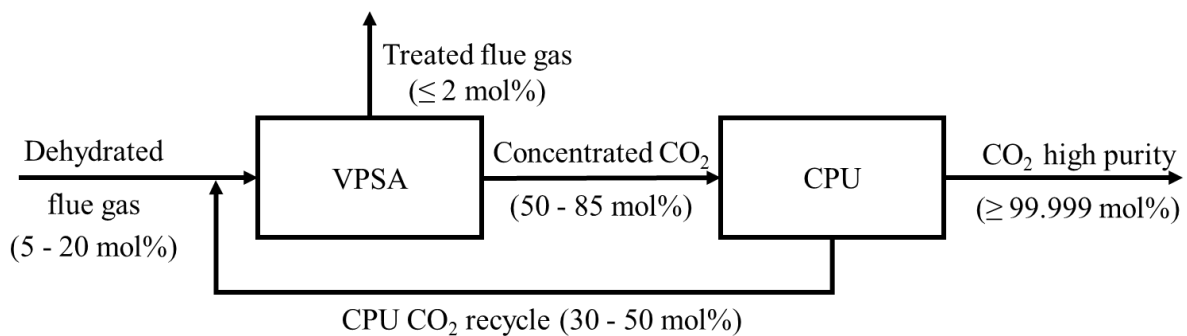
186 environments with higher CO₂ concentrations, and contributes to more sustainable and economically
187 viable carbon capture solutions.

188 In this work, a 2-bed VPSA was chosen to generate pre-concentrated CO₂ flux at a minimum of 50
189 mol%. This value corresponds to the entry level at which the CPU becomes energetically interesting.
190 For the CPU, a purity of 99.999 mol% is targeted in order to avoid any trace of undesirable compounds
191 for CO₂ transport or conversion operations. Aspen Plus® and Aspen Adsorption® V14 were used to
192 model cryogenic and VPSA units, respectively. Surrogate models, which convert process simulations
193 into mathematical representations, are employed to facilitate the optimization of the process, aiming to
194 analyze diverse performance indicators including energy consumption, cost, and CO₂ recovery. These
195 models play a pivotal role in identifying the most advantageous operational parameters for the processes.
196 The application of such tools in a hybrid setup stands as a noteworthy innovation, offering substantial
197 time savings in investigating simulated processes that entail computationally demanding calculations.
198 Optimizing two processes simultaneously provides an advantage over optimizing each process
199 individually to ensure finding the optimum point. This work provides a detailed energetic and economic
200 study of this innovative process, and a methodology for performing multi-objective optimization of a
201 complex, fully integrated process.

202 2 Details and design of the process

203 2.1 Process configuration

204 The studied process is a hybrid combination of a vacuum pressure swing adsorption and a carbon
205 purification unit used to capture the CO₂ from flue gases with a CO₂ concentration between 5-20 mol%
206 and a flow rate of 70,000 Nm³.h⁻¹ corresponding to around 1000 t.d⁻¹ of clicker production (see Figure
207 1). To prevent deterioration of the adsorption performance and ice formation in the CPU, the flue gas is
208 considered as dehydrated upstream of the process. To achieve the dehydration required for the VPSA
209 and the CPU, TSA with silica gel or alumina must be used to dry flue gas before the CO₂ capture unit
210 [57,58]. It is also necessary to consider potential treatments on a larger scale to remove pollutants that
211 could degrade the material, such as dusts, NO_x, SO_x, Hg, etc. In this study, a preliminary assumption is
212 to focus solely on nitrogen and carbon dioxide. The VPSA is used to concentrate CO₂ from the flue gas
213 at least 50 mol% CO₂ before remove the rest of the impurities in the CPU. The CPU purifies the CO₂
214 through the liquefaction of the flue gas, allowing to separate liquid CO₂ from the incondensable gases.
215 These are sent back to the VPSA to recover the CO₂ that has not liquefied in the CPU. Finally, a
216 minimum purity of 99.999 mol% is obtained at the output of the CPU. The total process CO₂ recovery
217 depends on the impact of CPU recycle on the VPSA. Traditionally, the target for capture processes is to
218 achieve 90% recovery even if in recent papers, this target increases to reach a value of 95% or more.
219 Nevertheless, this value could be higher while remaining economically viable. That's why in this study,
220 recovery will be an optimization objective.



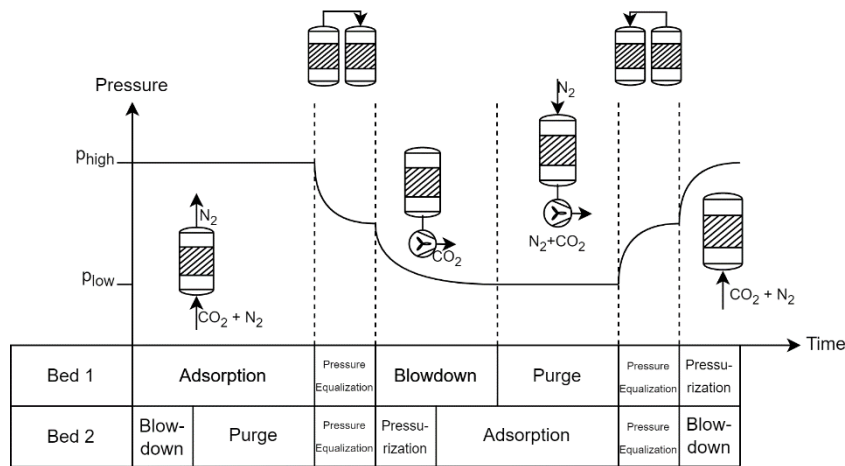
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Figure 1: Hybrid VPSA-CPU CO₂ capture process.

223 The objective of this work is to minimize the electrical consumption of the CO₂ capture process by
 224 globally optimizing the hybrid process, VPSA and CPU. Each process can be optimized for a specific
 225 CO₂ recovery and purity by minimizing the electrical consumption that is associated with a large part of
 226 the capture process cost. When the two processes are combined, the CO₂ recovery is fixed at the VPSA
 227 level, and the final CO₂ purity is determined with the CPU performance. This means that there is
 228 flexibility in the purity of the CO₂ at the VPSA output, which will have an impact on the electrical
 229 consumption. At fixed recovery, the more concentrated the CO₂ is, the higher the electrical consumption
 230 of the VPSA will be, but the lower the electrical consumption of the CPU will be. It is important to
 231 retrieve the right balance between the CO₂ purity and the electrical consumption of the VPSA and CPU
 232 in order to minimize the overall electrical consumption of the entire CO₂ capture process. Moreover, the
 233 recycled flux to the VPSA can modify the performances of the adsorption unit leading to different results
 234 in terms of purity, recovery, and energy consumption.

235 2.1.1 VPSA modelling

236 The first part of the process is a 2-bed VPSA unit performing the Skarstrom cycle with pressure
 237 equalization step [31]. Sequence of steps for one bed, in addition with the pressure profile is represented
 238 on Figure 2. The first step of the cycle is the adsorption where the flue gas is sent to the column to adsorb
 239 mainly the CO₂ and to obtain a nitrogen-rich gas at the outlet of the column. The column is then
 240 connected to the second column which is at lower pressure to equalize the pressure and save mechanical
 241 work of compression and vacuum. The pressure is further reduced in the blowdown step to desorb the
 242 CO₂ in the column and retrieve it. A part of the nitrogen-rich stream of the column in adsorption step is
 243 used during the purge step to flush the CO₂ from the second column and increase the amount of CO₂
 244 retrieved. Finally, the two columns are connected for the equalization of pressure, followed by a
 245 pressurization from the flue gas until the adsorption pressure is reached. In this cycle, the time of the
 246 blowdown step and the purge step must be equal to time of the adsorption step and pressurization step
 247 to keep the synchronization between the two beds.



248
249 *Figure 2: Sequence of steps and pressure profile for the cycle used in the VPSA unit.*

250 Zeolite 13X (UOP MOLSIV™) was chosen for its good CO₂/N₂ separation performance in dry
 251 conditions (CO₂ adsorption capacity, selectivity, etc.), the results already proven in simulation and pilot
 252 scale VPSA process for post-combustion CO₂ capture, and its commercial availability [43,44,46,47,59–
 253 61]. Adsorption isotherms, kinetics, and other parameters relative to zeolite 13X were obtained from
 254 literature data [62,63]. In these works, adsorption isotherms for CO₂ and N₂ are modelled with a dual-
 255 site Langmuir model with temperature dependency given by equations (S7) to (S9) in Supporting
 256 Information. Parameters of the adsorption isotherm model are given in Table 1 and are
 257 thermodynamically consistent which ensure a better representation of the co-adsorption as demonstrated
 258 by Farmahini et al. [62]. In addition, the affinity parameters for N₂ are equals ($b_0 = d_0$ and $\Delta H_1 = \Delta H_2$)

259 Other parameters relative to the adsorbent are given in Table 2. The adsorbent is assumed to have a
 260 spherical shape with a diameter of 3 mm. The packing density was derived from the crystal density of
 261 zeolite 13X (1403 kg.m⁻³) [62] and the inter- and intraparticle void fraction [63–65]. Tortuosity of the
 262 adsorbent is obtained from Hu et al. [63].

263 *Table 1: Adsorption isotherm parameters used for zeolite 13X (from [66]).*

Parameter	CO ₂	N ₂
q _{s1} [mmol.g ⁻¹]	1.44	1.44
b ₀ [bar ⁻¹]	3.59 × 10 ⁻⁵	2.89 × 10 ⁻⁷
ΔH ₁ [J.mol ⁻¹]	40.014 × 10 ³	30.67 × 10 ³
q _{s2} [mmol.g ⁻¹]	3.47	3.47
d ₀ [bar ⁻¹]	8.27 × 10 ⁻⁵	2.89 × 10 ⁻⁷
ΔH ₂ [J.mol ⁻¹]	40.491 × 10 ³	30.67 × 10 ³

264

265

Table 2: Geometric parameters of Zeolite 13X (from [67]).

Parameter	Value
Packing density [kg.m ⁻³]	645.24
Inter-particle void fraction [-]	0.37
Intra-particle void fraction [-]	0.27
Pellet diameter [mm]	3
Tortuosity [-]	2.6

266

267 To process the 70,000 Nm³/h of flue gas, five VPSA units are working in parallel to treat initially 14,000
 268 Nm³/h of flue gas. The volume of the bed used is equal to 80 m³ with an inner diameter of 3.24 m and
 269 length of 9.71 m filled with spherical beads of 3 mm diameter. The dimensions of the pilot were chosen
 270 to avoid the fluidization of the bed, and decrease the pressure drop of the units. The complete sizing
 271 procedure based on pressure drop and minimum fluidization velocity is described in Supporting
 272 Information.

273 The VPSA unit was modelled in Aspen Adsorption[®] V14 software using a 1D discretization in 30 nodes
 274 of the bed using the Van Leer scheme and the “unibed” approach which simulates a single bed to save
 275 simulation time [68]. Flowsheet used in the simulation software is represented in Figure S3 in
 276 Supporting Information. Plug flow is used for mass balance including axial dispersion, convective flow,
 277 accumulation in gas phase and accumulation in adsorbed phase represented by equation (S4) [30]. Axial
 278 dispersion coefficient is obtained with the correlation from Langer et al. [69] (equation (S11)). Linear
 279 driving force [70] given by equation (S14) is used to represent the adsorption kinetics. Macropore
 280 diffusion model is used to compute the kinetic coefficient (equation S15) with the parameters from

281 Table 2 [63]. Ergun equation is used for the momentum balance of the bed as represented in equation
 282 (S16). The bed is considered as non-isothermal with energy balance for the gas (equation (S17)), solid
 283 (S18), and wall of the bed (S19). The energy balance of the gas is composed of thermal conduction,
 284 convection, accumulation, heat generation from adsorption, gas-solid heat transfer, and gas-wall heat
 285 transfer. For the solid phase, only accumulation of heat in the solid is considered, neglecting the heat of
 286 the adsorbed phase. For the wall of the bed, accumulation, axial conduction, conduction across the wall
 287 and gas-wall heat transfer for the inside and outside of the column are considered [30,71]. The following
 288 correlations were implemented in Aspen Adsorption[®] V14 for the computation of the heat transfer
 289 coefficient:

- 290 • Heat transfer coefficient between solid and gas: correlation of Whitaker [48][72] given by
 291 equation (S20) which is valid for 20 < Re < 10,000 and 0.34 < ε_b < 0.78.
- 292 • Heat transfer coefficient between gas and wall: Correlation of Beek [72,73] (equation (S21))
 293 which is valid for 40 < Re < 2000.

294 • Heat transfer coefficient between wall and ambient: general heat transfer correlations for natural
 295 convection and radiation [72,74,75] represented by equation (S22) to (S25).

296 All the parameters used for the VPSA simulation are listed in Table S1 of Supporting Information. In
 297 addition, the gas properties (density, viscosity, heat capacity, heat conductivity) are determined with
 298 Aspen Properties V14 software using the following models :

- 299 • Redlich-Kwong-Soave equation of state for gas density [76].
- 300 • Chapman-Enskog-Brokaw with Wilke mixing rule for gas viscosity [77,78].
- 301 • Wassiljewa-Mason-Saxena model for heat conductivity [79].
- 302 • Polynomial model with data from [80] for gas heat capacity.

303 .

304 VPSA unit is evaluated with the purity and recovery of CO₂ obtained in addition to the electrical
 305 consumption. Purity is obtained by summing the amount of CO₂ obtained in the product section during
 306 one cycle, divided by the total amount obtained in this same section (equation (1)). VPSA recovery is
 307 the fraction of CO₂ retrieved at the outlet of the VPSA unit compared to the CO₂ in the flue gas. It is
 308 computed by the amount of CO₂ obtained in the product section divided by the amount of CO₂ in the
 309 feed gas (equation (2)) [31][33].

$$Purity_{VPSA} = \frac{\sum_{cycle} \dot{n}_{product} y_{CO_2 product}}{\sum_{cycle} \dot{n}_{product}} \quad (1)$$

$$Recovery_{VPSA} = \frac{\sum_{cycle} \dot{n}_{product} y_{CO_2 product}}{\sum_{cycle} \dot{n}_{feed} y_{CO_2 feed}} \quad (2)$$

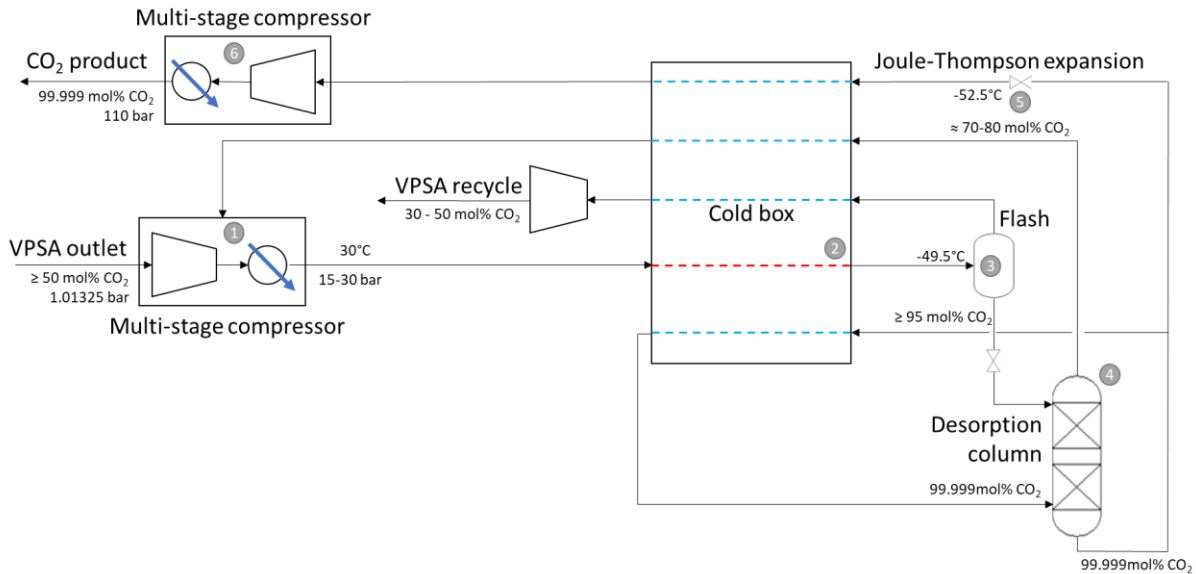
310 where \sum_{cycle} is the sum of the various time intervals in the cycle, \dot{n} is the molar flow rate (mol.s⁻¹) and
 311 y_{CO_2} the CO₂ molar fraction in the feed or in the product.

312 Cycles were performed until cyclic steady state was reached. During the pressure equalization steps, the
 313 flue gas is not treated by the VPSA unit. To take this into account, it is assumed that a buffer gas storage
 314 allows for the temporary regulation of the gas flow. VPSA purity and recovery are evaluated at the end
 315 of every cycle and compared with the values obtained during the previous cycle. The simulation is
 316 stopped when the difference is lower than 0.1% for both indicators. Seven parameters have been studied
 317 for the VPSA unit. The parameter bounds were chosen to cover a relatively wide range, considering the
 318 subsequent integration with the CPU. Among parameters, there are adsorption time [60 – 2000 s], purge
 319 time [10 – 1990 s], equalization time [10 – 50 s]. For these three parameters, a minimum time of 10
 320 seconds for each step, leading to a minimum adsorption time of 60 seconds. The maximum adsorption
 321 time was obtained by increasing the upper bound in order to ensure that the optimization results do not
 322 stick to the upper bound. The maximum purge time was adapted from the adsorption time minus 10
 323 seconds for blowdown. The maximum equalization time was set to 50 seconds since this step should be
 324 as fast as possible. In addition, adsorption pressure [1.01325 – 3 bar], blowdown pressure [0.01 – 0.5
 325 bar], feed flow rate [14,000 – 25,000 Nm³.h⁻¹] (extra flow rate above 14,000 Nm³.h⁻¹ is the recycle gas
 326 from the CPU and the factor [(*adsorption time* + *equalization time*)/*adsorption time*] considering the
 327 zero flow rate during the equalization step), purge flow rate [100 – 20,000 Nm³.h⁻¹] and feed CO₂
 328 concentration [5 – 27%] (the recycle gas from VPSA is concentrated between 30 and 50 mol% CO₂ that
 329 increases the concentration of the flue gas at the VPSA inlet) are also studied. For feed flow rate and
 330 CO₂ concentration, the upper bounds were obtained by preliminary simulations of the CPU unit giving
 331 the flow rate and CO₂ concentration of the recycled flow from the CPU to the VPSA unit. The purge
 332 time was always chosen to be lower than the adsorption time, and the difference between adsorption
 333 time and purge time (which is equal to blowdown time) must be at least 10 s. For pressurization, this
 334 step was included in the adsorption step by sealing the outlet of the adsorption bed at the beginning of

335 the adsorption step, increasing the pressure with the feed gas. When the pressure inside the bed reaches
 336 the desired adsorption pressure, the valve at the outlet of the bed is automatically opened.

337 2.1.2 CPU modelling

338 The second part of the process is the CPU. This unit is inspired by the Air Liquide Callide project
 339 [81,82] and based on the study performed by Costa *et al.* [83]. A schematic of this process is proposed
 340 on Figure 3. Six fundamental steps are present: (1) flue gas compression, (2) flue gas cooling, (3) CO₂
 341 vapor-liquid separation, (4) CO₂ purification, (5) cold generation and (6) CO₂ compression. This unit
 342 purifies the CO₂ pre-concentrated by the 5 VPSA units. The minimum concentration at the inlet of the
 343 CPU is 50 mol% CO₂ to stay energetically interesting.



344 Figure 3: Schematic plan of the CPU.
 345

346 The cryogenic unit plays a crucial role in purifying carbon dioxide (CO₂) and removes incondensable
 347 gases. This separation process is achieved by utilizing the unique properties of cryogenics, particularly
 348 the liquefaction of CO₂. To ensure efficient separation without the formation of dry ice (solid CO₂), a
 349 carefully controlled temperature limit of -54 °C is established. This temperature is deliberately kept just
 350 above the triple point of -56.6 °C at which CO₂ transitions between its solid, liquid, and gaseous phases.

351 The concentrated CO₂ from the 5 VPSA units passes through a multi-stage compression system that
 352 includes intercooling with water (1). To achieve the flue gas liquefaction, multi-stream brazed aluminum
 353 heat exchanger (BAHX) is employed (2). The effectiveness of this technology has been successfully
 354 demonstrated in previous projects such as the Callide project [81].

355 After liquefaction step, the liquid CO₂ is separated from non-condensable gases by using a flash
 356 separator (3). This separation step ensures that liquid CO₂ (> 95 mol%) enters the process. To avoid
 357 losing the coldness from these gases, it can be efficiently recovered and utilized through BAHX. These
 358 gases are then expanded to generate energy before being returned to the VPSA processes, optimizing
 359 the overall efficiency of the plant.

360 The liquid CO₂ is then fed into the desorption column (4). In this column, the impurities are effectively
 361 stripped by pure CO₂ vapor. This desorption process is fundamental to achieving a high CO₂ purity of
 362 99.999 mol%.

363 To further increase the efficiency of the plant, a fraction of the product liquid CO₂ is heated to provide
 364 pure CO₂ vapor to the column, while the remaining fraction is subjected to Joule-Thompson expansion
 365 (5). Then, the product CO₂ is compressed to reach the required supercritical pressure for injection into

366 the pipeline distribution network, typically 110 bar (6). The expansion process generates the
367 refrigeration required for liquefaction, contributing to the overall energy efficiency of the system.

368 Figure 4 is the modelling in Aspen Plus® V14 software. The Peng-Robinson equation of state [84] was
369 chosen to determine the thermodynamic properties of the fluid mixture. The binary interaction parameter
370 k_{ij} for CO₂-N₂ is -0.017 [85]. The first multi-stage compressor has 4 stages, resulting from an
371 optimization between CAPEX and OPEX using the cost calculation defined in the 2.3 section. Pressure
372 ratio is kept between 2 and 5 to limit the compressed gases temperature to a maximum of 200 °C [86].
373 Regarding the process cooling, two Joule-Thompson expansions are used to reduce the electrical
374 consumption thanks to the fact that a fraction of the liquid flow rate expand to a higher pressure in the
375 valve V2 than in the valve V3 which must generate a stream at -52.45°C. The produced CO₂ is
376 conditioned to a supercritical state to be transported at 110 bar. Thus, the CO₂ is compressed up to 72
377 bar with 4 stages of compression in order to be liquefied under the critical point before being pumped
378 up to 110 bar. This process part consumes less electricity (7% for water cooling temperature of 20 °C)
379 than a 5 stages compression as presented in [87]. Table 3 presents the various hypotheses defined for
380 CPU modelling.

381

Table 3: Assumption for the CPU modelling.

Assumptions	Value
Minimum temperature	-54 °C
Water cooling temperature	20 °C to 25 °C
BAHX pressure drop	0.45 bar
Heat exchanger pressure drop	0.1 bar
Desorption column packing	Mellapak 250Y

382

383 In this process, seven parameters are under scrutiny to optimize the efficiency of the integrated process.
384 The CO₂ concentration [50 – 85%] and gas flow rate [1,000 – 40,000 Nm³.h⁻¹] at the CPU inlet span a
385 broad range, accommodating various potential scenarios from the VPSA. Adjusting the pressure of the
386 cold box [15 – 30 bar] (compressor C4) plays a crucial role in modifying the liquid-vapor equilibrium
387 at the FL1 flash. This equilibrium significantly influences both the flow rate and the CO₂ concentration
388 of the recycled stream directed towards the VPSA.

389 The desorption column pressure [9 - 17 bar] and the mass fraction towards the column of splitter S1
390 [0.05 – 0.20] are fitted to achieve the desired CO₂ purity. Recycling the vapor emanating from the
391 column before compressor C4 is also a crucial step. To optimize the compression stages, the outlet
392 pressure of compressor C3 is strategically set in relation to the column pressure, considering pressure
393 losses. These parameters collectively influence the amount of vapor recirculated with the flue gas and
394 the pressure set for the initial Joule-Thompson expansion V3, important for process cooling.

395 Finally, the pressure of the second Joule-Thompson expansion [7 – 14 bar] and the mass fraction towards
396 the first Joule-Thompson expansion of splitter S1 [0.05 – 0.75] are systematically varied to fine-tune
397 the amount of refrigeration necessary for the efficient operation of the entire process.

382 2.2 Energy balance

383 Electrical consumption of each VPSA unit is due to compressor and vacuum pump, and for CPU from
 384 compressors and liquid pumps including an energy recuperation from the turbines. The electrical
 385 consumption for compressors and vacuum pumps is evaluated with equation (3) where p_{low} is the inlet
 386 pressure, and p_{high} is the outlet pressure. For vacuum pump, p_{high} is the atmospheric pressure.
 387 Isentropic efficiency (η_{iso-s}) is set to 85% for compressors. For vacuum pump, isentropic efficiency
 388 varies in function of the pressure and is calculated following equation regressed in the Subraveti *et al.*
 389 study [88]. The energy retrieved from the turbines of the CPU is evaluated with a similar equation (4)
 390 where p_{low} is the outlet of the turbine and p_{high} the inlet. The isentropic efficiency of the turbine is
 391 equal to 90%. For pumps, equation (5) is used with an efficiency of 72.5 %. The total electrical
 392 consumption of the hybrid unit by mass of CO₂ captured is given by equation (6) by summing the
 393 electrical consumption, and by dividing by the sum of CO₂ obtained.

$$\dot{W}_{compressor \& vacuum \ pump} = \frac{1}{\eta_{iso-s}} \dot{n} RT \frac{\gamma}{\gamma - 1} \left(\left(\frac{p_{high}}{p_{low}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \quad (3)$$

$$\dot{W}_{turbine} = \eta_{iso-s} \dot{n} RT \frac{\gamma}{\gamma - 1} \left(\left(\frac{p_{low}}{p_{high}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \quad (4)$$

$$\dot{W}_{pump} = \frac{1}{\eta_{iso-s}} \frac{\dot{m}}{\rho} (p_{high} - p_{low}) \quad (5)$$

$$Electrical \ consumption = \frac{\Sigma \dot{W}}{\dot{m}_{CO_2 \ captured}} \quad (6)$$

394 where \dot{W} the power rate (W), η_{iso-s} the isentropic efficiency, \dot{n} the molar flow rate (mol.s⁻¹), R the ideal
 395 gas constant (=8.314 J.mol⁻¹.K⁻¹), T the temperature (K), γ the heat capacity ratio, p the pressure (Pa),
 396 \dot{m} the mass flow rate (kg.s⁻¹), and ρ the density (kg.m⁻³).

397 2.3 Economic analysis

398 Method from Turton *et al.* [89] is used to estimate the CAPEX and OPEX of the hybrid unit. This method
 399 relies on a reference cost adjusted by the Chemical Engineering Plant Cost Index (CEPCI) (equation
 400 (7)) to actualize the cost according to the inflation. For 2022 year, the average CEPCI index was equal
 401 to 816.0 [90].

$$C_{actual} = C_{reference} \left(\frac{I_{actual}}{I_{reference}} \right) \quad (7)$$

402 where C is the cost (€), and I the CEPCI index (-).

403 CAPEX is estimated via the calculation of the bare module cost (C_{BM}) equations (8) using the purchased
 404 equipment cost (C_p^0) which is evaluated by equation (9), and a bare module factor (F_{BM}) which include
 405 direct and indirect costs. If this factor is not given, a pressure factor (F_p) and a material factor (F_M) are
 406 used instead. The pressure factor can be obtained with equation (10) for a heat exchanger, or with
 407 equation (11) for a vessel. Material factor depends on the material used for the equipment and is equal
 408 to 1 for carbon steel. Equations (8) to (11) use different coefficients (K_i , B_i , C_i) given in Table 4 [89].

$$C_{BM} = C_p^0 [B_1 + B_2 F_p F_M] = C_p^0 F_{BM} \quad (8)$$

$$\log_{10} C_p^0 = K_1 + K_2 \log_{10}(S) + K_3 [\log_{10}(S)]^2 \quad (9)$$

$$\log_{10} F_{p,hx} = C_1 + C_2 \log_{10}(p) + C_3 [\log_{10}(p)]^2 \quad (10)$$

$$F_{p,vessel} = \frac{\frac{p D}{2 St E - 1.2 p} + CA}{t_{min}} \quad (11)$$

409 where C_p^0 is the purchased equipment cost corresponding to the atmospheric operating pressure and
 410 using carbon steel construction, S is the size of the equipment, p is the pressure (bar), D is the diameter
 411 (m), t_{min} is the minimum allowable vessel thickness (0.0063 m), CA is the corrosion allowance (0.00315
 412 m), E is the weld efficiency (0.9), and St is the allowable stress for carbon steel (944 bar).

413 *Table 4: Capital cost variable of components (*: $F_p = 1$ for $p < 5$ barg).*

Equipment Type	K ₁	K ₂	K ₃	B ₁	B ₂	F _{BM}	C ₁	C ₂	C ₃
Compressors centrifugal	2.2897	1.3604	-0.1027	-	-	2.7	-	-	-
Floating head HX	4.8306	-0.8509	0.3187	1.63	1.66*	-	0.03881	-0.11272	0.08183
Turbines	2.2476	1.4965	-0.1618	-	-	1	-	-	-
Vertical towers and vessels	3.4974	0.4485	0.1074	2.25	1.82	-	-	-	-

414 The cost of the brazed aluminum heat exchanger and the vacuum pump cannot be estimated by the above
 415 equations since this exchanger is not reported in Turton *et al.* [89]. Instead, the costs are obtained by
 416 Aspen Economics software, for BAHX, using the volume of the exchanger calculated by the specific
 417 surface of the exchanger (2000 m⁻¹) [91] and the overall heat transfer coefficient (170 W.m⁻².K⁻¹) [54].
 418 Subraveti *et al.* [92] gives regression for vacuum pump cost with volumetric inlet flow rate. The
 419 adsorbent cost was obtained by considering a price for the zeolite at 1.50 €.kg⁻¹.

420 CAPEX is obtained by summing the bare module cost of each equipment of the unit. In addition, a
 421 contingency cost and fees cost factor is added to the CAPEX calculation as a protection against the
 422 uncertainties of the cost estimation of each equipment. Contingency cost relies on numerous factors such
 423 as the completeness of the process flowsheet, or the reliability of the data used for the cost estimation.
 424 As a rule of thumb, 15% of bare module is used for contingency factor, and 3% is used as fees factor if
 425 no other data is available. Therefore, the final CAPEX calculation is given by equation (12) [89].

$$CAPEX = 1.18 \sum C_{BM} \quad (12)$$

426 The value obtained for CAPEX is annualized considering a lifetime of twenty-five years for the unit and
 427 the inflation rate. Equation (13) gives the annuity cost of the unit, depending on the inflation rate and
 428 the number of years.

$$CAPEX_a = CAPEX \frac{i(1+i)^n}{(1+i)^n - 1} \quad (13)$$

429 where $CAPEX_a$ is the annuity cost (€), i is the inflation rate (6.5%) [93] and n is the number of years of
 430 annuity interest.

431 OPEX is estimated from different factors listed in Table 5. These factors used Utility Cost (C_{UT}),
 432 Operating Labor Cost (C_{OL}) which is dependent of the country of the installation, and CAPEX. Equation
 433 (14) gives the complete formula to compute the OPEX.

$$OPEX = 1.235 C_{UT} + 2.735 C_{OL} + 0.280 CAPEX \quad (14)$$

434 Finally, CO₂ capture cost can be calculated with the sum of the annuity of the CAPEX and the OPEX
 435 for one year of operation divided by the mass of CO₂ captured for one year (equation (15)).

$$\text{Capture cost } (\text{€ } t_{\text{CO}_2}^{-1}) = (\text{CAPEX}_a + \text{OPEX})/m_{\text{CO}_2 \text{ captured}} \quad (15)$$

436

437 *Table 5 Base case assumptions for OPEX (Cooling water and labor cost from [93]; other coefficients from [89])*

Parameter	Value
Utilities (C_{UT})	Electricity: Base case 100 €.MWh ⁻¹ with variation between 50 – 250 €.MWh ⁻¹ Cooling water: 0.025 € m ⁻³
Operating Labor Cost (C_{OL})	18 labors; 54,000 €.labor ⁻¹ .year ⁻¹
Direct supervisory and clerical labor	0.18 C_{OL}
Maintenance and repairs	0.06 CAPEX
Operating supplies	0.15 (0.06 CAPEX)
Laboratory charges	0.15 C_{OL}
Patents and royalties	0.03 OPEX
Local taxes and insurance	0.032 CAPEX
Plant overhead costs	0.6 (1.18 C_{OL} + 0.06 CAPEX)
Administration costs	0.15 (1.18 C_{OL} + 0.06 CAPEX)
Distribution and selling costs	0.11 OPEX
Research and development	0.05 OPEX
Depreciation	0.10 CAPEX

438 3 Optimization

439 Simulation of VPSA and CPU in Aspen software requires the resolution of several thousand of equations
 440 leading to long simulation times. Optimizing each independent process using heuristic optimization
 441 algorithms (such as genetic algorithms, particle swarm optimization, simulated annealing, etc.) requires
 442 a significant number of simulation points, which would result in very slow resolution. In this work, the
 443 linking of VPSA and CPU requires calculating a steady-state point before optimizing the overall process.
 444 Surrogate models have been developed for both units, allowing to bypass Aspen simulations after having
 445 built robust and precise surrogate models and drastically reducing the required computational time. This
 446 methodology has been already used and validated in several research in the field of CO₂ capture
 447 processes [94–96].

448 Table 6 summarizes the input ranges used to build surrogate models for each process. The first part of
 449 the table includes the inputs for one VPSA unit, while the second part includes inputs for the CPU. The
 450 gas flow rate and its CO₂ concentration are included as inputs in each process since they are modified
 451 after the integration of the two units.

452 *Table 6: Parameters for the surrogate models with lower and upper bounds (top part: VPSA, bottom part: CPU).*

Parameters	Definitions	Units	Lower bounds	Upper bounds
$C_{\text{CO}_2\text{-FG}}$	Inlet CO ₂ concentration from flue gas	mol%	5	27
F_{FG}	Inlet flue gas flow rate of VPSA	Nm ³ .h ⁻¹	14,000	25,000
t_{ads}	Adsorption time	s	60	1500
t_{purge}	Purge time	s	10	1490
t_{equ}	Pressure equalizer time	s	10	50
F_{purge}	Purge flow rate	Nm ³ .h ⁻¹	100	20,000
p_{ads}	Adsorption pressure	bar	1.01325	3
P_{blow}	Blowdown pressure	bar	0.01	0.5
$C_{\text{CO}_2\text{-VPSA}}$	Inlet CPU CO ₂ concentration from VPSA	mol%	50	85
F_{VPSA}	Inlet CPU pre-concentrated flow rate from VPSA	Nm ³ .h ⁻¹	1,000	40,000
p_{C4}	Cold box pressure	bar	15	30
p_{V1}	Desorption column pressure	bar	9	17
p_{V2}	Second Joule-Thompson valve pressure	bar	7	14
α_1	Mass fraction towards desorption column	-	0.05	0.20
α_2	Mass fraction towards first JT valve	-	0.05	0.75

453 3.1 Surrogate model

454 Several mathematical models can be used to construct a surrogate model from simulation data. One of
 455 the simplest models widely used is the second-order polynomial approximation represented by the
 456 equation (26) [97,98].

$$\hat{f}(x, a, \alpha) = a_0 + \sum_{i=1}^m a_i x_i + \sum_{i=1}^m \alpha_{ii} x_i^2 + \sum_{i=1}^{m-1} \sum_{j=i+1}^m \alpha_{ij} x_i x_j \quad (16)$$

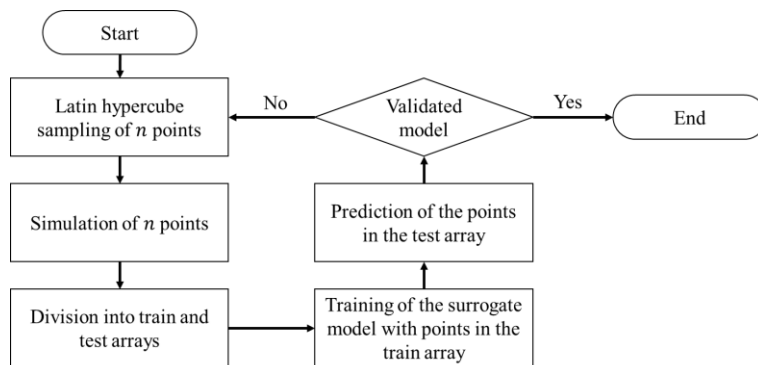
457 where \hat{f} is the estimation of the response by the model, a and α the coefficients of the polynomial with
 458 a_0 being a constant, x the parameter (t_{ads} , t_{purge} , etc.) and m the number of parameters.

459 Unfortunately, for complex model, second-order polynomial approximation gives unsatisfactory results
 460 and require the use of other surrogate models. The Kriging method is a popular model for engineering
 461 problem, giving satisfactory results for the approximation of time-consuming simulation [98]. In a
 462 general way, Kriging models are composed of a deterministic term $F(x)$ (constant term, linear or
 463 quadratic model of parameters such as equation (16)), and a stochastic term $Z(x)$ (equation (17)). The
 464 main assumption of Kriging model is to consider a spatial correlation between the responses to the model
 465 (which implies to consider the responses as random variables, even if they come from a determinist
 466 simulation software), with a known correlation function between the variables. Therefore, the prediction
 467 of an unknow point can be done by using this correlation function, and the distance between the new
 468 point and the known points [98–100].

$$\hat{f}(x) = F(x) + Z(x) \quad (17)$$

469 Different correlation functions can be used to construct the Kriging model. A list of frequently employed
 470 functions is available in [98]. In this work, the choice of the correlation function is done empirically by
 471 testing different functions until satisfactory results are obtained.

472 The models were constructed following the flowchart in the Figure 5. A total of n ($= 100$) points were
 473 generated with a Latin hypercube sampling using the Enhanced Stochastic Evolutionary algorithm
 474 [101], which allows for a semi-random distribution of points to ensure comprehensive coverage within
 475 the system bounds. The points were simulated with their respective tools and divided into two arrays to
 476 build the model with the first array (80% of data) and validate it with the second array (20% of data).
 477 The Surrogate Modelling Toolbox (SMT) [102] is used to construct both the surrogates of VPSA and
 478 CPU in Python.



479
 480 *Figure 5: Algorithm for surrogate model creation.*

481 For recovery and purity, the transformation described by (18) was applied to train the surrogate model
 482 with u the transformed data, z the training data, and ϵ a numerical perturbation equal to 0.0001. This
 483 transformation improves the robustness of the optimization procedure as stated by Beck et al. [103].
 484 Recoveries and purities are obtained by applying the inverse transformation to the surrogate prediction.

485 For energy consumption, the transformation given by (19) was applied to avoid negative value from the
 486 surrogate model [104].

487

$$u = \log\left(\frac{z}{(1 + \epsilon)1 - z}\right) \quad (18)$$

$$u = \log(z + 1) \quad (19)$$

488

489 Different indicators are used to quantify the fitting of the model with the validation points: coefficient
 490 of determination (R^2), mean absolute error (MAE), median absolute error (MedAE) and root mean
 491 squared error (RMSE) [97,98]. Equations 28 to 31 give the definition of the indicators.

$$R^2 = 1 - \frac{\sum_i^n (y_i - \hat{y}_i)^2}{\sum_i^n (y_i - \hat{y}_{mean})^2} \quad (20)$$

$$MAE = \frac{1}{n} \sum_i^n |y_i - \hat{y}_i| \quad (21)$$

$$MedAE = median(|y_1 - \hat{y}_1|, \dots, |y_n - \hat{y}_n|) \quad (22)$$

$$RMSE = \sqrt{\frac{1}{n} \sum_i^n (y_i - \hat{y}_i)^2} \quad (23)$$

492 where y is a calculated value from the surrogate and \hat{y} is a value from the Aspen simulations.

493 These indicators are divided by the difference between maximum and minimum of the values they are
 494 measuring. This normalization process results in dimensionless metrics, which can be better understood
 495 and compared across different scenarios. The model is considered validated when its R-squared value
 496 exceeds 97.5% and MedAE is less than 2% after normalization. MedAE was chosen among the different
 497 indicators due to the robustness of this indicator against outliers results.

498 3.2 VPSA and CPU linking.

499 Since the surrogate models of the two processes are independent, it is necessary to define an algorithm
 500 to link the two processes together. For each input array, a steady-state point will be calculated.
 501 Specifically, for a total flow rate and a concentration of CO_2 in the flue gas, when the inputs are fixed,
 502 the VPSA system produces a stream with a certain CO_2 concentration and flow rate that is processed in
 503 the CPU, and the CPU returns a gas flow containing residual CO_2 back to the VPSA inlet, which
 504 modifies the concentration and flow rate of the incoming stream to the VPSA (Figure 6). The system is
 505 considering to be in steady state when the variation in flow rate and concentration of the recycled stream
 506 between the CPU and the VPSA is smaller than a certain tolerance (set to 10^{-3} conserving concentration
 507 and flow rate unit). Section 3 of the supporting information present the cycle steady-state for inlet CO_2
 508 concentration and flow rate of both unit.

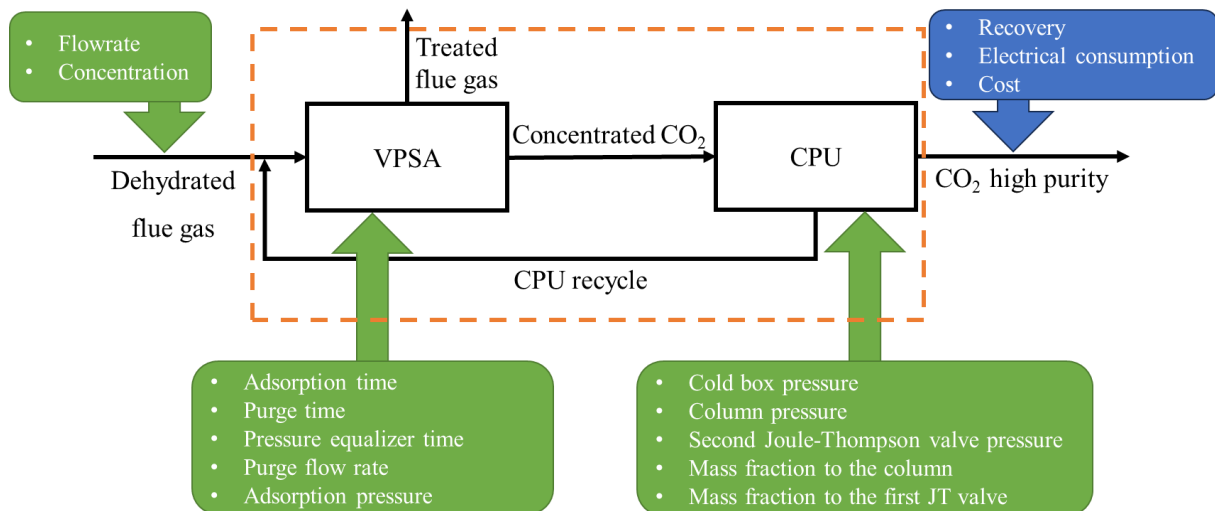


Figure 6: Linking VPSA+CPU with inputs and outputs.

509
510

511 The CO₂ recovery in the coupled process can be calculated as the quotient of the quantity of CO₂
512 captured as it emerges from the CPU in relation to the incoming CO₂ flow prior to its combination with
513 the CPU recycle stream. Furthermore, the electrical consumption of the entire process is the sum of
514 electrical consumption across its constituent processes, and the cost is intricately linked to the CAPEX
515 and OPEX associated with each individual process.

516 3.3 Sensitivity analysis

517 Impacts of the different parameters on the complete unit were studied with a sensitivity analysis by
518 computing the Sobol's total order indices for recovery and electrical consumption. Total order indices
519 indicate relative importance of the different parameters with higher values for the most important
520 parameters [105]. Estimation of indices use a Monte-Carlo process which requires the evaluation of CO₂
521 recovery and electrical consumption for multiple conditions. Surrogate modelling described in section
522 3.2 was used to evaluate the Sobol indices associated with the steady state point of global VPSA and
523 CPU process.

524 The python library Salib [106] was used to evaluate the total order indices with the model of VPSA and
525 CPU developed. To take into account the different constraints between the parameters of the two units,
526 the analysis method was modified according to [107] with an acceptance-rejection sampling method
527 allowing to use the Sobol method for non-rectangular domains ensuring a more accurate representation
528 of the interplay between the parameters of the VPSA and CPU process.

529 3.4 Optimization algorithm

530 The objective of this study is to optimize a complex process with multiple objective functions, resulting
531 in an irregular surface containing local minima. To address this challenge, U-NGSA-III (Unified non-
532 dominated Sorting Genetic Algorithm III) genetic algorithm is chosen as it is known for its effectiveness
533 in handling multi-objective problems [108]. U-NGSA-III builds upon the NGSA-III algorithm and
534 enhances its performance through the introduction of new tournament pressure function that is the
535 selection method of individuals.

536 NGSA-III, an evolution of NGSA-II, brings significant advances to the field of multi-objective
537 optimization. It contains sophisticated mechanisms for preserving diversity, improving exploration and
538 exploitation, and efficiently finding Pareto-optimal solutions. The algorithm uses non-dominated sorting
539 to categorize solutions into distinct Pareto fronts, each representing a group of solutions that cannot be
540 improved in one objective without affecting another.

541 By preserving diversity among solutions, U-NGSA-III provides a comprehensive representation of the
 542 trade-off space that allows decision makers to select the most appropriate solutions based on their
 543 preferences. The algorithm uses genetic operators such as selection, crossover, and mutation to steer the
 544 population toward the Pareto-optimal bounds, allowing efficient exploration and convergence to a
 545 diverse set of optimal solutions.

546 In summary, the choice of U-NGSA-III demonstrates its capability to address the challenges posed by
 547 multi-objective optimization, offering enhanced performance compared to its predecessor, NGSA-II. Its
 548 ability to efficiently explore the Pareto frontiers and maintain diversity among solutions makes it a
 549 valuable tool for tackling complex optimization tasks. To enhance the optimization of the VPSA and
 550 CPU, the Python library Pymoo [109] is employed.

551 4 Results and discussions

552 The surrogate models play a role in approximating and streamlining the complexities of the processes.
 553 Upon successful validation of the surrogate models, the subsequent step involves an analysis of process
 554 optimization for each component. This investigation culminates in a comprehensive assessment of the
 555 coupled process, encompassing both energy and economic considerations. This evaluation provides
 556 insights into the performance and sustainability of the integrated system, offering a complete perspective
 557 on its potential for real-world applications.

558 4.1 Surrogate models building and process analysis

559 4.1.1 VPSA process

560 A large number of successful simulations (namely 5280) have been performed to construct the surrogate
 561 model of the VPSA unit. To improve the calculation time, the Aspen Adsorption process is parallelized
 562 across the 8 cores of the PC. As explained in section 3.1, 4244 simulations have been used to construct
 563 the surrogate model, and 1056 simulations have been used to validate the model. A Kriging model was
 564 constructed using a polynomial function for the deterministic term, and the Matérn (3/2) kernel for the
 565 stochastic term. The model was then validated by using the different indicators presented in section 3.1.
 566 The indicators values for the different results are given in Table 7. CO₂ purity and CO₂ recovery of
 567 VPSA are defined in equation (1) and (2). Equation (6) gives electrical consumption calculation.
 568 Maximum energy consumption of compressor and maximum flow rate of vacuum pump are information
 569 used to calculate the CAPEX of the VPSA.

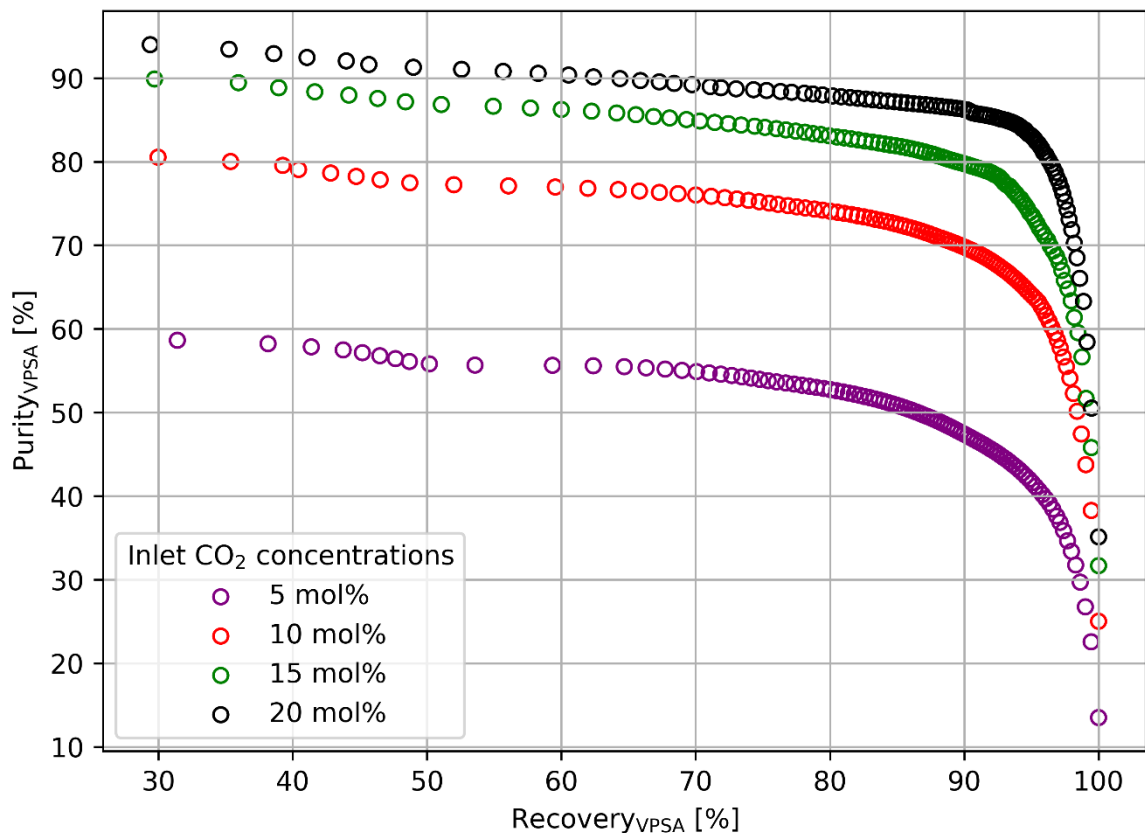
570 *Table 7: Values of indicators for the surrogate model of VPSA.*

	Purity_{VPSA}	Recovery_{VPSA}	Electrical consumption	Maximum energy consumption of compressor	Maximum flow rate of vacuum pump
R ²	97.5%	98.0%	97.8%	99.9%	98.1%
MAE	1.58%	1.39%	1.94%	0.27%	1.94%
RMSE	3.12%	3.71%	3.77%	5.07%	0.03%
MedAE	0.84%	1.57%	0.90%	0.14%	0.13%

571
 572 The values obtained indicate a good representation of the validation points by the surrogate model,
 573 showing a R² value higher than 97.5%, and MedAE (and MAE) lower than 2%. Purity and maximum
 574 energy consumption of energy compressor have a good representation with high R², and low MAE and
 575 MedAE. For Purity, RMSE is higher than MAE and MedAE due to some outlier degrading the value
 576 of this indicator. Recovery and maximum flow rate of vacuum pump have a similar R² value, but other
 577 indicators are higher for the flow rate due to a larger error from the model. Energy consumption is the
 578 least well-represented result of the VPSA surrogate with a R² slightly higher the stop criterion described
 579 in 3.1. Nevertheless, the MedAE is similar to the purity which indicates that the value of R² is diminished
 580 by some outlier which is confirmed by the high value of RMSE.

581 The surrogate model of the VPSA unit was used to evaluate the pareto of VPSA recovery and purity at
 582 different CO₂ concentrations in the inlet flue gas for a flow rate of 14,000 Nm³.h⁻¹. Pareto plot is given
 583 in Figure 7 for a CO₂ concentration of 5, 10 ,15 and 20%. As observed, the VPSA unit can reach high
 584 recovery for all CO₂ concentrations. The maximum CO₂ purity obtained in the unit increases with the
 585 inlet CO₂ concentration. For all CO₂ inlet concentrations, a sharp decrease of purity is observed as the
 586 VPSA recovery increases. The decrease of purity is stepper between 95 and 100% recovery for the
 587 VPSA due to an increase of purge time to recover all the CO₂ adsorbed.

588 An observation reveals that, at a 5% CO₂ concentration level, only recoveries lower than 85% allow to
 589 reach the value of 50 mol% of CO₂ for the CPU. This implies that the current configuration may render
 590 this flue gas treatment impossible to reach the target of 95% recovery and purity. Nevertheless, it is
 591 imperative to account for the impact of the CPU recycle, as it has the potential to increase the feed
 592 stream's concentration, thereby increasing the possibility of achieving higher purity levels at the VPSA's
 593 outlet.



594 Figure 7: Pareto plot of the VPSA unit for different CO₂ molar fractions in the flue gas with a flow rate of 14,000 Nm³.h⁻¹.
 595

596 4.1.2 CPU process

597 Among the CPU inputs used (detailed in Table 6) to build the surrogate of the CPU process, some of
 598 them cannot be considered because they give results outside of the constraints. Among 24,200 points
 599 tested, 2,628 have satisfied the constraints. Thus 2102 points are used to build the surrogate model and
 600 526 have been used to validate the model. A Kriging model was constructed using a polynomial function
 601 for the deterministic term, and the Gaussian for the stochastic term. The model was then validated by
 602 using the different indicators presented in section 3.1. The indicators values for the different results are
 603 given in Table 8. Equation (6) gives electrical consumption calculation for the CPU. Flow rate and CO₂
 604 concentration to VPSA are the information of the recycle stream that go to VPSA. CAPEX is calculated
 605 for the complete CPU process and the cooling water flow rate is part of utility in the OPEX.

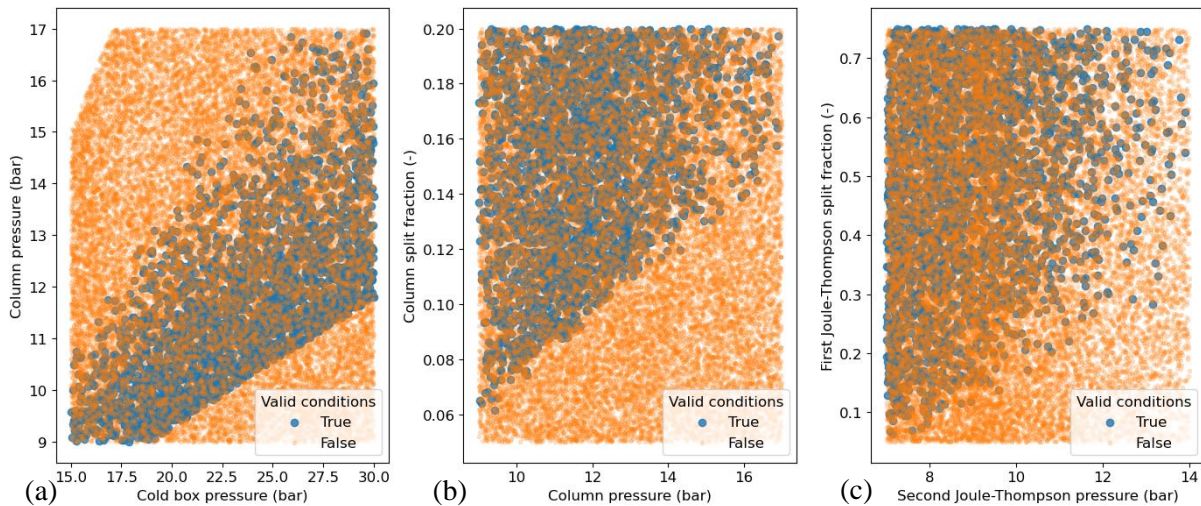
Table 8: Value of indicators for the surrogate model of CPU.

	Electrical consumption	Flow rate to VPSA	CO ₂ concentration to VPSA	CAPEX	Cooling water
R ²	99.9%	99.9%	99.9%	99.9%	99.9%
MAE	0.1%	0.1%	0.1%	0.1%	0.6%
RMSE	0.5%	0.1%	0.1%	0.2%	1.0%
MedAE	0.1%	0.1%	0.1%	0.1%	0.3%

607

608 The calculated indicators show an excellent mathematical representation of the CPU modelled in Aspen
 609 Plus® V14. During the data analysis, attention was given to ensure an appropriate distribution of points
 610 within the defined bounds for various parameters. This analysis revealed distinct physical constraints
 611 associated with relationships between two specific parameters. Figure 8 highlights three pairs of
 612 parameters that exhibit these physical limits. It shows comparisons among the 24,200 simulations,
 613 categorizing the points that either meet or fail to meet these constraints.

614 Figure 8 (a) illustrates the relationship between the cold box pressure and the column pressure. The
 615 limit in the upper-left corner is associated with insufficient cooling input into the system, while the one
 616 in the bottom-right corner is linked to excessive expansion between the two pressures, causing the stream
 617 to drop below -54 °C. Figure 8 (b) relates column pressure to the mass fraction returning to it. If the
 618 pressure is too high and the CO₂ vapor flow at the bottom of the column is too low, this leads to
 619 hydrodynamic column issues. Figure 8 (c) connects the pressure of the second Joule-Thompson
 620 expansion with the mass fraction going to the first Joule-Thompson expansion. If there is insufficient
 621 flow to this expansion and the pressure drop in the second expansion is too low, there is a lack of cold
 622 flow to the cold box. These limits are incorporated during optimization by adding constraints to prevent
 623 the system from going beyond what is physically possible.



624

625

626

Figure 8: Physical limits driven by conditions in the process between parameters (a) Cold box pressure/Column pressure –
 (b) Column pressure/Column split fraction – (c) Second Joule-Thompson pressure/First Joule-Thompson split fraction.

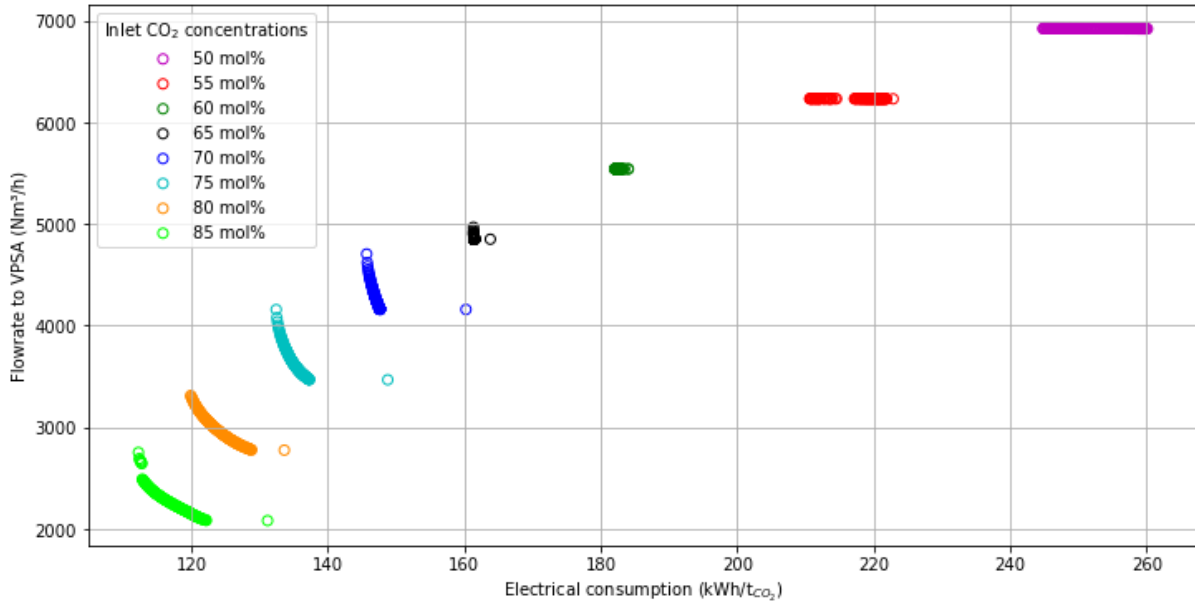
627 Optimizing the CPU with an inlet flow rate of 10,000 Nm³.h⁻¹ and varying concentrations ranging from
 628 50 to 85 mol% CO₂ demonstrates an interesting trend (Figure 9). As the CO₂ concentration in the feed
 629 from the VPSA increases, the electrical consumption is decreasing, which presents a promising energy-
 630 saving prospect for the CPU. These findings are in line with the broader observations made across
 631 various capture units, all of which point towards reduced electrical consumption as CO₂ concentrations
 632 rise.

633 Furthermore, an interesting correlation emerges in terms of the recycled flow. This flow is directly
 634 linked to the decreasing concentration of nitrogen within the system. The reducing nitrogen

635 concentration implies a reduction in the volume of non-condensable components exiting the cold box
636 during the flash separation process from the liquid CO₂.

637 By definition, the higher the concentration of CO₂ in the VPSA feed, the more energetically
638 advantageous it becomes for the CPU. However, in our quest for optimization, it remains crucial to
639 determine the precise threshold at which these two processes, VPSA and CPU, reach their optimal
640 balance, ensuring the most efficient and energy-effective operation.

641



642
643 *Figure 9: Pareto plot of optimization between electrical consumption and flow rate to VPSA for a stream of 10,000 Nm³.h⁻¹*
644 *at different inlet CO₂ concentrations.*

645 After analyzing the parameters used for optimizing CPU performance, some interesting trends emerge
646 regarding electricity consumption: (i) when the pressure in the cold box decreases, the electrical
647 consumption also decreases, while the flow rate towards the VPSA unit increases, (ii) the cooling
648 temperature of the flue gas is constant and (iii) thanks to the higher pressures operation, more CO₂ turns
649 into a liquid form resulting in a lower flow rate to the VPSA unit.

650 The column pressure tends to approach its limit to the cold box pressure reducing the energy needed to
651 recompress vapor from the column. Another key factor of optimization involves the minimization of the
652 mass fraction directed towards the column for the desorption. This approach ensures an optimal flow
653 rate to operate the column while simultaneously mitigating product loss, particularly with regards to
654 CO₂ recirculation.

655 Additionally, optimizing the performance of the second Joule-Thompson valve is also important for
656 achieving the lowest electrical consumption while maintaining a robust refrigeration output.
657 Simultaneously, minimizing the mass fraction allocated to the first Joule-Thompson valve, which
658 operates at the lowest pressure, is paramount for achieving optimal electrical consumption.

659 In conclusion, this comprehensive analysis reveals intricate relationships between various parameters
660 and electrical consumption in CPU optimization. These findings highlight the importance of carefully
661 tuning these parameters to strike a balance between process performance and energy efficiency.

662 4.2 Sensitivity analysis

663 Sobol's total order indices for the coupling were determined for CO₂ recovery and energy consumption
664 with surrogate models. Results obtained are represented in Figure 10 for different CO₂ concentrations

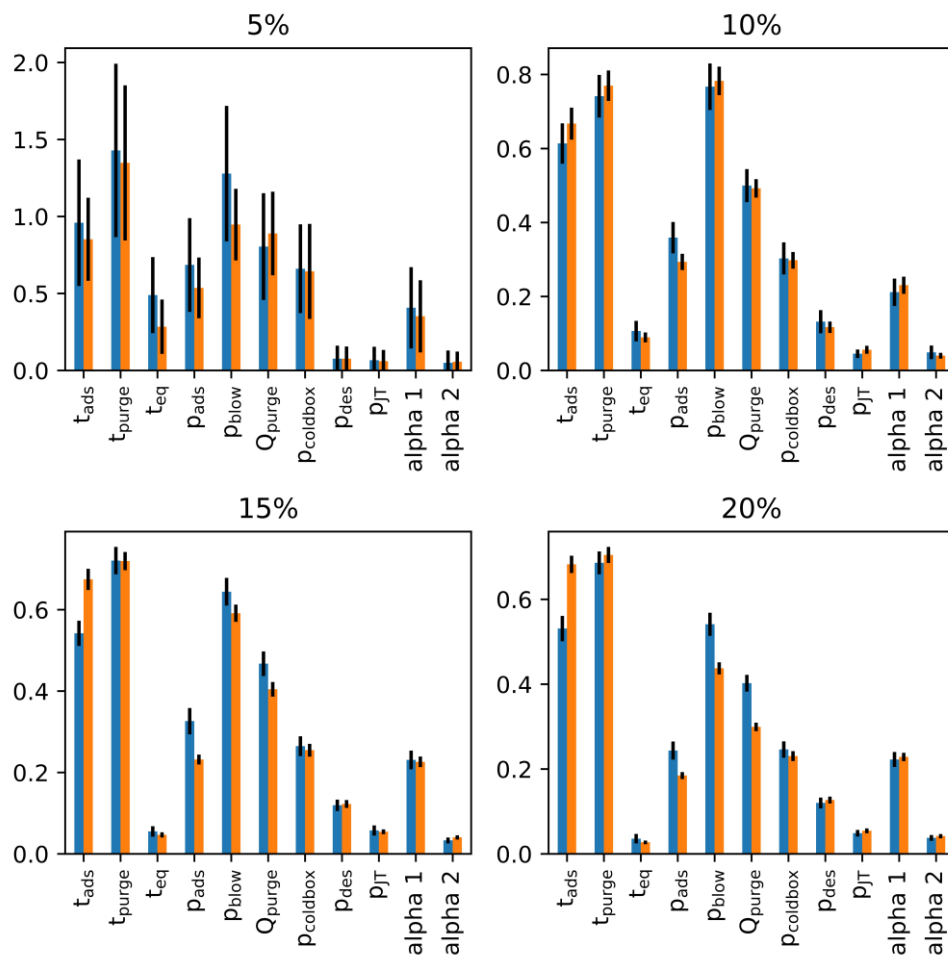
665 in the flue gas. Uncertainties indices for the 5% case are higher due to the purity requirement of 50%
666 for the CPU leading to numerous samples out of bounds compared to higher CO₂ concentration.

667 For all the CO₂ concentrations, adsorption and purge times are two important parameters with high
668 indices (around 0.8) for both recovery and energy consumption except for the 20% case where the
669 indices of adsorption time are lower for recovery than energy consumption. The link with purge time is
670 straightforward since an increase of purge time will lead to a better desorption of CO₂ and thus a better
671 recovery but also to an increase of energy consumption and decrease of purity due to the nitrogen flux
672 which can affect the CPU performance. Adsorption time also change the amount of CO₂ inside the
673 adsorption bed which can influence recovery and purity of VPSA unit. Adsorption time and purge time
674 can also have a combined effect since blowdown time is equal to adsorption time less purge time. A
675 higher blowdown time can increase the amount of CO₂ recovered from the adsorption bed. Nevertheless,
676 total order indices do not give any information on interactions between parameters. As expected,
677 equalization time only affects the results for the 5% case and has very low indices for higher CO₂
678 concentrations, this step being dedicated to energy recovery. Due to the minimum purity required for
679 CPU, the adsorption pressure for the 5% case is always close to 3 bar which can explain why the pressure
680 equalization is more important in this case to reduce the energy consumption. The effect on recovery
681 can be caused by the change of flow rate in the VPSA inlet due to the equalization time (see section
682 2.1.1). This effect could be less important for higher CO₂ concentrations. Effect of adsorption pressure
683 on recovery and energy consumption can easily be interpreted as the increase of adsorbed amount in
684 zeolite 13X with the increase of pressure which increase the recovery. In addition, the rise of pressure
685 increases the power of the feed compressor in the VPSA unit. The effect of adsorption pressure on
686 recovery decreases as the CO₂ concentration in the flue gas increases due to the shape of adsorption
687 isotherms having a plateau at higher partial pressure of CO₂. Therefore, an increase of adsorption
688 pressure is less impacting on the performance of the VPSA unit. Blowdown pressure is more important
689 than adsorption pressure for both recovery and purity. In fact, this parameter is as important as the
690 adsorption time or purge time. The impact of blowdown pressure on recovery can be explained by the
691 sharp change of adsorbed amount at low pressure on the CO₂ adsorption isotherm of zeolite 13X.
692 Therefore, low blowdown pressure leads to higher working capacity in the bed which increases the
693 performance of the VPSA process. Nevertheless, decreasing blowdown pressure increases the energy
694 consumption of the process. Since the efficiency of the vacuum pump is lower than the efficiency of
695 compressor, the effect of blowdown pressure is more important on the energy consumption of the
696 process than adsorption pressure. Purge flow rate is an important parameter for all the CO₂ concentration
697 with indices higher than adsorption pressure. An increase of purge flow rate allows to recover more CO₂
698 from the adsorption column but decrease the purity. This affects the performance of the CPU and
699 increase the flow rate across the vacuum pump of the VPSA unit and the CPU compressors which
700 increase the overall energy consumption.

701 From the CPU side, cold box pressure is one of the key variables at 5% CO₂ concentration (0.6) and
702 becomes less important at higher CO₂ concentration. The effect of this parameter on energy consumption
703 is easily understood since a rise of pressure increases the energy consumed by the multi-stage
704 compressor of the CPU. This pressure also determines the liquid-vapor equilibrium of the mixture in the
705 flash separator in the CPU, and thus modify the recirculated flow send to the VPSA units. This is
706 particularly critical for the 5% case where the recirculated flow can strongly enhance the performance
707 of VPSA by increasing the CO₂ concentration of the flue gas. The desorption pressure has a constant
708 effect (0.15) on recovery and energy consumption for all the CO₂ concentrations studied. Desorption
709 pressure directly affects the compression ratio between compressors C3 and C4 (see Figure 4) and thus
710 energy consumption of the CPU. This pressure can also slightly change the vaporization temperature in
711 the desorption column, impacting the recirculating flux to the exchanger and the overall equilibrium in
712 the flash which could explain the impact on recovery. The Joule-Thompson expansion pressure is one
713 of the less impacting parameters (less than 0.1). This expansion is used to provide the cold source for
714 the CPU, but the pressure of this step does not affect the overall efficiency of the coupling between

715 VPSA and CPU. The two last parameters are the fraction from the desorption column used for stripping
 716 (α_1) and the fraction send to the Joule-Thompson valve (α_2). The first fraction plays an important role in
 717 the recovery and energy consumption of the coupling with an index of more than 0.2 which is as
 718 important as cold box pressure for 10, 15 and 20% case. The amount of gas used in the desorption
 719 column will directly impact the energy consumption of the CPU with an increase of flow rate in
 720 compressor C4 (Figure 4), and will indirectly impact the recovery and energy consumption by changing
 721 the liquid-vapor equilibrium in the flash unit. Parameter α_2 has a low and similar impact to the pressure
 722 of the Joule-Thompson expansion and will affect the cold source of the CPU unit.

723 In a general way, recoveries and energy consumptions seem to be mainly driven by the adsorption time,
 724 purge time, and blowdown pressure (indices around 0.6). For higher CO₂ concentration the other main
 725 variables are adsorption pressure, purge flow rate, cold box pressure, desorption pressure, and α_1 with
 726 indices between 0.2 and 0.4. Equalization time, Joule-Thompson expansion pressure and α_2 have a
 727 limited effect on the recoveries and energy consumptions of this unit. These variables could be
 728 eliminated in a parametric study with a limited impact if a similar unit must be studied.



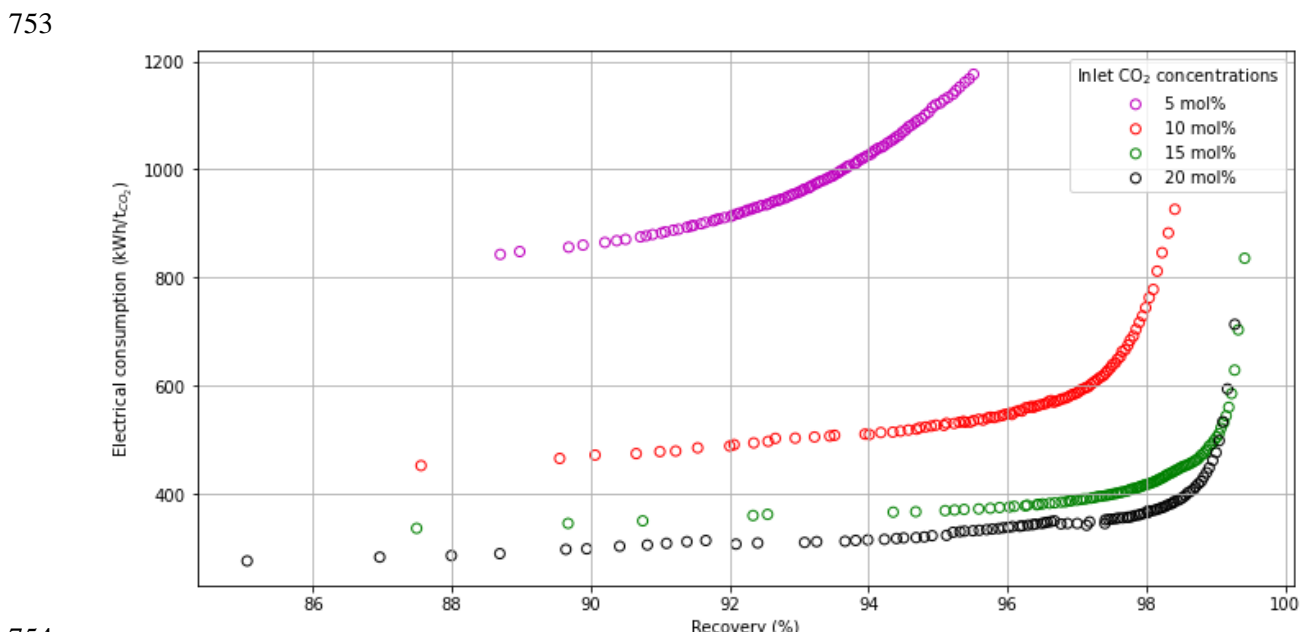
729
 730 *Figure 10: Sobol's total order indices determined for recovery (blue) and energy consumption (orange) obtained for the*
 731 *coupling of VPSA and CPU with a CO₂ molar fraction in the flue gas of 5, 10, 15 and 20% for a flow rate of 70,000 Nm³.h⁻¹.*

732 4.3 Multi-objective optimization of the complete process

733 With both surrogate models now effectively established and validated, the optimization for the VPSA +
 734 CPU coupling can be performed. The focus will be on optimizing both recovery and electrical
 735 consumption. The primary objective is to maximize the recovery process while concurrently minimizing
 736 electrical consumption. A range of inlet concentrations, varying from 5 to 20 mol% with 5 mol%
 737 increments, for a flue gas of 70,000 Nm³.h⁻¹, will be examined.

738 Figure 11 displays the results of the combined process optimization. The higher the concentration of
 739 CO₂ in the inlet flue gas, the less electricity is consumed. To achieve the highest recovery rates, it is
 740 necessary to increase electrical consumption. As the results demonstrate, recovery rates approaching
 741 99% are achievable thanks to VPSA technology. Therefore, it is reasonable to inquire about the desired
 742 recovery rate. To address this question, it is essential to consider the electricity prices and carbon taxes
 743 in order to determine the optimum recovery point. Gaps in the pareto front come from the algorithm
 744 approach of the NGS-III that provides results close to the optimal point. In addition, the pareto plot
 745 between energy consumption and productivity is represented in Section 4 of Supporting Information.

746 A noticeable discrepancy in electrical consumption is observed for the 5% concentration compared to
 747 the others. This variance is attributed to a more substantial compression of flue gases at the entrance of
 748 the VPSA, and low blowdown pressure to increase the working capacity of the VPSA pilot enhancing
 749 adsorption of CO₂ with the same amount of adsorbent. Furthermore, the requirement to achieve a 50%
 750 CO₂ purity imposes operating conditions that are not particularly energy-optimal for the VPSA. This
 751 constraint also results in an inability to attain a 99% recovery, as it is no longer valid beyond a 95.5%
 752 recovery threshold.



754 *Figure 11: Pareto plot of the optimization between electrical consumption and global CO₂ recovery for different inlet CO₂*
 755 *concentrations.*
 756

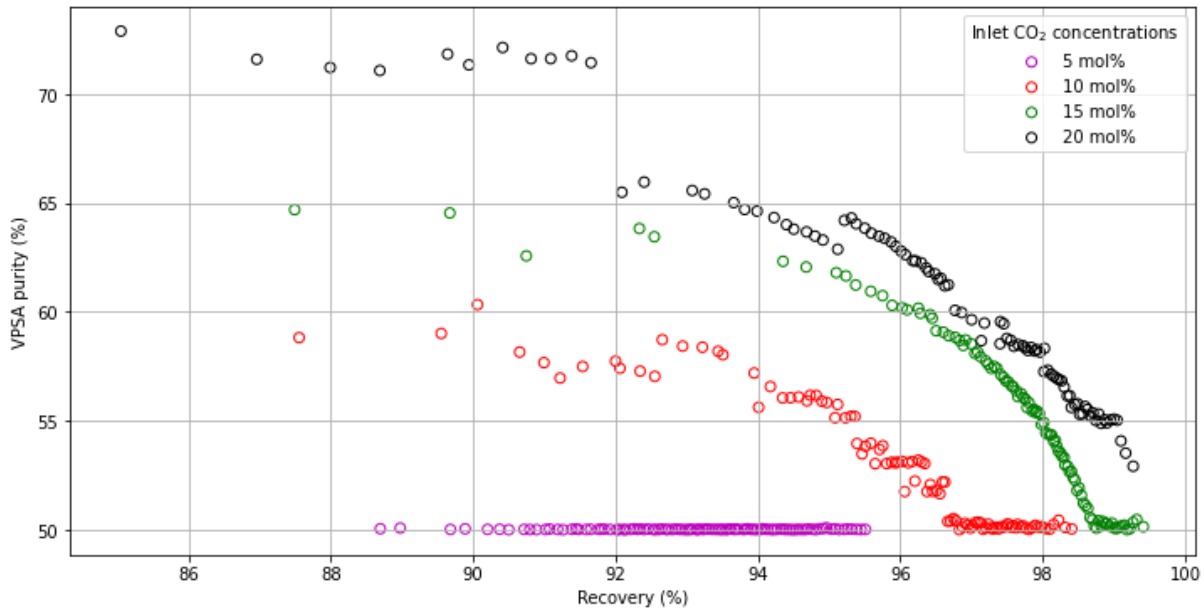
757 When analyzing the variation of CPU parameters, it becomes evident that the pressure in the cold box
 758 is relatively low, between 17 and 22 bar, compared to the CPU-alone optimization. This observation
 759 suggests that it is advantageous to increase the flow rate directed towards the VPSA unit, concurrently
 760 enhancing the concentration of CO₂ in this stream. Consequently, this strategy leads to a greater
 761 reduction in consumption on the VPSA side, thanks to a stream that is enriched in CO₂ compared to the
 762 initial flue gas, despite an overall increase in the flow through the VPSA.

763 In general, the other parameters exhibit similar trends as seen in the standalone CPU optimization,
 764 although with relatively consistent outcomes throughout the recovery evolution. Thus, it is likely more
 765 relevant to focus on optimizing the VPSA, which appears to maintain a relatively stable operational
 766 point. A comprehensive study of the parameter impact will subsequently be conducted to further delve
 767 into this discussion.

768 By analyzing the purity of the output from the VPSA in relation to recovery (Figure 12), it becomes
 769 evident that purity is highest at lower recovery levels which correspond to lower electrical consumption
 770 rates. This phenomenon is characteristic of VPSA systems, where an increase in purity is accompanied

771 by a decrease in recovery. To achieve recovery exceeding 90%, it is therefore necessary to reduce the
 772 purity at the VPSA output, resulting in an increase in CPU-side consumption. The constraint of
 773 minimum 50% of purity from the VPSA unit is also visible in Figure 12, especially for the 5% case.

774



775
 776 *Figure 12: CO₂ purity of the output from the VPSA as a function of CO₂ recovery for different inlet CO₂ concentrations.*

777 The volumetric flow rate entering the CPU experiences an upward trend corresponding to increasing
 778 concentrations (Table 9). This increment is attributable to the increase of CO₂ amount in the flue gas
 779 which increase the volume of gas sent to the CPU unit for a same recovery and purity of the VPSA unit.
 780 In addition, a correlation between flow rate and recovery can be found, where a higher recovery results
 781 in more CO₂ being captured by the VPSA and subsequently directed to the CPU.

782 *Table 9: Inlet and outlet from VPSA and CPU for different inlet CO₂ concentrations.*

		5 mol%		10 mol%		15 mol%		20 mol%	
		Min	Max	Min	Max	Min	Max	Min	Max
CPU inlet flow rate	Nm ³ .h ⁻¹	6,960	7,570	11,960	16,940	16,600	28,850	18,950	38,450
Recycled flow rate to VPSA	Nm ³ .h ⁻¹	6,000	7,170	9,860	16,180	9,200	22,000	10,200	30,000
VPSA inlet concentration	CO ₂ mol%	7.6	7.8	13.6	14.9	18.6	21.6	22.4	26.2

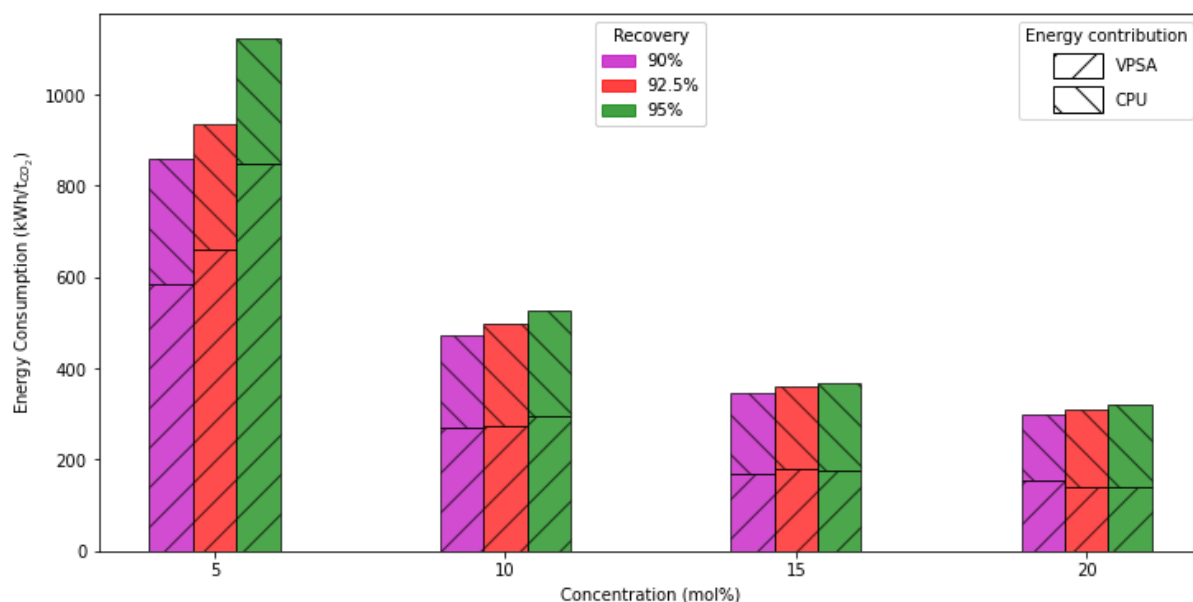
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784 The recycled stream directed back to the VPSA is enriched with a concentration ranging from 30 to 50
 785 mol%. The post-cold box temperature of the flue gas is carefully set to adhere to the minimal temperature
 786 threshold, ensuring the prevention of dry ice formation. Consequently, the liquid-vapor equilibrium at
 787 the flash is mainly influenced by the pressure of the flue gas. At lower pressures, the vapor phase exhibits
 788 the highest concentration of CO₂. The CO₂ concentration in the gas stream entering the CPU from the
 789 VPSA plays a fundamental role in determining, at a given pressure, the volumetric flow rate returning
 790 to the VPSA (Table 9). This nuanced understanding of the interdependencies between pressure,
 791 temperature, and concentration elucidates the intricate dynamics of the system, offering valuable
 792 insights for further optimization and refinement.

793 Hence, the concentration at the VPSA inlet is enhanced through this recycling stream (Table 9). This
 794 augmentation significantly improves the VPSA performance by elevating the partial pressure of CO₂,
 795 thereby improving the adsorption process. This enhancement permits to achieve recoveries exceeding
 796 90% across all cases, consequently attaining a purity of 50% at the VPSA outlet.

797 An interesting aspect that emerges from this optimization work is that there are several points beyond
 798 the conventional recovery rate of 90%. A more detailed study of specific scenarios can be conducted by
 799 considering different recovery levels such as 90%, 92.5% and 95%. Figure 13 compares the electrical
 800 consumption from VPSA and that from the CPU. For the 5 mol% case, VPSA consumes significantly
 801 more than the CPU, accounting for around 60% of the total consumption. For 10 and 15 mol% recovery,
 802 the ratio is smaller and close to 50%. For the 20 mol%, the situation reverses, with the CPU becoming
 803 the more consumptive component. Furthermore, as the desired recovery rate increases, the ratio of CPU
 804 consumption to VPSA consumption also rises. This observation is ultimately linked to the purity of the
 805 output stream from VPSA, which decreases, as presented in Figure 12.

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Figure 13: Energy consumption of VPSA and CPU at several recovery for different inlet CO₂ concentrations.

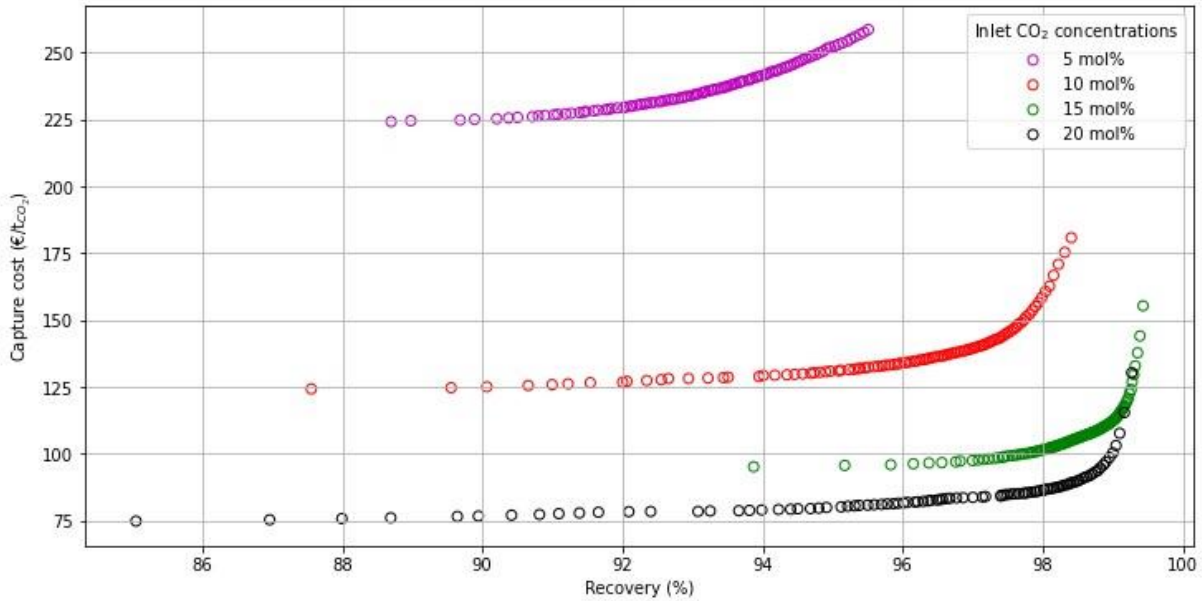
809 4.3.1 Techno-economic analysis

810 The main objective of this work is minimizing the electrical consumption of the entire VPSA-CPU
 811 process. For this type of installations, operational costs significantly outweigh fixed annual costs.
 812 Nevertheless, it is imperative to conduct cost estimations to assess the feasibility of this process and
 813 enable meaningful comparisons with other methods.

814 Being highly dependent on electrical consumption, the price of electricity per kilowatt-hour will have a
 815 substantial impact on the cost. Carbon taxation, on the other hand, serves to isolate an optimal recovery
 816 point since it is directly linked to the quantity of emitted CO₂.

817 Figure 14 illustrates the capture costs as a function of CO₂ recovery. It is noticeable that there is a
 818 substantial gap between the costs for a flue gas concentration of 5 CO₂ mol% compared to the other
 819 concentrations. These costs follow the same trend as the electrical consumption curves. This is attributed
 820 to the significant proportion of the cost allocated to electrical consumption, accounting for more than
 821 90% when electricity costs are considered equal to 100 €.MWh⁻¹. Similar to Figure 11, the difference is
 822 more pronounced for the 5% concentration since the costs are primarily driven by electrical
 823 consumption. As for electricity consumption, the cost sharply increases when the recovery approaches
 824 99% due to the diminution of purity.

825



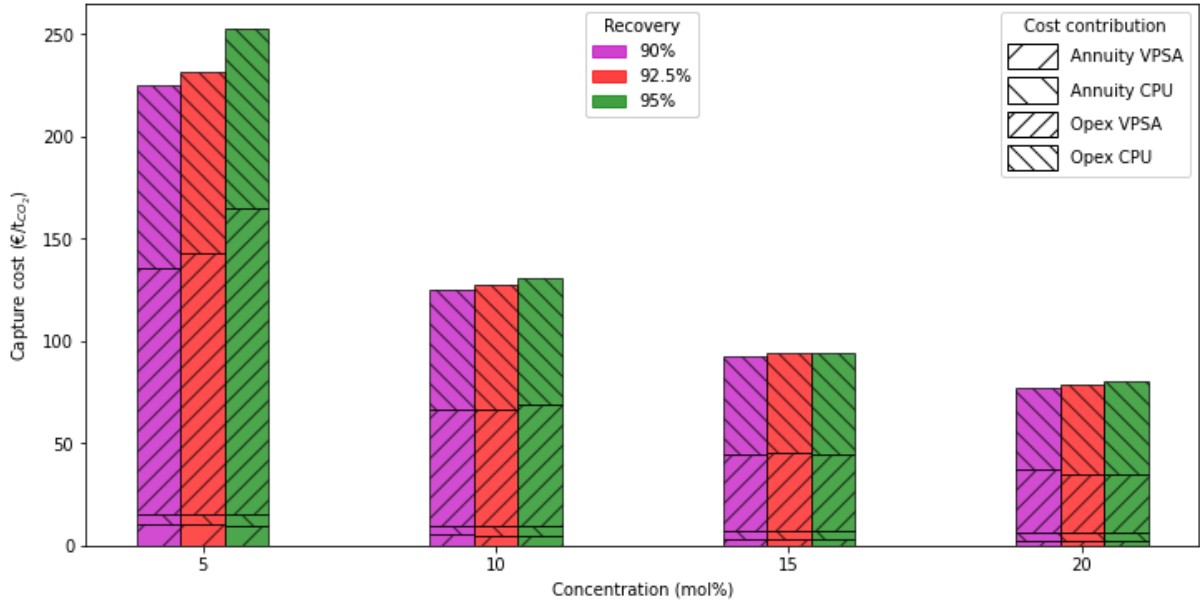
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827

Figure 14: CO₂ capture cost as a function of CO₂ recovery for different inlet CO₂ concentrations.

828 Figure 15 illustrates the diverse contributions of CAPEX and OPEX for both the VPSA and CPU units.
829 In the overall cost structure, the CAPEX component constitutes a noteworthy portion, ranging between
830 5% and 10%. Notably, for the 5% concentration, the VPSA CAPEX surpasses the CPU one, which
831 differs from other cases where the CPU's CAPEX stands as the most substantial contribution.

832 Turning attention to OPEX, a pronounced pattern emerges. The preeminent share of costs emanates
833 from the VPSA, particularly within the concentration range of 5% to 10%. However, as the
834 concentration escalates to 15 and 20%, the CPU assumes a dominant role in driving overall operational
835 expenses. This shift in the cost dynamics can be attributed to the pronounced impact of electricity costs
836 within the operational expenditure framework.

837 Understanding the nuanced interplay between CAPEX and OPEX contributions is crucial for optimizing
838 the economic viability of the integrated VPSA and CPU system. It not only underscores the financial
839 implications of different concentration scenarios but also emphasizes the importance of addressing
840 specific cost drivers, particularly electricity expenses, to enhance the economic efficiency of the overall
841 carbon capture process.



843
844
845

Figure 15: CAPEX annualized (annuity) and OPEX contribution of VPSA and CPU at several for different inlet CO₂ concentrations.

846 Considering the carbon tax for uncaptured CO₂, an optimum can be determined for a CO₂ recovery
847 value. Per ton of CO₂, the total cost, including the CO₂ capture costs and the carbon tax, can therefore
848 be calculated as follows:

$$Total\ cost = \frac{CO_2\ recovery}{100} CO_2\ capture\ cost + \frac{(100 - CO_2\ recovery)}{100} carbon\ tax \quad (24)$$

849 The evolution of total cost as a function of recovery and carbon tax for various concentrations is
850 presented in Figure 16. During 2023, carbon tax of EU-ETS varying between 77.39 and 100.34 €·tCO₂⁻¹
851 [110]. The interval of the carbon tax is considered between 70 to 130 €·tCO₂⁻¹. Different scenarios emerge
852 based on the flue gas CO₂ concentration to determine the financially optimal recovery. Considering an
853 electricity price of 100 €·MWh⁻¹, the cost optimum is below 90% recovery for the different cases. As
854 the carbon tax rate increases, the optimum recovery rate tends to approach higher levels.

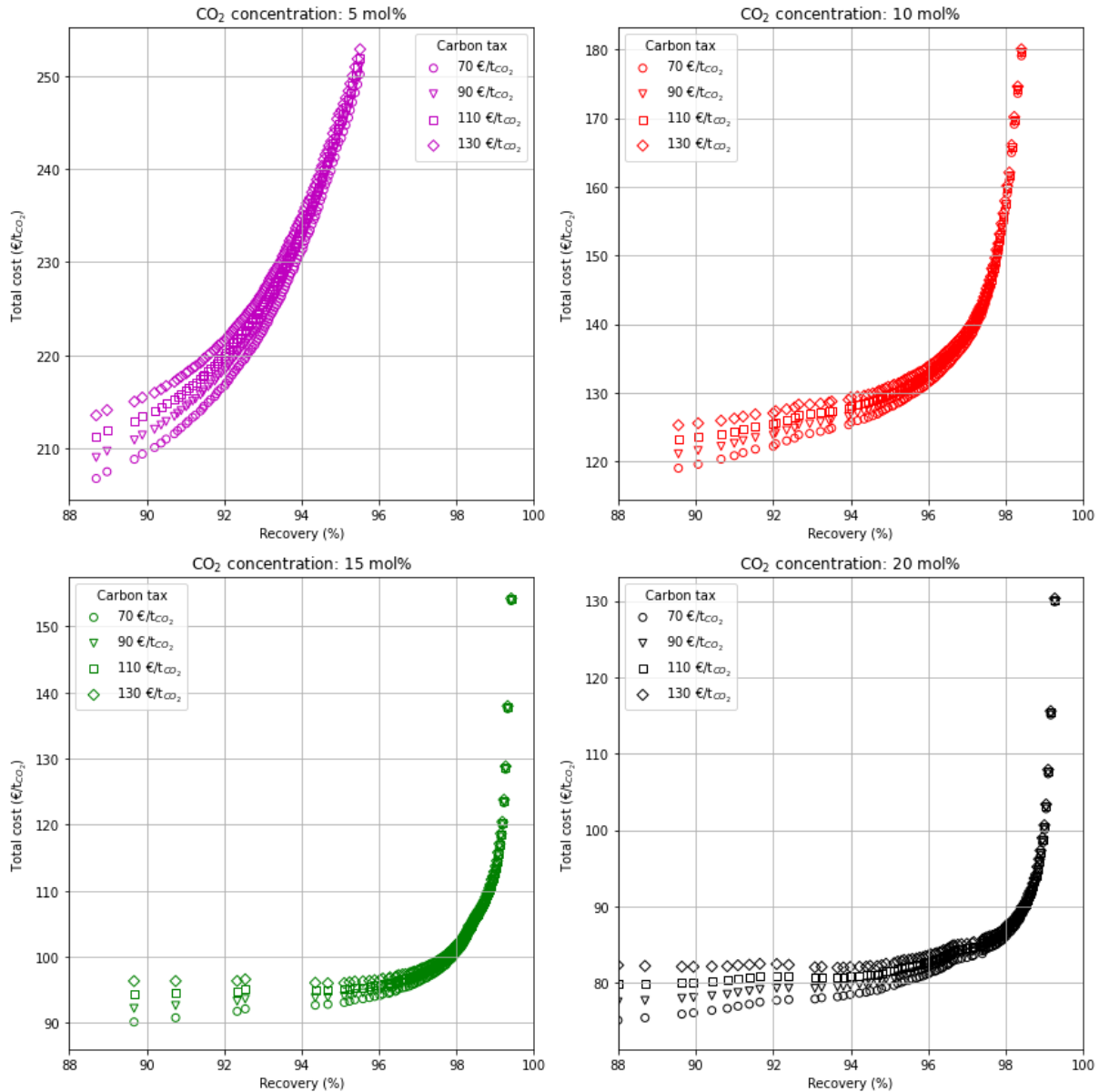


Figure 16: Evolution of total cost as a function of CO₂ recovery and carbon tax for different inlet CO₂ concentrations (electricity price: 100 €/MWh⁻¹).

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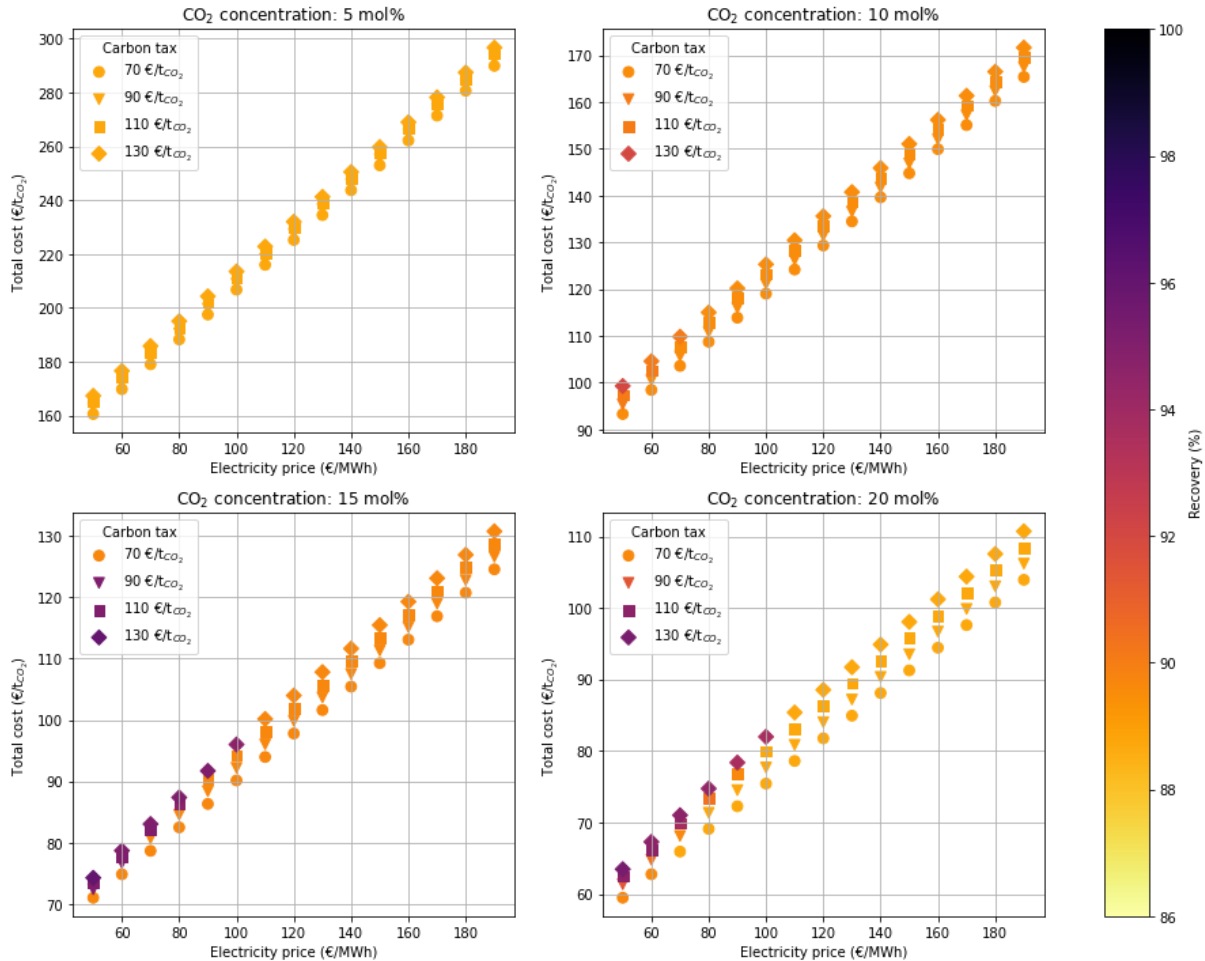
859 4.3.2 Electricity price variation

860 The fluctuation of electricity prices is a topic of utmost importance in the fields of energy and economics.
861 This variability is influenced by a multitude of complex factors, including the availability of energy
862 resources, the production costs, the demand, the government policies, the international energy market
863 fluctuations, and the technological advancements. In this study, the process under investigation
864 consumes only electricity. To examine the impact of electricity prices on the total process cost, it was
865 varied from 50 to 200 €/MWh. Electricity price variation will have an important impact on the optimum
866 recovery at minimal total cost. Figure 17 displays the minimum total cost according to equation (24) as
867 a function of carbon tax and CO₂ concentration within this range of electricity prices. Notably, the
868 optimal recovery rate is higher for lower electricity prices.

869 For the 5% concentration, this technology demonstrates a substantial cost disadvantage over the carbon
870 tax. Consequently, it is presently not prudent to consider such installations for concentrations at this low
871 level. This process become interesting for 10% concentration for a high carbon tax (> 130 €/t_{CO2}) and a

872 low electricity price ($< 50 \text{ €/MWh}$). However, for other concentrations, if the electricity cost remains
 873 below 100 €/MWh^{-1} and the carbon tax is at least 100 €/tCO_2^{-1} , this technology proves to be relatively
 874 compelling. Furthermore, achieving a recovery rate exceeding 90% remains economically viable and
 875 attractive.

876



877
 878 *Figure 17: Optimum total cost for several carbon tax in function of the electricity price and the CO₂ inlet concentrations.*

879 **4.3.3 Environmental impact of the electricity source**

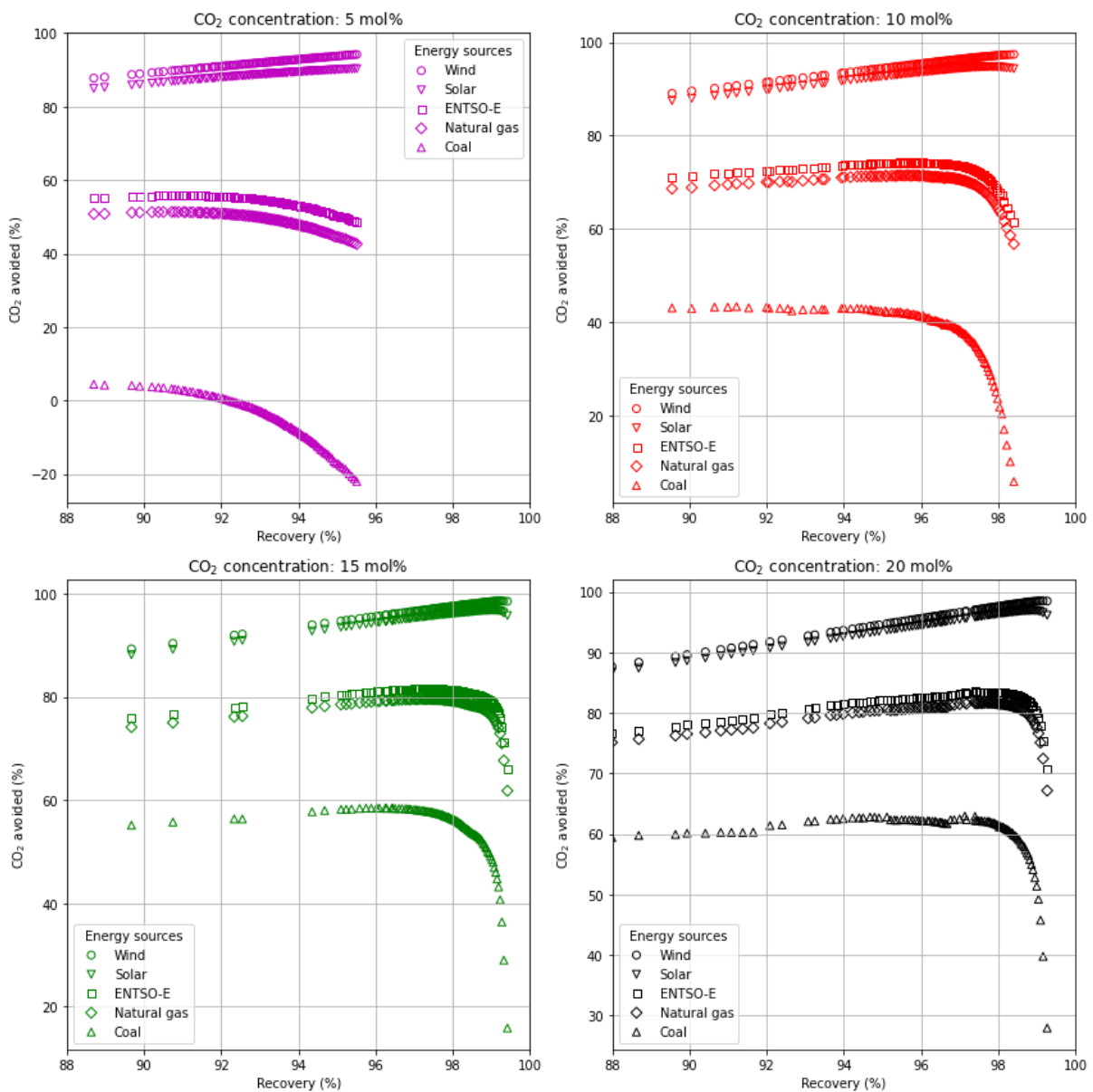
880 The environmental impact, in terms of CO₂ avoided, of a fully electric carbon capture unit is assessed
 881 considering diverse electricity sources. The incorporation of an integrated electric-driven carbon capture
 882 system signifies a pivotal advancement in sustainable technology. The comprehensive analysis
 883 encompasses an evaluation of the environmental ramifications associated with the electricity sources
 884 powering the carbon capture unit. This investigation serves to elucidate the broader environmental
 885 implications of deploying electric-based carbon capture technologies and emphasizes the critical
 886 significance of opting for environmentally sound energy sources to augment the overall sustainability
 887 of carbon capture processes. Conventional sources, including coal, natural gas as well as renewable
 888 alternatives such as wind are scrutinized. Furthermore, the European electricity mix (ENTSO-E) is
 889 considered in the analysis to assess the impact on current energy producers. Solar production emissions
 890 are close to the wind production emissions.

891 Figure 18 illustrates the dynamic trajectory of CO₂ avoided, representing the captured CO₂ minus the
 892 emissions associated with electricity production. This is normalized against the total quantity of CO₂
 893 present in the initial flue gases.

$$CO_2 \text{ avoided} = \frac{CO_2 \text{ captured} - CO_2 \text{ emitted by power production}}{CO_2 \text{ flue gas}} \quad (25)$$

894 Across various concentrations, the influence of a purely wind-powered source on recovery is negligible,
 895 resulting in CO_2 avoided levels closely mirroring the recovery rates. Emissions linked to the European
 896 electricity mix closely approximate those of a natural gas power plant. The trend in CO_2 avoided is
 897 capped at over 98% for different concentrations. Notably, at a 90% CO_2 recovery rate, there is a
 898 discernible decrease of 34%, 18%, 13%, and 11% attributable to emissions from the European mix for
 899 concentrations ranging from 5% to 20%, respectively. For the different cases, a peak in CO_2 avoided
 900 signifies that reaching higher recovery levels, necessitating increased energy input, may not be the most
 901 optimal scenario when the energy source is highly polluting. For the coal at 5 mol% concentration, the
 902 values of CO_2 avoided are relatively compromised compared to the initial recovery rates, showing a
 903 higher production of CO_2 than all the captured CO_2 due to important electricity consumption for
 904 recovery higher than 92%.

905



906
 907 *Figure 18: CO_2 avoided as a function of recovery and carbon tax for different inlet CO_2 concentrations. (Emissions factor of*
 908 *electricity ($kg_{CO_2} \cdot kWh^{-1}$): Wind = 0.011; European Network of Transmission System Operators (ENTSO-E) = 0.399; Natural*
 909 *gas = 0.450; Coal = 1.000)*

910 5 Conclusion

911 The present study investigates the integration of a vacuum pressure swing adsorption process and a
912 carbon purification unit for a hybrid CO₂ capture plant. This approach offers significant advantages,
913 including a high CO₂ recovery facilitated by VPSA and the production of CO₂ with high purity thanks
914 to CPU considering various inlet CO₂ concentrations ranging from 5% to 20%. What makes this process
915 particularly appealing is its reliance on electricity, ensuring a sustainable and environmentally friendly
916 operation and its production of CO₂ matching with all specification needed for CO₂ transportation.

917 The use of surrogate models for optimization allowed to explore various objectives, such as energy,
918 cost, and CO₂ recovery. The optimization process reveals the intricate interplay between inlet
919 concentrations, recovery rates, and electrical consumption. Notably, the study identifies the trade-off
920 between recovery and electricity consumption, emphasizing the need to balance these factors to achieve
921 an economically viable and environmentally effective carbon capture process. A recovery exceeding
922 90% can be achieved across different flue gas concentrations. Furthermore, the electrical consumption
923 decreases as the CO₂ content in the feed gas increases, providing a valuable insight into energy
924 efficiency.

925 The techno-economic analysis emphasizes the significance of minimizing electrical consumption for
926 economic feasibility. The study incorporates considerations of electricity prices and carbon taxes,
927 revealing the effect of these factors on the overall cost structure. The identification of optimal recovery
928 points under different cost scenarios provides crucial information for decision-making and process
929 design.

930 Taking into consideration the total cost of the process, encompassing CAPEX, OPEX, and the impact
931 of carbon taxes, an inflection point in the recovery levels was identified. This minimum tends towards
932 higher recoveries as carbon taxes rise, underlining the economic and environmental incentives for
933 increased carbon capture.

934 Additionally, by analyzing the sensitivity of the optimal recovery to variations in electricity prices
935 (ranging from 50 to 200 €·MWh⁻¹), a 10% absolute difference in the optimal recovery value can be
936 achieved. This flexibility is essential for adapting the process to changing economic and regulatory
937 conditions.

938 One can draw the conclusion that a concentration of 5% is not economically viable, in contrast to other
939 concentrations. For scenarios where the electricity price is below 100 €·MWh⁻¹ and the carbon tax
940 exceeds 100 €·t_{CO₂}⁻¹, the total capture costs average at 123, 95 and 80 €·t_{CO₂}⁻¹ for 10%, 15% and 20%
941 CO₂ concentrations in the flue gas, respectively.

942 This underscores the economic feasibility and attractiveness of the technology for concentrations above
943 5%, as it aligns with favorable conditions in terms of electricity costs and carbon taxes. Notably, the
944 cost dynamics demonstrate a clear dependency on concentration levels, emphasizing the importance of
945 considering such factors in the strategic planning and decision-making process for implementing carbon
946 capture technologies.

947 The analysis of the electricity source revealed that the closer one gets to a low-carbon emission energy
948 mix, the more the recovery corresponds to the CO₂ avoided. It is essential, therefore, to consider the
949 nature of electricity production for optimal reduction of carbon emissions; otherwise, a high-recovery
950 operation might be less optimal than lower recoveries.

951 The sensitivity analysis using Sobol's total order indices sheds light on the key parameters driving
952 recovery and energy consumption. The results underscore the dominant influence of adsorption time,
953 purge time and blowdown pressure, with their importance varying based on CO₂ concentration. This

954 understanding enables researchers and practitioners to focus on critical parameters for future
955 optimization efforts.

956 In summary, the research provides a comprehensive understanding of a hybrid CO₂ capture process and
957 offers valuable insights into optimizing it for efficiency, cost-effectiveness, and environmental
958 sustainability. These findings will undoubtedly contribute to the advancement of carbon capture
959 technology and its role in mitigating climate change and reducing greenhouse gas emissions.

960 CRedit authorship contribution statement

961 Alexis Costa: Conceptualization, Methodology, Software, Investigation, Data curation, Writing -
962 original draft, Writing - review & editing, Visualization. Arnaud Henrotin: Conceptualization,
963 Methodology, Software, Investigation, Data curation, Writing - original draft, Writing - review &
964 editing, Visualization. Nicolas Heymans: Conceptualization, Methodology, Investigation, Writing -
965 review & editing, Visualization. Lionel Dubois: Writing - review & editing. Diane Thomas: Writing -
966 review & editing. Guy De Weireld: Conceptualization, Validation, Writing - review & editing,
967 Supervision.

968 Declaration of competing interests

969 The authors confirm that there are no conflicts to declare.

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