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Should VPSA and membranes join forces? A techno-economic assessment of a VPSA-membrane hybrid process for post-combustion CO₂ Capture

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Abstract

The cost of capture is a key barrier to the widespread deployment of CO₂ capture and storage (CCS). Hybrid processes combine more than one CO₂ capture technology, typically two, with the goal of improving the capture performance. This work investigates the techno-economic potential of a hybrid vacuum pressure swing adsorption (VPSA) and membrane concept as an end-of-pipe post-combustion CO₂ capture solution. The assessment encompasses a range of cases in terms of flue gas characteristics (representative of a wide spectrum of industrial applications), materials, and economic inputs. For each of the cases studied, the optimal process design is identified, which leads to the minimum cost to avoid CO₂ emissions. The performance of the hybrid process is benchmarked against mature standalone technologies – absorption, membranes, and VPSA. The results indicate that the VPSA-membrane hybrid process has the potential to become an attractive solution at low-to-medium CO₂ concentrations in the flue gas (up to ca. 14%vol.) among the technologies compared, especially when there is no heat supply available on-site. The availability of clean and affordable electricity underpins the competitiveness of the hybrid process against absorption, while, in the opposite case, the area of interest diminishes. Finally, the utilization of metal-organic frameworks such as IISERP MOF2 instead of commercial adsorbents such as a zeolite 13X, showed a promising potential to further reduce the cost of capturing CO₂ with the hybrid process (15- 20% reduction in the low-to-medium CO₂ concentrations).

1 Introduction

The carbon budget for limiting global warming to 1.5°C is rapidly diminishing, and realistic roadmaps to meet global mitigation targets necessarily rely more and more on deep emissions reductions together with negative emissions [1]. Industrial sectors present significant challenges to reduce emissions down to zero and beyond, while remaining competitive. CO₂ capture and storage (CCS) can be a relevant solution for decarbonizing power generation and industry sectors [2]. However, several barriers prevent the timely widespread deployment of CCS, one of them being the high cost of CO₂ capture. There are multiple technologies for post-combustion CO₂ capture from power plants and industrial flue gases at different maturity levels. Chemical absorption with solvents is arguably the most mature technology [3]. The main advantage of chemical solvents is that it is possible to reach both high CO₂ purities (>99%) and capture ratios (>90%). The chemistry at the contactors level offers high CO₂ selectivity for gas separation. However, the regeneration step typically requires high specific energy input (mainly in the form of heat for solvent regeneration) and needs solvent management due to amine degradation as well as significant auxiliary equipment [4]. It is a technology demonstrated at industrial scale (TRL 8-9) [5] (>0.4 MtonsCO₂/year) in a single process. Other important aspects of the technology include the potential

environmental impact of emissions (when using amines) and potential equipment corrosion. The cost of capture using this technology benefits from economies of scale [6]. The heat supply scenario, normally in the form of steam for amine solvents, is crucial to evaluate the techno-economic performance of chemical solvents when integrated into industrial processes. When waste heat is readily available on-site, the total CO₂ avoidance cost (CAC) is usually much lower compared to the scenario where steam must be generated using a separate boiler solely for operating the CO₂ capture process [6].

Among the emerging technologies, permeation membrane technology is the most mature [7], with polymeric membranes reaching TRL levels of at least 7 [5]. Several advantages of membranes include their flexibility and modularity. The nature of the gas separation makes membranes electricity-driven, electricity that is primarily used to drive compressors and vacuum pumps to generate the driving force for CO₂ separation. However, there are many trade-offs in design that limit their performance. It is challenging to achieve high CO₂ purity and CO₂ capture ratios (CCR) in a single stage, and normally complex (multi-stage) arrangements with high feed pressures or permeate vacuums are needed to achieve design targets of high CCR (>90%) and sufficient CO₂ purity (>95%). They present poor energy and cost performances at low feed CO₂ concentration in the gas. As a result, most membranes are cost-attractive when starting from relatively high CO₂ concentrations (from ca. 15-20%) [8] and considering at relatively moderate CCRs (ca. 50-70%) [7]. Another technology for CO₂ capture, based on solid sorbents, is adsorption technology. Adsorption processes capture CO₂ by leveraging pressure swing adsorption (PSA) or temperature swing adsorption (TSA) to adsorb CO₂ and regenerate the sorbent. These processes have attracted increased interest in recent years, as demonstrated by a rapid increase of their TRL levels, reaching TRL at least of 6 and 5-7 for PSA and TSA, respectively [5]. PSA shows competitive energy penalties for a range of CO₂ concentrations in the feed gas; however, cost-wise, the technology appears attractive at medium-to-high CO₂ concentration levels [9]. TSA schemes are more suitable for lower CO₂ concentrations [10,11] and there is a growing interest for more advanced reactor technologies such as moving beds [12] and rotating beds [13]. This work will focus on PSA processes, in particular those relying on vacuum (VPSA). There are a few issues that impede the successful deployment of this technology as a standalone CO₂ capture process. It might be challenging to deliver high CO₂ purity and CCR simultaneously in a single step [14]. This requires the need for systems with complex designs and large plant sizes, involving several adsorption columns coordinated in a train as well as several hundreds of trains working in parallel [9]. In addition, deep vacuum levels are often needed that might be challenging to implement in industrial settings.

Hybrid processes for CO₂ capture have been proposed as promising concepts. A hybrid process is a process combining two or more technologies to achieve the separation performance targets (CO₂ purity and CO₂ capture ratio), and possibly impurities content [15]. The technologies involved can be combinations of absorption, membranes, adsorption, low-temperature gas separation, etc. Significant technology development has occurred already (e.g., membranes – cryogenic hybrid reached a TRL of at least 6, PSA – cryogenic hybrid of 6-9) [5]. The typical configuration of a hybrid process involves the technologies deployed in series [15], but there are other arrangements involving parallel configurations or more advanced arrangements, including complex recycle loops or heat and material integration with the upstream point source CO₂ emitting process [15]. In a hybrid process with configuration in series, there are normally two main steps:

- i) Bulk removal step or the "first-step" technology: provides the bulk removal of CO₂ - acting as CO₂ concentrator step;
- ii) Purification step or the "second-step" technology: provides with the required purification - raising the CO₂ purity to the requested level from an already concentrated stream.

Several hybrid processes, particularly VSA-membrane configurations, have been considered in the literature. In most of these studies, the emphasis has been on energy performances [15]. Membranes and

PSA processes can be considered as technologies suited to bulk separation. A hybrid process was proposed by Warmuzinski et al. [16] consisting of an upstream VPSA unit and a downstream membrane separation stage. For flue gas purification VPSA unit with pressure slightly above atmospheric and vacuum, the adsorbent selection is important in terms of adsorption capacity for CO₂ and selectivity with respect to the other components. In that work, a zeolite 13X and an activated carbon are suggested as adsorbent materials. Further works have explored this concept based on experimental work and modelling and simulation approaches [17] [18]. Jashik et al. claim that such hybrid process is flexible enough to improve both energy efficiency and adsorbent productivity in comparison with standalone VSA or membrane systems [19]. Another work has addressed combinations of these two technologies in an advanced arrangement that differs from series hybrid processes [20], and recent developments show the willingness of membrane and adsorption technology providers to develop hybrid processes: a version of this hybrid was tested at a scale of ca. 20 ton CO₂/day at the site for emerging technologies at Technology Centre Mongstad in Norway [21]. In a preliminary analysis, Montañés et al. showed the arrangement VPSA-membrane appears to be more competitive than the arrangement with membrane as first step or bulk separation step (membrane-VPSA) [22]. The main findings from the literature review are summarized in Table S1 in the supporting information. After the literature review, the following statements and insights apply as a basis for this work:

- Membrane section has lower energy consumption per ton CO₂ captured if CO₂ concentration at inlet exceeds 20%. Therefore, previous published works have focused on VPSA as first step instead of membrane as first step.
- Most previous works addressing this membrane-adsorption concepts consider flue gas with 10-15%vol. CO₂ content based on coal power plant (real or simulated).
- Adsorbent selection is important in terms of adsorption capacity for CO₂ and selectivity the other components. Zeolites 13X and AC are mostly suggested and applied in the literature.
- The studies include mostly commercial polymeric membranes (material properties) in the assessment of hybrid concepts.
- Industry developments claim that membrane-adsorption could be a competitive technology (also in comparison to chemical absorption with amine solvents), and there are ongoing demonstration activities ca. 20 TPD in a process that integrates both technologies.

Overall, it was noted that a systematic approach to address energy and techno-economic performances of hybrid processes is lacking in the literature [22,23]. While reduced specific energy consumption for capture is relevant, technology screening of hybrid concepts must be addressed by means of techno-economic assessment in order to identify applications where they could be cost-attractive, as clearly demonstrated in [6][8]. Techno-economic assessment (TEA) allows to incorporate trade-off between CAPEX and OPEX, relevant when optimizing and comparing technologies. In addition, TEA is required for fair comparisons [6]. A consistent TEA to identify the potential and application niches of these concepts is generally lacking in the literature. This work is the first step in addressing this gap by presenting a systematic TEA of a hybrid concept combining adsorption and membrane CO₂ capture processes; refer to Figure 1 for a schematic representation of the hybrid configuration. The aim is to identify if there is a niche of industrial applications where the hybrid process could potentially be competitive or outperform mature CO₂ capture technologies (chemical absorption with 30%wt MEA) or emerging standalone technologies (multi-stage polymeric membranes and VPSA). In other words, in this work, we address the following research questions:

- Can hybrid concepts combining VPSA and membrane become cost competitive? If so, under what conditions?

- Are the potential application niches of the technology affected by factors such as scale and geographic location?
- Can advanced materials supported by suitable process configurations bolster the potential niche?

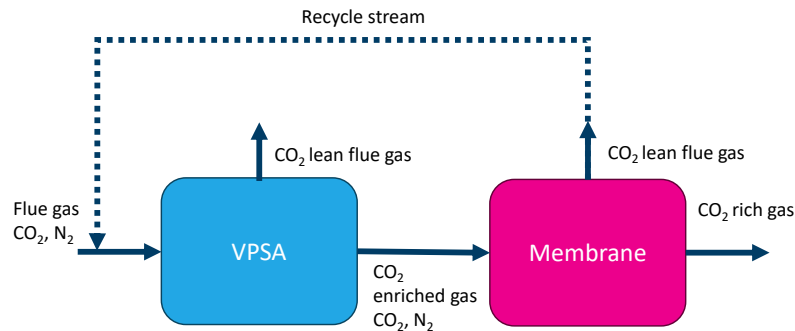


Figure 1. Schematic representation of the VPSA-membrane hybrid process.

The paper is structured as follows. First, the methodology adopted for the work is outlined in section 2, including insights into the models used, the techno-economic and optimization framework and the key performance indicators. Section 3 presents the matrix of cases and the benchmark technologies, which constitute the basis for the analysis on the potential of the hybrid process. The results obtained are presented and discussed in section 4, also analyzing the effect of geographic location and alternative materials. The key findings of the work are summarized in section 5.

2 Methodology

In this work, we assess a hybrid separation process that consists of an upstream bulk removal step acting as CO₂ concentrator step and a second step where the more concentrated stream can be further enriched to yield a permeate stream containing at least 95 vol.% of CO₂. The first step is selected to be a VPSA process, while the second step consists of a multi-stage membrane system [22]. A techno-economic framework to optimize the performance and assess the potential of the VPSA-membrane hybrid process is developed. In particular, a process modelling (section 2.1 and 2.2) and cost estimations (section 2.3) framework are established and integrated in order to optimize (section 2.4) and assess the hybrid process.

2.1 VPSA process model

A five-step VPSA cycle, presented in Figure S1 in the supporting information, is considered for the bulk removal of CO₂ in the first step of the hybrid process configuration. In contrast to standard VPSA cycles, which are designed to achieve high CO₂ purity and recovery in a single stage, this cycle aims to concentrate CO₂ to moderate purities while achieving a very high CO₂ recovery. The cycle consists of adsorption (ADS), heavy reflux (HR), counter-current blowdown (BLO), light product purge (PUR), and light product pressurization (LPP) steps. In the adsorption step, the feed gas is introduced in the column at high pressure, P_H , where the separation is achieved by preferential adsorption of CO₂ in the column. The HR step occurring at P_H after adsorption increases the partial pressure of CO₂ in the column before regeneration. The HR step is introduced to enable the target CO₂ purities for diluted CO₂ feed gases, by increasing its partial pressure which would otherwise be challenging to achieve. Subsequently, the pressure in the column is reduced to vacuum (P_L) using a vacuum pump in the BLO step to collect the CO₂-containing stream as a feed stream for the membrane process (the purification step of the hybrid process). The purpose of the PUR step at P_L after counter-current blowdown is to flush the column with

N_2 and completely regenerate the column by removing residual CO_2 from the column. This flushed-out stream is fed back to the heavy reflux step, thereby improving the CO_2 recovery in the process. Note that vacuum pumps are assumed to remove the gas in the BLO and PUR steps based on constant volumetric flow rates, as observed in realistic conditions and consistent with other studies reported in the literature [24,25]. Finally, the column is pressurized back to P_H by using the light product from the adsorption step in the LPP step. This cycle is a modified version of the six-step dual reflux cycle proposed in the literature [9,25].

The five-step cycle is evaluated based on three different adsorbent materials: 1) commercial zeolite 13X, widely regarded as a benchmark adsorbent for CO_2 separation from flue gases, 2) activated carbon, a cheap and abundantly available commercial adsorbent commonly used in different industrial gas separations, and 3) IISERP MOF2, a metal-organic framework that is not yet commercialized, but extensively used in assessing the potential of VPSA processes for post-combustion CO_2 capture [9,26,27]. The adsorption isotherms on these materials are described using the competitive dual-site Langmuir isotherm (DSL) model. Their isotherm parameters have been retrieved from the literature and are tabulated in Table S2 in the supporting information. Table S3 in the supporting information lists the physical properties of adsorbent materials.

Data-driven models leveraging artificial neural networks (ANNs) are considered for simulating the five-step VPSA cycle. Conventional rigorous adsorption models based on a set of nonlinear partial differential equations are computationally very expensive and time-consuming [26,28,29], making them unsuitable for use within integrated techno-economic optimization routines, where thousands of process simulations must be performed for each optimization. Compared to rigorous process models, data-driven models are orders of magnitude faster to train and deploy within the optimization routines [28]. As a result, the use of machine learning models has become increasingly common to calculate the process performance of VPSA processes rapidly [28–31]. For this study, an ANN model of the five-step cycle VPSA process was developed, trained and validated. Insights on the model development, including the modelling assumptions adopted, are presented in section S3 in the supporting information.

2.2 Membrane process model

The membrane gas separation consists of multiple steps in series (one or two stage membrane) [7]; refer to Figure S2 in the supporting information that shows a simplified flowsheet of a two-stage membrane process for CO_2 capture. The CO_2 -rich gas stream leaving the VPSA process is compressed and sent to a membrane where a permeate stream is produced with a higher CO_2 purity by the pressure difference governed by a vacuum pump as CO_2 is preferentially transported across the membrane compared to other components in the flue gas. The high-pressure retentate gas from the membrane is depressurized to the targeted outlet pressure through an expander while producing work, where applicable. Each stage consists of a membrane unit and its own intercoolers and rotating equipment.

The most mature permeate membrane technologies for CO_2 capture available today are based on polymeric materials [3]. In this work, mature membrane (i.e., MTR Polaris) is considered in the process (permeance: $5.94 \text{ (Sm}^3/\text{m}^2\text{barh)}$, selectivity: 50 (-)) [8]. The membrane process models and optimization method utilized in this framework were presented in previous publications [7,32]. The model employs a methodology for systematic and consistent design of membrane processes for post-combustion capture [33]. The design methodology relies on underlying process models for the membrane separator and the rotating equipment. The membrane module is modelled as a binary component separator in cross-flow configuration with plug flow on the feed side and negligible mixing on the permeate side [34]. Pressure drops are neglected. The model accommodates binary (CO_2/N_2) mixtures to reflect the current availability

of experimental data. Rotating equipment are modeled as isentropic expansions/compressions of an ideal gas. An isentropic efficiency is applied to account for irreversibility. The approach is accurate to approx. $\pm 1\%$ for compressors, expanders and heat exchanger duties and approx. $\pm 5\%$ for the vacuum pump in the range of pressures considered [34]. Table S4 in the supporting information summarizes the key process parameters of the membrane modules.

2.3 Techno-economic assessment framework

The cost evaluation methodology is based on a systematic techno-economic assessment (TEA) framework. The complete TEA framework model consists of approaches for the evaluation of CAPEX and OPEX. As commonly used in literature for aspirational Nth-of-a-kind plant, for the CAPEX, a bottom-up approach (BUA) is employed to estimate the total capital requirement (TCR) as illustrated in Figure 2. The OPEX are calculated based on utilities consumption and standard factors, mainly accounting for maintenance and labor costs. The TEA has been developed in a consistent manner following the principles and guidelines presented in the work by Roussanaly et al. [6]. The assessment in this work considers only the CO₂ capture element of a CCS chain, excluding conditioning and transport for use or storage required in a case-specific and complete CCS chain. The TEA models to estimate the cost of the capture processes have been developed and applied in a consistent fashion irrespective of using the CO₂ capture technologies (membrane, VSA and MEA) as standalone solutions or in a hybrid configuration.

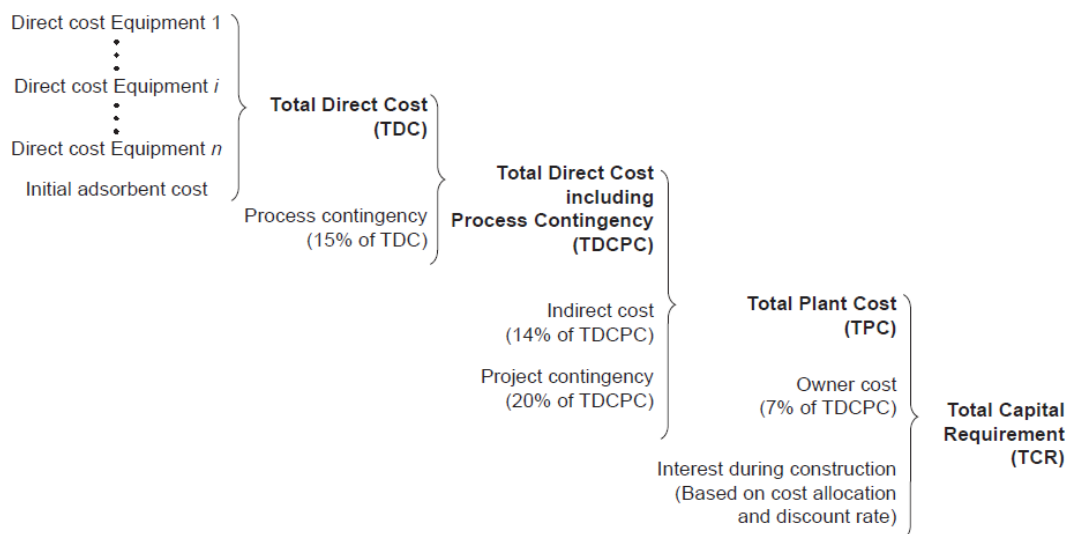


Figure 2. Bottom-up approach for calculating capital costs [24].

The approaches used for the two capture processes are as follows:

- **VPSA process:** The TEA methodology embedded in the VPSA process is presented in [24]. Equipment-specific cost functions are developed to estimate the direct cost terms (the main equipment included in the analysis are adsorption columns, vacuum pumps and compressors). Factors to consider indirect costs, process contingencies, and more are applied to obtain the TCR. The cost of the adsorbent material has been set to 1500 €/t for the Zeolite 13X (based on commercially available samples), 1000 €/t for the activated carbon (based on commercially available samples) and to 16640 €/t for IISERP MOF2 (based on the costing method from [24]). The adsorption cost parameters are summarized in Table S5 in the supporting information.
- **Membrane process:** For the membrane processes, the total direct cost with process contingencies is first evaluated, based on the cost model presented in Roussanaly et al. [35]. This also includes an update in the corresponding cost year based on the Chemical Engineering Plant Cost Index (CEPCI).

Factors to consider indirect costs, process contingencies, and more are applied to obtain the TCR. The investment cost parameters for the membrane utilized in this work are summarized in Table S6 in the supporting information.

The operating cost of the hybrid capture system is assessed based on two components: i) the annual fixed operating cost and ii) the annual variable operating cost.

- VPSA process: For the VPSA unit, fixed operating costs include maintenance, insurance, and labour costs. In addition, the cost for replacement of the adsorbent material is considered. In particular, the lifetime of the adsorbent beds has been set to 5 years.
- Membrane process: For the membrane modules, fixed operating costs include maintenance, insurance, and labour costs. A 5-year membrane module lifetime is considered, with a replacement cost of 9.4 €/m².

The annual variable operating cost of the VPSA and membrane system is based on utility consumption considering an electricity price from the relevant grid, specific values are reported in section 3.

Additional information is available in section S7 in the supporting information.

2.4 System optimization

A system optimization framework is developed to identify the optimal hybrid process design accounting for the mutual influences of the two capture technologies [36]. All decision variables listed in Table 1 constitute the input to the optimization process. The objective of the optimization is to minimize the CO₂ avoidance cost (CAC) of the VPSA-membrane hybrid process. Two constraints are applied, namely a minimum CO₂ purity constraint ($\geq 95\%$ vol.) and a minimum CCR constraint ($\geq 90\%$ at system level). This optimization framework has a superstructure including an option for recycling the retentate gas from the membrane stage(s). If stream recycle is indeed considered, the entirety of the retentate gas from the membrane stage(s) is recycled to the inlet of the VPSA process. Thus, when membrane retentate stream is recycled to the VPSA, the recovery of the VPSA process step alone determines the overall (system) CO₂ capture ratio. A schematic representation of the system optimization methodology applied for the design of the hybrid process is shown in Figure 3.

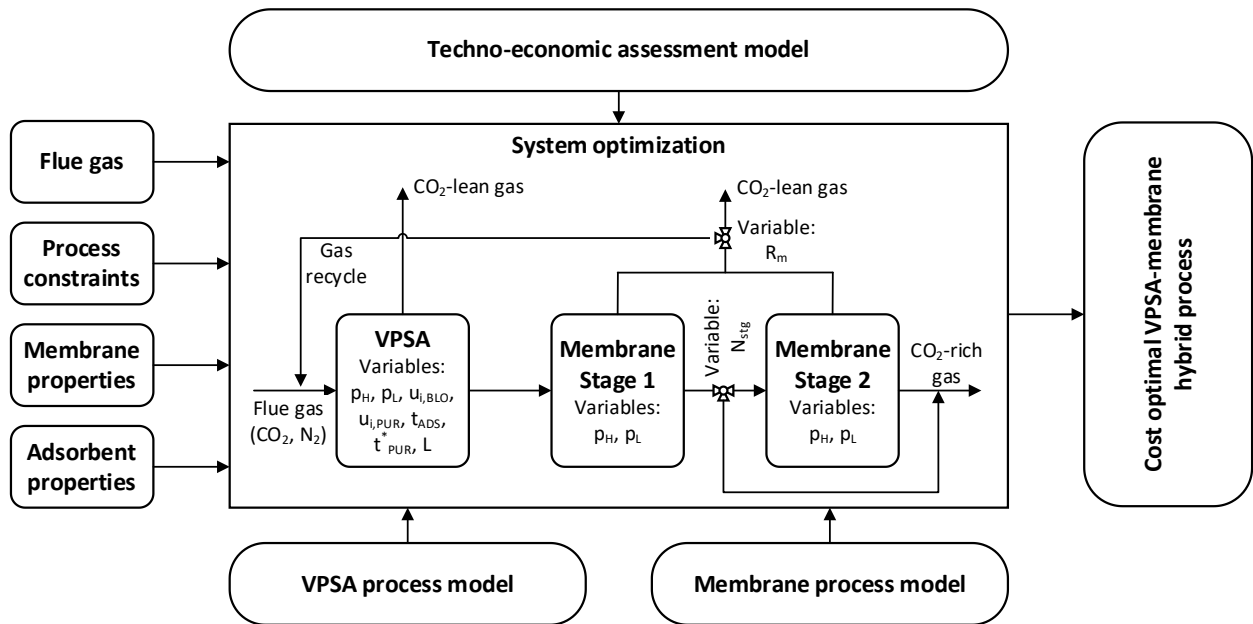


Figure 3. Flowchart of the system optimization methodology for cost-optimal design of the VPSA-membrane hybrid process.

The variables as well as the bounds for optimization are reported in Table 1, for a total of 13 variables.

The optimization was performed using a genetic algorithm (i.e., `geneticalgorithm2` – version 6.8.5) available from a Python [37] library:

- Population size equal to 60 times the number of optimization variables considered.
- Number of generations considered was 200.

Table 1. List of optimization variables and related bounds.

Variable	Symbol	VPSA	Membrane stg 1	Membrane stg 2 [†]
High pressure level (bar)	ρ_H	1.05 – 3.6	1.1 – 50	1.1 – 50
Low pressure level (bar)	ρ_L	0.01 – 0.5	0.2 – 0.9	0.2 – 0.9
Interstitial velocity outlet blowdown step (m/s)	$u_{i,BLO}$	0.45 – 2.5	N/A	N/A
Interstitial velocity inlet purge step (m/s)	$u_{i,PUR}$	0.2 – 1.0	N/A	N/A
Adsorption step time (s)	t_{ADS}	100 – 500	N/A	N/A
Factor for purge step time [‡]	t_{PUR}^*	0.1 – 0.99	N/A	N/A
Length column (m)	L	6 – 9	N/A	N/A
Number of membrane stages	N_{stg}	N/A	1 – 2	
Recovery from membrane stages [‡]	R_m	N/A	0.4 – 0.95	

[†]These variables apply only if $N_{stg} = 2$

[‡]The actual purge step time is calculated as: $t_{PUR} = (t_{ADS} - t_{LPP}) \cdot t_{PUR}^*$

[‡]This variable applies only when gas recycle is implemented in the system superstructure for the optimization framework.

3 Benchmarking the hybrid process

In order to evaluate the relative potential of the VPSA-membrane hybrid process, three CO₂ gas separation technologies are chosen as benchmark:

- Multi-stage membrane: A multi-stage membrane technology based on polymeric materials (i.e., MTR Polaris) is considered as benchmark (with same membrane properties as reported in section 2.2.). A 2-stage or 3-stage configuration is designed depending on the case studied with a possibility to include recycle of the retentate gas from the last stage.
- VPSA: A VPSA process using zeolite 13X as adsorbent material (same as in section 2.1) is considered as benchmark. A 6-step cycle with dual reflux proposed in the literature [38] is utilized as earlier evaluations have shown performances over a large range of conditions [9].
- Chemical absorption with 30%wt. MEA: The chemical absorption benchmark results are based on the work presented by Subraveti et al. [39]. Two scenarios for heat supply are considered: (1) steam for CO₂ capture generated by a natural gas-fired boiler and (2) steam for CO₂ capture generated by process waste heat. This is relevant as some industries, and specific industrial sites or clusters might have waste heat available onsite, while in others heat might be supplied by an ad-hoc steam boiler, possibly burning fossil fuels [40].

A matrix of cases, combination of feed CO₂ concentration and flue gas volumes, is established to be representative of a wide range of relevant industrial¹ applications and, hence, allow understanding at which conditions the VPSA-membrane hybrid process is cost competitive – Table 2 illustrates the range of cases considered. The main parameters varied are:

- Feed CO₂ concentration: spanning from 3.5 to 30% (on a dry volumetric basis) to represent the typical range of industrial sites: from around 3.5% typical of, e.g., metal industries; 10%-15% typical of, e.g., waste-to-energy, biomass boilers and stacks in refineries; 18%-20% typical of, e.g., cement kilns and steam methane reforming flue gas; and up to 30% in typical of, e.g., some stacks of steel mills. The flue gas is simplified as a binary mixture of N₂ and CO₂. Therefore, the assessment does not take into consideration aspects of feed gas moisture and impurities.
- Scale: The scale of the CO₂ capture plant affects its economics, as well as the relative performance with respect to different capture technologies due to differences in economies of scale. The two flue gas flowrates considered – 200 t/h and 2000 t/h – represent a small/medium industrial site and a large industrial site, respectively.

Table 2. Matrix of cases: combination of feed CO₂ concentration and flue gas scale.

Matrix of cases		CO ₂ feed concentration (vol.%)						
		3.5%	10%	12.5%	15%	18%	22%	30%
Flue gas flow rate (t/h)	200	Main KPI: CO ₂ avoidance cost (€/t _{CO2})						
	2000							

One of the factors potentially influencing the relative performance of capture processes is the geographic location. In fact, the location of an industrial site determines the electricity price and the CO₂ emission intensity of electricity, in turn affecting the economics. To account for this effect, three geographic locations are considered, where the electricity prices [41] and related emission intensity [42] are listed in Table 3 (the values reported are averages for the year 2020).

¹ With term "industrial applications", this study exclude power plants cases where the power or heat required by the capture technology would be extracted from the power plant itself thus reducing the electricity production of the power plant.

Table 3. Electricity prices and emission intensity of the three geographic locations considered.

Geographic location	Electricity price [41] (€/MWh)	Emission intensity [42] (kg_{CO2}/MWh)
European Union average	76	231
Norway	27	11
Germany	107	311

The assessment is based on key performance indicators (KPI)s. The main KPI used in the study is the CO₂ avoidance cost (CAC) [43], calculated as the ratio between the sum of the annualized capital expenditures (CAPEX) and the annual operational expenditures (OPEX), and the annualized amount of CO₂ emissions avoided:

$$\text{CAC} \left[\frac{\text{€}}{\text{t}_{\text{CO}_2}} \right] = \frac{\text{Annualised CAPEX} + \text{Annual OPEX}}{\text{Annual amount of CO}_2 \text{ avoided}} \quad (1)$$

Compared to the also commonly used CO₂ captured cost, the CO₂ avoidance cost includes the impact of CO₂ emissions associated with energy (heat and/or power) consumption linked to the CO₂ capture process. The CO₂ avoided costs for reference MEA technology were retrieved from Subraveti et al. [44] for the two different cases considered, representing two different options to supply heat. The source of steam supply has a substantial impact on the overall CO₂ avoided costs obtained using the MEA solvent [44] and this variation is taken into account when comparing the techno-economic performance of hybrid configurations with a MEA.

The specific energy consumption (SEC) is another important performance metric. The SEC is calculated as follows (note that in this case the denominator is the amount of CO₂ captured by the capture technologies):

$$\text{SEC} \left[\frac{\text{kWh}}{\text{kg}_{\text{CO}_2}} \right] = \frac{\text{Power consumption to run the CO}_2 \text{ capture processes}}{\text{Mass flow rate of CO}_2 \text{ captured}} \quad (2)$$

The SEC is utilized in this work to compare the performance of the electricity driven CO₂ capture technologies, namely PVSA, multi-stage membrane and hybrids based on VPSA-membrane. No direct comparison is considered with heat driven technologies like chemical absorption with MEA.

4 Results and discussions

In this section, the optimal designs obtained for the VPSA-membrane hybrid process are reported, benchmarked and discussed. All cases described in section 3 are considered.

The hybrid process is optimized for all cases with and without recycling to understand the implications of the two design strategies. While recycling the retentate stream from the membrane process has potential to improve the energy performance of the hybrid system, it also increases complexity and control challenges. Quantifying the impact of recycling is critical in evaluating these trade-offs. An example of a full set of results with and without recycling is provided in Table S8 in the supporting information. The following insights could be gained:

- Gas recycle allows to reduce the energy requirements (especially at low CO₂ concentrations), while it tends to increase the CAPEX due to the increased volumes of gas treated by the capture technologies.
- Gas recycle is more useful at lower CO₂ concentrations. At higher CO₂ concentrations the difference between the cases becomes minimal.
- Optimal hybrid designs implementing gas recycle achieve higher CO₂ recoveries [36].

For the remainder of the paper, the results presented will be those returning the minimum CAC (either with or without gas recycle). The same applies also to the multi-stage membrane system used as the benchmark.

4.1 Base case

The base case considers a zeolite 13X as adsorbent material and MTR Polaris technology for the membrane stage(s) of the hybrid process. The electricity price and CO₂ intensity are those representative of European Union for large consumers. Tables S9 and S10 in the supporting information provide a complete set of the results obtained (including the different CO₂ concentrations and the two scales) for the VPSA-membrane hybrid process.

The results show that VPSA pre-concentrates CO₂ between 39% and 70% in the hybrid process, depending on the original concentration in the flue gas. This concentrated flue gas is subsequently fed to the membrane process. Figure 4A illustrates how the CO₂ purification effort is distributed between the two technologies for the different industrial cases (i.e., the different CO₂ concentrations in the flue gas) for the large-scale scenario (i.e., 2000 t/h of flue gas). A single industrial scale (large-scale) is shown as the simulations for the small-scale (200 t/h of flue gas) returned a very similar trend.

For diluted CO₂ sources (i.e., 3.5% CO₂ in the flue gas), the optimal intermediate purity is about 39%: the VPSA process struggles to reach higher purities in an efficient manner. Although at such low intermediate purity the CAPEX of membrane step will be significantly higher, the additional energy penalty (i.e., OPEX) required for achieving higher purities balances out the potential reductions in CAPEX. The optimality of minimizing the OPEX at these conditions is also confirmed by the significant advantage obtained by implementing gas recycle (CAC equal to 69 and 75 €/t with and without recycle, respectively), which indeed reduces OPEX at the expense of larger CAPEX. For more concentrated CO₂ sources (i.e., 10% to 30%), the optimal intermediate purity increases from 50 to 70%. Larger intermediate purity translates in lower separation duty required to the membrane step, which in fact necessitates of two stages only at the 3.5% CO₂ case. For less diluted CO₂ streams a significant reduction in CAPEX can be observed both in absolute terms (from 32 €/t to 11 €/t) and in relative terms (from 47% of the total cost to 31%) – see Table S11 in the supporting information for the cost breakdown of all cases simulated. The simplified gas separation process at high inlet CO₂ concentrations also decreases the positive effect of gas recycle. The results show that recycling the gas stream is an efficient strategy for medium-to-low CO₂ concentrations in the flue gas (see Tables S9 and S10 in the supporting information where recycling is cost-efficient up to 22% inlet CO₂ concentration). All in all, it can be argued that it is cost-optimal for the VPSA step to take on an increasingly larger role in the separation and purification process – the cost for the VSA process alone constitutes the 78% of the total hybrid process cost at 3.5% CO₂, while it reaches a maximum of 83% at 18% CO₂. The comparison between the cost of the VPSA step and the cost of the membrane step confirms this (see Figure 4B).

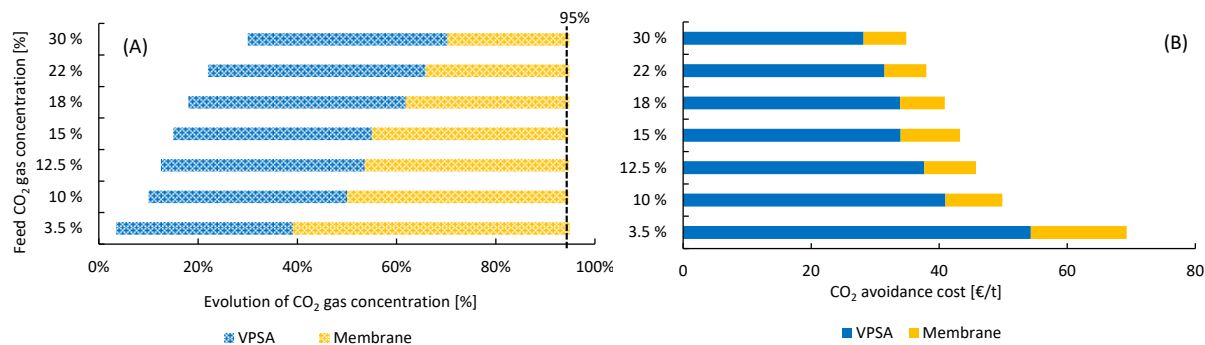


Figure 4. (A) Evolution of CO₂ concentration between each step of the hybrid process. (B) Contribution to total CO₂ avoidance cost of VPSA and membrane steps. Large industrial scale (i.e., 2000 t/h of flue gas).

Figure 5A and Figure 5B illustrate the cost results for the two flue gas scales considered, 200 t/h and 2000 t/h, respectively. The CAC from the hybrid process is compared with that from the benchmark technologies presented in section 3: standalone membrane (2 or 3 stages), standalone VPSA and MEA-based absorption with steam supplied either from natural gas (NG) or from waste heat (WH) available from the industrial processes. The figures also show the areas where a given technology appears to be the most cost-efficient: green for the VPSA-membrane hybrid, orange for the standalone membrane, blue for the standalone VPSA and black for MEA using a NG boiler. For this visualization with colored areas the results of MEA with waste heat were not considered for two reasons - the related CAC is consistently lower than alternatives (apart at very high CO₂ concentrations, i.e., > ≈25%) and the availability of waste heat is case specific.

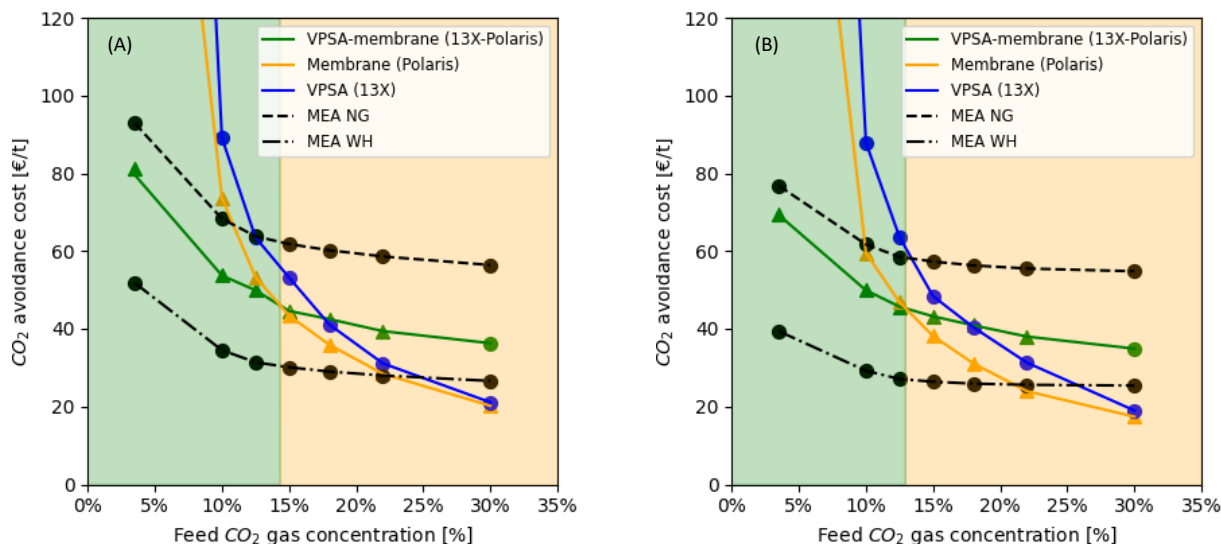


Figure 5. Cost results of VPSA-membrane hybrid process at the different CO₂ concentration cases and the two industrial scale considered: (A) 200 t/h and (B) 2000 t/h of flue gas. The performances of the benchmark technologies are also included. For the VPSA-membrane hybrid process and for the standalone membrane process the triangles indicate designs implementing a gas recycle scheme. The circles indicate designs not implementing a gas recycle scheme. The areas of the figure are colored depending on the most cost-competitive process in that range of conditions: green for the VPSA-membrane hybrid, orange for the standalone membrane, blue for the standalone VPSA and black for MEA using a NG boiler.

The VPSA-membrane hybrid process is the preferable solution at low concentrations, while membranes become more efficient at high concentrations. Such observations are consistent at both scales. VPSA shows a similar trend as membranes but at higher cost levels, hence there are no areas where it is cost-efficient. The hybrid process appears to be more cost-efficient than MEA even at fairly low concentrations (i.e., 3.5%) when heat needs to be produced with a NG boiler. It is also interesting to note that the cost of the VPSA-membrane hybrid process does not increase exponentially at low concentrations as it is the case for membranes and VPSA as standalone technologies, at least for the CO₂ concentration range considered in this study (note that standalone VPSA is not able to achieve the CO₂ specifications requested in terms of recovery and purity at 3.5 %CO₂ inlet concentration).

The hypothesis when developing a hybrid concept is that such an arrangement would combine technologies so to put them in the conditions to operate efficiently. This is expected to translate into an improved energy performance with respect to standalone technologies. Figure 6 compares the specific energy requirement (SEC) of the VPSA-membrane hybrid process with that of the membranes and VPSA benchmarking processes for the matrix of cases at the largest industrial scale. MEA is not included as it is a heat-driven process, and a direct comparison with power-driven technologies can be misleading. The expected trend is obtained for standalone membrane and VPSA processes, where the SEC decreases with feed CO₂ concentration. A steep change is also observed in the low CO₂ concentration area. While the trend is the same, the relative performance of membranes and VPSA changes across the CO₂ concentrations tested. However, the gap remains small in most cases and, arguably, within the uncertainty connected to the optimization. The VPSA-membrane hybrid process exhibits a much more stable trend. This is the result of the increased design flexibility granted by a hybrid configuration, where two processes can be tuned. As previously discussed, at diluted CO₂ concentrations it is optimal to minimize the energy requirement (i.e., OPEX) at the expense of increased capital investments (i.e., CAPEX). The hybrid configuration provides supplementary degrees of freedom to pursue such optimality in comparison to standalone capture processes, for example targeting low intermediate CO₂ purity. When the CO₂ inlet concentration increases, and the focus gradually shifts towards limiting the CAPEX, the hybrid configuration can be rearranged to accommodate the new process requirements for achieving minimum cost. All in all, the hybrid process is competitive from an energy consumption perspective in a large region. Membranes and VPSA processes become more energy efficient only at relatively high CO₂ concentrations.

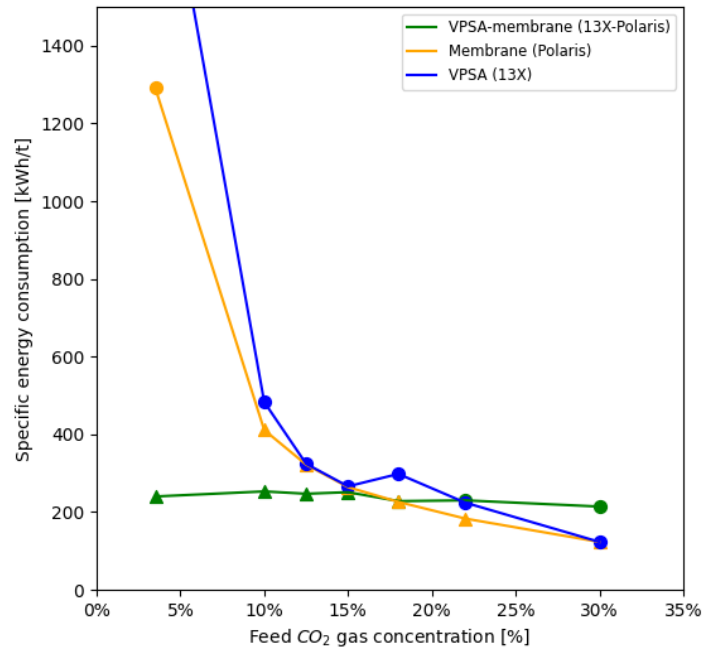


Figure 6. Energy results of VPSA-membrane hybrid process at the different CO₂ concentration cases. The performances of the benchmark technologies are also included. For the VPSA-membrane hybrid process and for the standalone membrane process the triangles indicate designs implementing a gas recycle scheme. The circles indicate designs not implementing a gas recycle scheme. The larger industrial scale is considered (i.e., 2000 t/h of flue gas).

4.2 The impact of geographic location

The energy consumption affects the economics of the capture process both as an OPEX term and as a contributor to indirect CO₂ emissions (hence affecting the CO₂ avoidance). These two aspects are accounted for by the electricity price and by the CO₂ emission intensity of electricity, respectively. Both parameters are dependent on where the industrial plant is located. To assess this effect on the potential of the VPSA-membrane hybrid process, simulations were performed considering two additional geographical locations, i.e. Norway and Germany. Norway represents a country characterized by relatively low electricity prices and emission intensity (27 €/MWh and 11 kg_{CO2}/MWh), while Germany is a country characterized by relatively high electricity prices and emission intensity (107 €/MWh and 311 kg_{CO2}/MWh). A complete set of results for the VPSA-membrane hybrid process at different geographic locations is provided in Table S12 and S13 in the supporting information.

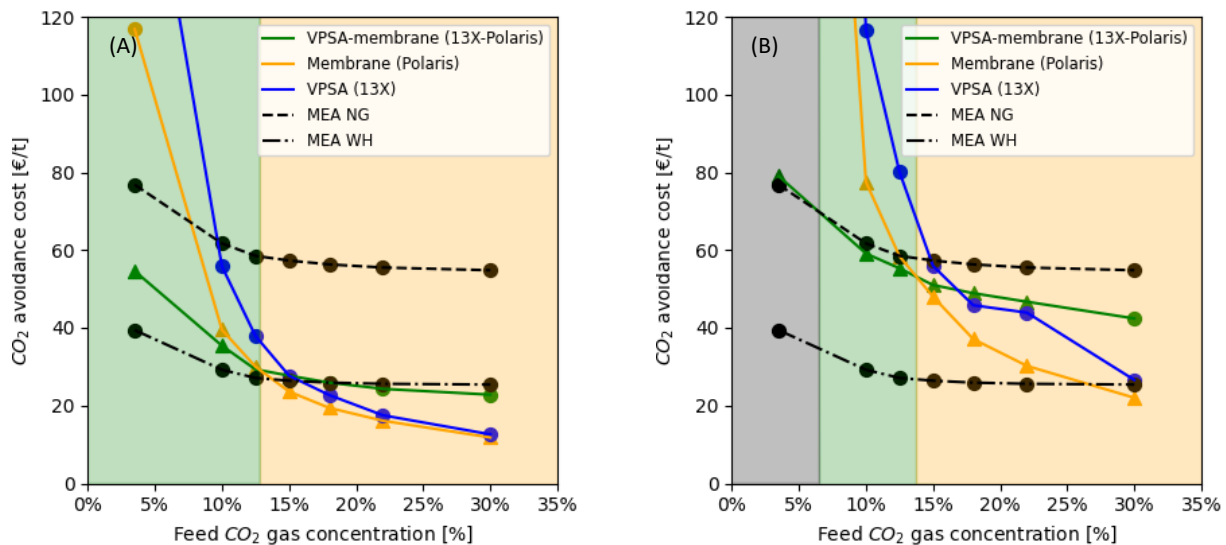


Figure 7. Cost results of VPSA-membrane hybrid process at the different CO₂ concentration cases for two alternative geographic locations: (A) Norway and (B) Germany. The performances of the benchmark technologies are also included. For the VPSA-membrane hybrid process and for the standalone membrane process the triangles indicate designs implementing a gas recycle scheme. The circles indicate designs not implementing a gas recycle scheme. The areas of the figure are colored depending on the most cost-competitive process in that range of conditions: green for the VPSA-membrane hybrid, orange for the standalone membrane, blue for the standalone VPSA and black for MEA using a NG boiler. The larger industrial scale is considered (i.e., 2000 t/h of flue gas).

Figure 7A and Figure 7B illustrate the cost results for the large industrial scale, assuming the industrial plant is located in Norway or Germany, respectively. The effect of electricity price and CO₂-intensity due to geographical location on the MEA-based cases is negligible as the technology is heat-driven. Conversely, a significant effect on the VPSA-membrane hybrid, on membranes and on VPSA can be observed and, therefore, on their relative performance. The availability of cheap and clean electricity, as is the case in Norway, benefits the utilization of power-driven technologies (see Figure 7A). This means that the hybrid process, as well as VPSA and the membrane processes, become even more competitive compared to MEA-based capture using a natural gas boiler and even outperform MEA-based capture using waste heat at relatively high concentrations. However, the relative performance of the hybrid against membranes and VPSA remains almost unchanged, with a minor increase in the area where membranes are more cost-efficient compared to the base case results based on an average European electricity mix. A very different picture is obtained for the German case. The higher price and carbon footprint of electricity impair the competitiveness of power-driven technologies. MEA becomes the preferred solution at low concentrations (up to around 6% CO₂), while the membrane process is the most cost-efficient option for CO₂ concentrations above 14%. This means that the hybrid VPSA-membrane process is the most cost-efficient option for CO₂ concentration between 6 and 14% but there is only a small cost improvement compared to the reference MEA process. Thus, the applicability of the hybrid process for a German electricity mix (or similar) is marginal at best.

4.3 Alternative materials

The results presented in the previous sections rely on well-established materials and technologies. In particular, a zeolite 13X was used as adsorbent material, and the MTR Polaris was used as membrane technology. However, alternatives have been proposed in the literature and showed promise of improved performances [26,45]. That is the case of IISERP MOF2, which outperformed zeolite 13X for post-

combustion CO₂ capture from steam-methane reformer flue gas [24], as well as demonstrated to be a cost-efficient option at several other conditions [9]. Another option considered with respect to VPSA is that of using activated carbons as adsorbent material. Activated carbons are cheap materials that perform sufficiently well for mild gas separation requirements, for instance when the target purification level is not very high, as is the case in a hybrid configuration. Therefore, activated carbon was deemed as a potentially interesting option to investigate. Technological advancements concerning the membrane step of the hybrid process were not investigated since, as shown in Figure 4B, the impact on the overall cost is limited.

To assess the potential improvements connected to the utilization of alternative materials, simulations for the hybrid process were carried out with IISERP MOF2 and activated carbon. The parameters to model the adsorbent materials were obtained from the literature [26,46]. A complete set of results for the VPSA-membrane hybrid process with IISERP MOF2 and activated carbon are provided in Table S14 and S15, respectively, in the supporting information.

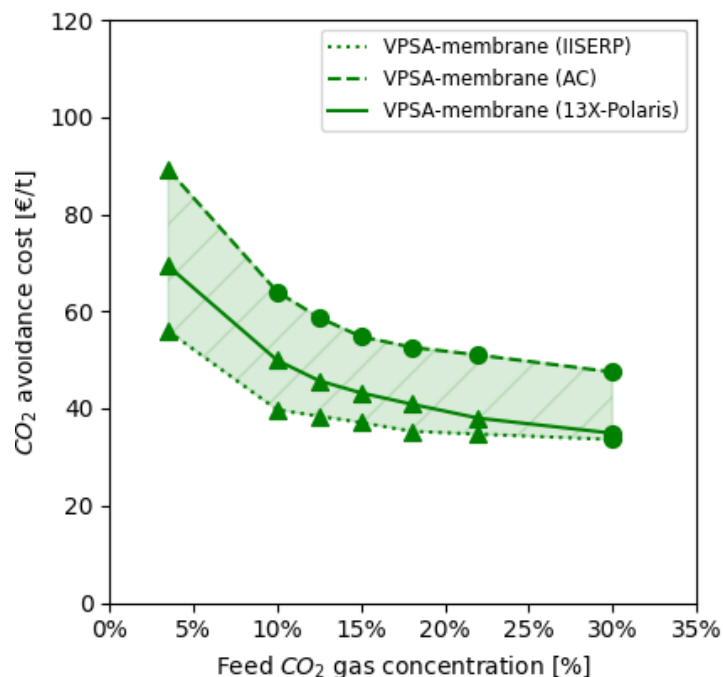


Figure 8. Cost results of VPSA-membrane hybrid process at the different CO₂ concentration cases considering alternative materials. The performances of the benchmark technologies are also included. The triangles indicate designs implementing a gas recycle scheme. The circles indicate designs not implementing a gas recycle scheme. The larger industrial scale (i.e., 2000 t/h of flue gas) and average European electricity parameters are considered.

The optimal costs obtained are shown in Figure 8. The simulations assume large industrial scale and average European electricity parameters. The utilization of alternative adsorbent materials has a meaningful effect on the results, either positive (i.e., IISERP MOF2) or negative (i.e., activated carbons). The range of possible costs is large throughout the entire region tested but especially at low CO₂ concentrations (up to 32 €/t at 3.5% CO₂). IISERP MOF2 is consistently the best-performing adsorbent with relative cost reductions between 15% and 20% for the low-to-medium CO₂ concentrations, while activated carbon is consistently the worst-performing one. The results indicate that it is important, at least in this small sample of cases, to rely on efficient materials even though they might be more expensive – an overview of the adsorbent costs used is provided in Table S5 in the supporting information. It can be

argued that the development and utilization of advanced adsorbent materials will improve the economic performance of the VPSA-membrane hybrid process. However, technological advancements will be available also for the standalone technologies, making difficult to conclude on the evolution of the relative performance gap between the set of technologies examined.

5 Conclusions

This work presents a detailed assessment of a hybrid concept for post-combustion CO₂ capture based on VPSA and membrane technology (VPSA bulk removal as first step and membrane purification as second step). A techno-economic analysis framework was established, integrating process models of the capture technologies, a systematic methodology for cost estimations and a robust system optimization framework. Process optimization was performed for a matrix of cases, representative of a wide range of relevant industrial applications. The techno-economic performance of the VPSA-membrane hybrid process was compared to that of standalone capture technologies, namely absorption with MEA, multi-stage membrane systems and VPSA. The obtained results suggest that:

- The hybrid concept has the potential to be a cost-efficient solution mainly in a low-to-medium range of CO₂ concentration in the flue gas (up to \approx 14%vol.), irrespective of the scale of the industrial application. In such applications it appears to be a cost-efficient solution against the benchmark technologies, especially if no waste heat is available for the absorption process.
- The VPSA-membrane hybrid process potential is affected by the geographic location of the industrial site, which in turn affects factors such as the availability of clean and affordable energy. Cases where electricity is a low-cost and low-carbon footprint commodity boost the performance of power-driven technologies such as the VPSA-membrane hybrid process. In the opposite case, heat-driven technologies such as absorption gain competitiveness.
- The VPSA-membrane hybrid process cost competitiveness is consistent at both scales (200 t/h and 2000 t/h) considered in this study. However, considering the modular nature of VPSA and membrane processes, it is reasonable to argue that this hybrid process technology can be expected to be even more attractive than non-modular technologies when applied to flue gas stacks of relatively low scale.
- The utilization of an advanced adsorbent material, supported by suitable process configurations, can bolster the performance of the hybrid process, and offer promises to further reduce the cost of capturing CO₂.

All in all, a significant potential niche of industrial applications is identified for the VPSA-membrane hybrid process. In other words, based on the results from the assessment in this work, VPSA and membrane process technology developers for CO₂ capture should join forces to provide a cost-efficient alternative to chemical absorption capture and their corresponding standalone in the low-to-medium range of CO₂ concentration in industrial flue gases. Even more so for industrial cases where there is no waste heat available, and there is access to clean and affordable electricity. In future work, the analysis will be expanded to encompass alternative options, mixing and matching suitable technologies in promising hybrid configurations, with the ultimate goal of providing an extensive mapping of techno-economic potential of hybrid processes for CO₂ capture.

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