Supporting information

S1. Literature review on hybrid processes

Table S1 summarizes the main findings from the literature review performed on hybrid processes based on PSA and membrane CO_2 separation technologies.

Table S1. Literature review on hybrid processes based on PSA and membrane CO_2 separation technologies.

Concept	*Feed Gas*	*Configuration*	*Method*	*First step*	*Second step*	*Main outcome*
Membrane/PSA [1]	*15% CO_2* *400 to 500 Nl/min*	*Membrane-adsorption with PSA*	*Experimental:* *150 days operation*	*Membrane unit concentrates feed stream from 15% to 40%* *Permeation pressure* *5 to 7 atm* *Effective membrane are 40 m^2*	*PSA produces purified CO_2 rich gas pressurization,* *Adsorbent: zeolite molecular sieve 13X* *Steps: adsorption, blowdown, rinse, and desorption steps*	*The results state that the membrane unit satisfies as a pre-treatment or enrichment process for PSA.* *Production rate of carbon dioxide to be 110 Nl/min with its purity up to 40% and recovery up to 60%* *Production of 20 Nl/min with the purity of carbon dioxide higher than 99.5%, and its recovery of 45 to 50%* *Need to further optimize process*
PSA/membrane [2]	*15% CO_2 concentration (CO_2/N_2)* *7.5 m3(STP)/h*	*PSA/membrane*	*Experimental basis and simulations*	*PSA separation unit* *Adsorbents: Zeolites 13X (ZMS) and Activated carbons (AC)* *Steps: feed, concurrent depressurization, purge with CO_2 rich stream, counter current depressurization, vacuum regeneration with purified gas, counter current repressurization with N_2.* *70% CO_2 (20% flow rate) with 100% recovery.*	*Membrane polymeric (commercial modules)* *Feed 70 vol% CO_2 and 30vol% N_2* *Flow rate 1.2 m3(STP/h)* *Permeate CO_2 concentration (91.5 to 95.5%CO_2) for transmembrane Δp (0.5 to 1.5 to 2.5 bar)*	*Describes challenges to be addressed and possible directions:* *For flue gas purification PSA unit with pressure slightly above atmospheric and vacuum* *Adsorbent selection is important in terms of adsorption capacity for CO_2 and selectivity the other components. Zeolites and 13X and AC are suggested.* *CO_2 outlet concentration of 50-80 vol.%. In the membrane section, this stream can be further enriched to yield a permeate stream containing 90 -99vol.% of CO2. The recycle of the retentate, with a content of 20-60vol.% of CO2, to the inlet of the hybrid system will lead to an almost complete recovery of carbon dioxide.*
PSA/membrane [3]	*12% CO_2 dry* *5–10m3(STP)/h*	*VSA/membrane*	*Experimental work with parametric testing*	*Four column VBSA process* *Feed 1.1 bar and vacuum ca. 0.15 to 0.2 bar* *Adsorbent material Zeolite 13X* *12% to 70% CO_2*	*Commercial membrane modules* *Polymeric, Air Liquid*	*The experimental energy consumption (in excess of 4.1MJ/kg of CO_2 captured) is obtained in the pilot. Pilot feasibility.* *Rough estimates show that for higher capacities, it can to a value as low as 1.7MJ/kg of CO_2.* *Need rigorous multiparameter optimization.*
PSA/membrane [4]	*13.3% CO_2* *(3500–9500m3(STP)h−1)*	*VSA/membrane*	*Modelling and simulations with validated models* *KPIs: CO_2 purity, CO_2 recovery, adsorbent productivity, energy consumption and amount of CO_2 captured*	*Four column VSA process Feed 1.1 bar and vacuum ca. 0.15 to 0.2 bar* *Adsorbent material Zeolite 13X* *12% to 70% CO_2*	*Commercial membrane modules* *Polymeric, Air Liquid* *70 to 90-95% CO_2*	*Competitive (energy) in comparison with VSA or membrane* *Energy consumption does not exceed 2 MJ/kgCo2 and could be lowered to 1.54-1.56 MJ/kg/Co2 with proper VSA cycle step time or area of membrane* *Claims it is a flexible solution* *Claims next step is finding optimal conditions before moving into technoeconomic optimization*
PSA/membrane [5]	*Not applicable as only membrane step is studied*	*VSA/membrane*	*Experimental and modelling investigation of membrane second step in this hybrid concept*	*Not included in assessment, as focus is on membrane as part of this hybrid*	*Two commercial membrane modules* *PRISM PA1020/Air Products and* *UBE UMS-A5*	*Separation properties of the polysulfone membrane in the context of CO_2 capture from flue gases were comprehensively analyzed* *Applicability in a hybrid system depends on the investment outlays and is the subject of ongoing optimization investigations.*

S2. VPSA process cycle

Figure S1 shows the VPSA 5-step process cycle selected as first step of the hybrid process.

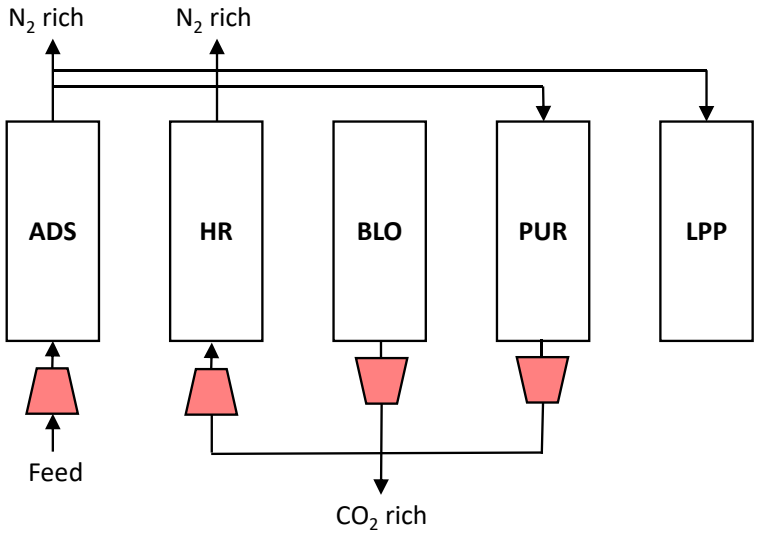

Figure S1. VPSA 5-step process cycle, working as bulk removal step in the hybrid process.

S3. Artificial neural network VPSA model

To generate relevant data for training ANN models, a rigorous one-dimensional mathematical model comprising a set of nonlinear partial differential equations (PDEs) developed in-house based on model equations in Haghpanah et al. [6] is employed. The model accounts for both mass and energy balances within the adsorption column and follows the assumptions used in Subraveti et al. [7]. These assumptions include the ideal gas law governing the gas phase, axially dispersed plug flow for the bulk fluid phase, uniform column and adsorbent properties, Ergun's equation accounting for the pressure drop, linear driving force model characterizing the solid phase mass transfer with macropore controlled kinetics, instantaneous gas-solid thermal equilibrium, and adiabatic process operation. The model equations, boundary conditions, and simulation parameters used in this study can be found in Subraveti et al. [7]. The process model is numerically solved, based on the standard approach proposed by Haghpanah et al. [6], where the spatial terms in the PDEs are discretized into 30 finite volumes using a total variation diminishing (TVD) scheme with a van-Leer flux limiter. The resulting ordinary differential equations (ODEs) are then solved using the in-built "solve_ivp" ode solver in Python 3.10, which employs the implicit multi-step variable order method. The process simulations are initialized with feed composition and continued until the process reaches a cyclic steady state (CSS).

The criterion for CSS is when the overall mass balance error of the VPSA cycle is less than 1%. This approach has been extensively used in adsorption process studies [7,8] and has been validated experimentally elsewhere [9,10].

The ANN models constructed in this study have a feedforward, fully connected architecture consisting of one input layer with 8 neurons, two hidden layers with 20 neurons each, and a single output layer with one neuron. A *tanh* activation function was used in the hidden layers, and a linear activation was used in the output layer. The inputs to the ANN are 8 process decision variables, which include the CO_2 composition in the flue gas and 7 process operating conditions, namely, adsorption pressure (P_H), low pressure (P_L), adsorption step time (t_{ADS}), light product purge step time (t_{PUR}), counter-current blowdown vacuum pump velocity (v_{BLO}), light product purge inlet velocity (v_{PUR}), and column length (L). Individual ANN models are trained for each output, which are process performance indicators, namely, CO_2 purity, CO_2 recovery, VPSA power consumption per single train, and other process features that form inputs to the scale-up and cost models. These features include counter-current blowdown step duration (t_{BLO}), volumetric flow rate of light product purge vacuum pump (S_{PUR}), and inlet molar flow rate (N_{ADS}). To sum up, 6 ANN models, each with 8 process decision variables as inputs, are constructed for every adsorbent investigated.

For training ANN models, an initial design of experiments (DoE) is performed on the process decision variables covering a wide range of design space. Decision-variable samples are generated based on Latin hypercube sampling and are then evaluated in the rigorous process model to calculate the desired outputs. Around 1200 unique combinations of the input variables generated using the Latin hypercube sampling, along with the corresponding outputs, were used as samples in the training of ANN models. The ANN models were trained using Bayesian regularization with the backpropagation algorithm in Python. An independent dataset of 600 samples was used to test the accuracy of the trained models. This procedure is repeated for each adsorbent. A test R2>0.98 was obtained for all ANN models in the validation, indicating a high degree of accuracy of the ANN models.

S4. Membrane two-stage process

Figure S2 shows the process flowsheet of the membrane two-stage CO_2 gas separation selected as second step of the hybrid process.

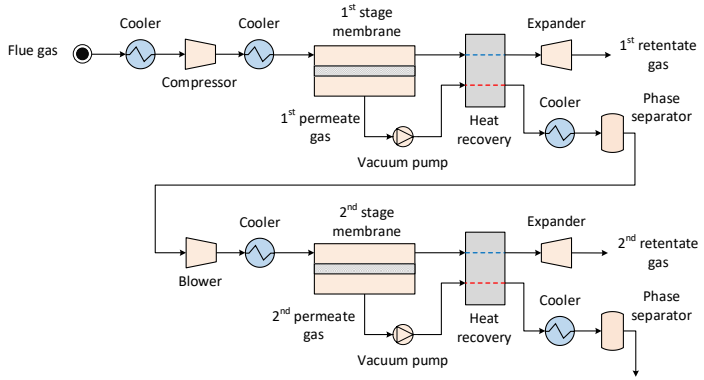

Figure S2. Membrane two-stage CO_2 gas separation process flowsheet

S5. VPSA process model parameters

The adsorption equilibria for the adsorbents studied in the paper are described in terms of the competitive dual-site Langmuir (DSL) isotherm model:

$$q_i^* = \frac{q_{sb,i} b_i c_i}{1 + \sum_i b_i c_i} + \frac{q_{sd,i} d_i c_i}{1 + \sum_i d_i c_i}$$

where q_i^* is the equilibrium solid-phase loading of the component i, $q_{sb,i}$ and $q_{sd,i}$ are the saturation capacities for the two sites and, b_i and d_i are the temperature dependent adsorption equilibrium constants:

$$b_i = b_0 e^{\left(-\frac{\Delta U_{b,i}}{RT}\right)}$$

$$d_i = d_0 e^{\left(-\frac{\Delta U_{d,i}}{RT}\right)}$$

where $\Delta U_{b,i}$ and $\Delta U_{d,i}$ are the internal energies of the two sites. The DSL parameters used are reported in Table S2, while the physical properties of the adsorbents are reported in Table S3**.**

Table S2. Parameters for the dual-site Langmuir isotherm models describing the adsorption behavior of the adsorbents selected.

Input parameters	**Unit**	**Zeolite 13X** [7]	**IISERP MOF2** [7]	**Activated carbon** [11]
CO_2				
q_{sb}	mol/kg	3.09	3.29	0.59
q_{sd}	mol/kg	2.54	1.89	7.51
b_0	m^3/mol	8.65×10^{-7}	9.39×10^{-8}	-
	1/bar	-	-	4.05×10^{-5}
d_0	m^3/mol	8.65×10^{-7}	5.23×10^{-7}	-
	1/bar	-	-	1.68×10^{-4}
ΔU_b	J/mol	-36641	-31135	-31400
ΔU_d	J/mol	-35690	-31135	-19800
N_2				
q_{sb}	mol/kg	3.09	3.29	0.16
q_{sd}	mol/kg	2.54	1.89	41.3
b_0	m^3/mol	2.69×10^{-6}	2.55×10^{-7}	-
	1/bar	-	-	8.34×10^{-3}
d_0	m^3/mol	2.69×10^{-6}	2.55×10^{-7}	-
	1/bar	-	-	7.98×10^{-12}
ΔU_b	J/mol	-15170	-11890	-14300
ΔU_d	J/mol	-15170	-11890	-50000

Table S3. Physical properties of adsorbent materials.

Physical properties	**Unit**	**Zeolite 13X** [7]	**IISERP MOF2** [7]	**Activated carbon** [11]
Adsorbent density	kg/m^3	1130	938	481
Specific heat capacity	J/kg/K	1070	1070	1050
Particle void fraction	-	0.35	0.35	0.35
Particle diameter	mm	1.5	1.5	1.5

A bed void fraction of 0.37 is selected for all cases.

S6. Membrane process model parameters

The membrane properties and process parameters are reported in Table S4.

Table S4. Process parameters of the membrane process. The parameters of the membrane benchmark optimization are also presented.

Input parameters	Unit	Value
Membrane carbon capture ratio	%	90
Membrane temperature	°C	30
CO_2 Permeance	Sm^3/m^2barh	5.94
Selectivity	P(A)/P(B) [-]	50
Feed temperature	°C	30
Feed pressure	bar	1.01
Feed CO_2 concentration	mol%	Varying
Retentate product temperature	°C	Varying
Retentate product pressure	bar	1.01
Permeate product temperature	°C	30
Minimum permeate product pressure	bar	0.2
CO_2 upgraded gas pressure	bar	1.01
Permeate product CO_2 concentration	mol%	>95%
Compressor		
Maximum pressure ratio	-	4
Outlet pressure	bar	<50 bar
Isentropic efficiency	%	80
Motor efficiency	%	98.1
Expander		
Outlet pressure	bar	1.01
Isentropic efficiency	%	85
Generator efficiency	%	98.1
Vacuum pump		
Minimum operating vacuum pressure	bar	0.2
Isentropic efficiency	%	75
Motor efficiency	%	98

S7. Cost model parameters

The cost parameters for the VPSA process are reported in Table S5.

Table S5. Cost parameters of the techno-economic analysis model utilized for costing the VPSA process.

Investment cost parameters	Unit	Value
VPSA module		
Adsorbent material [7]	€/t	1500 (13X), 1000 (AC), 4440 (IISERP)
Adsorbent material lifetime	y	5

The direct costs of individual VPSA process equipment were estimated using cost functions developed and validated with Aspen Economic Process Analyzer®. More details can be found in Subraveti et al [7].

$$Column\ direct\ cost\ (€) = e^{\left(0.4148 \cdot diameter\ (m) + 0.0738 \cdot \frac{L}{D}\ (-) + 0.0231 \cdot p_{max}\ (bar) + 10.8079\right)}$$

$$Compressor\ direct\ cost\ (€) = 121.412 \cdot \left(inlet\ flow\ rate\ (m^3/h)\right)^{0.900} \cdot 1.032^{p_{max}\ (bar)}$$

$$Vacuum\ pump\ direct\ cost\ (€) = 423.9 \cdot \left(inlet\ flow\ rate\ (m^3/h)\right)^{0.653} + 30000$$

The cost parameters for the membrane process are reported in Table S6.

Table S6. Cost parameters of the techno-economic analysis model utilized for costing the membrane process.

Direct cost of individual components	Unit	Value
1st stage compressor	€/kW	860
2nd stage compressor	€/kW	480
3rd stage compressor	€/kW	340
Expander	€/kW	530
Vacuum pump	€/kW	740
Cooler	€/m^2	340
Membrane Framework		
Reference area	m^2	
Area scale power	-	
Reference pressure	bar	55.0
Pressure scale power	-	0.875
Framework reference cost	€	267000
Membrane Module		
Membrane module cost	€/m^2	46.9
Membrane module lifetime	y	5.0
Membrane module replacement cost	€/m^2	9.38

The replacement of adsorbent materials and membrane modules is accounted for as an operational cost, occurring at the end of the respective lifetime (5 years in both cases). No performance degradation is considered within the lifetime.

The common cost parameters are reported in Table S7.

Table S7. Common cost parameters of the techno-economic analysis model utilized for costing the hybrid CO_2 capture process. Three geographic locations are considered, where the electricity prices and related emission intensity are determined: European Union (EU), Norway (NO) and Germany (DE).

Investment cost parameters	**Unit**	**Value**
Cost factors		
Direct cost-to-TCR factor	-	1.95
Operating cost parameters	**Unit**	**Value**
Overall parameters		
Discount rate	%	8
Years of operation	year	25
Utilization rate first year	%of time	65
Utilization rate second year	%of time	85
Utilization rate other years	%of time	85
Annual fixed maintenance cost	% of CAPEX/y	4.24
Utility cost		
Cooling water cost	€/m^3	0.025
Electricity cost	€/MWh	26.5 (NO), 76.2 (EU), 106.5 (DE)
Climate impact of electricity	$kgCO_2$/MWh	10.8 (NO), 230.7 (EU), 311 (DE)
Labour cost		
Number of operators	-	1
Number of shifts	-	5
Operator cost	k€/y	60

The annual maintenance cost was calculated as 2.0% of the total plant cost (TPC) of which the maintenance labour cost accounts for 40%. The annual insurance and location taxes, which include overhead and miscellaneous regulatory fees, were set to 2% of TPC. The labour costs were calculated based on the assumption that the hybrid CO_2 capture unit requires 5 operators (5 shift pattern with 1 operator per shift as adsorption processes are highly automated) with an annual salary of 60 k€ per person. Administrative costs were set to 30% of the operating and maintenance labour cost.

S8. Optimization results with and without gas recycle – base case

Table S8 illustrates the results optimal obtained by the VPSA-membrane hybrid process with and without gas recycle and using European average values for price and footprint of electricity. The large industrial scale (i.e., 2000 t/h of flue gas) is considered.

Table S8. Full set of results (with and without gas recycle) for the VPSA-membrane hybrid process in Europe and for the larger industrial scale (i.e., 2000 t/h of flue gas)

CO_2 conc.	Recycle	CO_2 purity	CO_2 recovery	SEC (kWh/t)	CAPEX (€/t)	OPEX (€/t)	CAC (€/t)
3.5 %	N	94.9 %	90.0 %	307	33	43	75.2
	Y	94.9 %	92.3 %	240	32	37	69.3
10 %	N	95.0 %	90.0 %	280	19	34	52.3
	Y	94.7 %	92.5 %	253	19	31	49.9
12.5 %	N	94.4 %	90.0 %	301	16	33	49.3
	Y	94.8 %	91.8 %	247	16	29	45.7
15 %	N	94.4 %	90.0 %	263	15	30	44.7
	Y	94.6 %	94.5 %	251	14	29	43.2
18 %	N	94.6 %	90.0 %	248	13	28	40.8
	Y	94.8 %	92.2 %	228	14	27	40.9
22 %	N	94.8 %	90.0 %	221	12	26	38.5
	Y	94.8 %	92.5 %	224	12	26	38.0
30 %	N	94.9 %	90.0 %	214	11	24	34.9
	Y	94.8 %	93.7 %	215	12	25	36.3

S9. Optimization results – base case

Table S9 illustrates the optimal results obtained by the VPSA-membrane hybrid process using European average values for price and footprint of electricity. The small industrial scale (i.e., 200 t/h of flue gas) is considered. A breakdown for the two hybrid steps is included.

Table S9. Optimal results for the VPSA-hybrid process in Europe and for the smaller industrial scale (i.e., 200 t/h of flue gas).

		VPSA			Membrane				Hybrid			
CO_2 conc.	Recycle	CO_2 purity	CO_2 recovery	CAC (€/t)	no. stages	CO_2 purity	CO_2 recovery	CAC (€/t)	CO_2 purity	CO_2 recovery	SEC (kWh/kg)	CAC (€/t)
3.5 %	Y	37.4 %	93.7 %	59.6	2	95.0 %	83.6 %	21.5	95.0 %	93.7 %	265	81.1
10 %	Y	52.8 %	92.1 %	42.2	1	94.8 %	84.1 %	11.5	94.8 %	92.1 %	282	53.7
12.5 %	Y	51.3 %	94.3 %	38.8	1	94.8 %	80.0 %	11.1	94.8 %	94.3 %	259	49.9
15 %	Y	56.5 %	93.2 %	36.9	1	94.7 %	82.7 %	7.7	94.7 %	93.2 %	234	44.6
18 %	Y	62.9 %	91.0 %	35.7	1	94.6 %	88.8 %	6.8	94.6 %	91.0 %	216	42.5
22 %	Y	63.3 %	94.0 %	33.2	1	95.0 %	85.6 %	6.2	95.0 %	94.0 %	220	39.4
30 %	N	68.8 %	93.6 %	28.8	1	94.8 %	96.2 %	7.5	94.8 %	90.0 %	211	36.3

Table S10 illustrates the optimal results obtained by the VPSA-membrane hybrid process using European average values for price and footprint of electricity. The large industrial scale (i.e., 2000 t/h of flue gas) is considered. A breakdown for the two hybrid steps is included.

Table S10. Optimal results for the VPSA-hybrid process in Europe and for the larger industrial scale (i.e., 2000 t/h of flue gas).

		VPSA			Membrane				Hybrid			
CO_2 conc.	Recycle	CO_2 purity	CO_2 recovery	CAC (€/t)	no. stages	CO_2 purity	CO_2 recovery	CAC (€/t)	CO_2 purity	CO_2 recovery	SEC (kWh/kg)	CAC (€/t)
3.5 %	Y	39.1 %	92.3 %	54.3	2	94.9 %	84.3 %	15.0	94.9 %	92.3 %	240	69.3
10 %	Y	50.0 %	92.5 %	41.0	1	94.7 %	73.1 %	8.9	94.7 %	92.5 %	253	49.9
12.5 %	Y	53.6 %	91.8 %	37.7	1	94.8 %	80.0 %	8.1	94.8 %	91.8 %	247	45.7
15 %	Y	55.0 %	94.5 %	34.0	1	94.6 %	87.3 %	9.3	94.6 %	94.5 %	251	43.2
18 %	Y	61.8 %	92.2 %	33.9	1	94.8 %	88.1 %	7.0	94.8 %	92.2 %	228	40.9
22 %	Y	65.8 %	92.5 %	31.5	1	94.8 %	91.5 %	6.5	94.8 %	92.5 %	224	38.0
30 %	N	70.3 %	93.6 %	28.2	1	94.9 %	96.2 %	6.7	94.9 %	90.0 %	214	34.9

Table S11 illustrates the cost breakdown into CAPEX and OPEX of the optimal results presented in Table S10.

Table S11. Cost breakdown into CAPEX and OPEX of the optimal results for the VPSA-hybrid process in Europe and for the larger industrial scale (i.e., 2000 t/h of flue gas).

		VPSA			Membrane			Hybrid		
CO_2 conc.	Recycle	CAPEX (€/t)	OPEX (€/t)	CAC (€/t)	CAPEX (€/t)	OPEX (€/t)	CAC (€/t)	CAPEX (€/t)	OPEX (€/t)	CAC (€/t)
3.5 %	Y	28.2	26.1	54.3	4.1	10.9	15.0	32.3	37.0	69.3
10 %	Y	16.4	24.5	41.0	2.3	6.6	8.9	18.8	31.1	49.9
12.5 %	Y	14.3	23.4	37.7	2.0	6.1	8.1	16.3	29.4	45.7
15 %	Y	12.2	21.8	34.0	2.2	7.1	9.3	14.4	28.8	43.2
18 %	Y	12.3	21.6	33.9	1.7	5.2	7.0	14.1	26.8	40.9
22 %	Y	10.8	20.7	31.5	1.6	4.9	6.5	12.4	25.6	38.0
30 %	N	9.4	18.8	28.2	1.5	5.2	6.7	10.9	23.9	34.9

S10. Optimization results – Norway

Table S12 illustrates the optimal results obtained by the VPSA-membrane hybrid process using Norwegian values for price and footprint of electricity. The large industrial scale (i.e., 2000 t/h of flue gas) is considered. A breakdown for the two hybrid steps is included.

Table S12. Optimal results for the VPSA-hybrid process in Norway and for the larger industrial scale (i.e., 2000 t/h of flue gas).

		VPSA			Membrane				Hybrid			
CO_2 conc.	Recycle	CO_2 purity	CO_2 recovery	CAC (€/t)	no. stages	CO_2 purity	CO_2 recovery	CAC (€/t)	CO_2 purity	CO_2 recovery	SEC (kWh/kg)	CAC (€/t)
3.5 %	Y	31.2 %	91.3 %	42.2	2	95.5 %	88.0 %	12.4	95.5 %	91.3 %	351	54.6
10 %	Y	38.6 %	92.1 %	24.6	2	95.1 %	92.3 %	10.8	95.1 %	92.1 %	357	35.4
12.5 %	Y	52.7 %	96.7 %	24.8	1	94.9 %	78.8 %	4.5	94.9 %	96.7 %	302	29.3
15 %	Y	57.2 %	93.9 %	22.9	1	95.0 %	87.3 %	4.9	95.0 %	93.9 %	298	27.7
18 %	N	63.4 %	94.1 %	20.9	1	94.8 %	95.6 %	5.1	94.8 %	90.0 %	305	25.9
22 %	N	66.3 %	93.4 %	19.8	1	94.9 %	96.4 %	4.5	94.9 %	90.0 %	278	24.3
30 %	N	70.0 %	93.5 %	19.1	1	94.9 %	96.2 %	3.7	94.9 %	90.0 %	267	22.8

S11. Optimization results – Germany

Table S13 illustrates the optimal results obtained by the VPSA-membrane hybrid process using German values for price and footprint of electricity. The large industrial scale (i.e., 2000 t/h of flue gas) is considered. A breakdown for the two hybrid steps is included.

Table S13. Optimal results for the VPSA-hybrid process in Germany and for the larger industrial scale (i.e., 2000 t/h of flue gas).

		VPSA			Membrane				Hybrid			
CO_2 conc.	Recycle	CO_2 purity	CO_2 recovery	CAC (€/t)	no. stages	CO_2 purity	CO_2 recovery	CAC (€/t)	CO_2 purity	CO_2 recovery	SEC (kWh/kg)	CAC (€/t)
3.5 %	Y	40.0 %	91.7 %	60.7	2	95.0 %	80.5 %	18.3	95.0 %	91.7 %	237	79.0
10 %	Y	42.4 %	92.8 %	44.5	1	94.2 %	67.8 %	11.9	94.2 %	92.8 %	184	56.3
12.5 %	Y	50.2 %	91.5 %	42.1	1	94.5 %	83.0 %	13.2	94.5 %	91.5 %	203	55.3
15 %	Y	54.0 %	93.2 %	41.2	1	94.6 %	79.8 %	9.8	94.6 %	93.2 %	230	51.0
18 %	Y	61.4 %	91.3 %	40.5	1	94.9 %	86.6 %	8.4	94.9 %	91.3 %	227	48.9
22 %	Y	64.7 %	92.7 %	39.5	1	94.8 %	88.2 %	7.2	94.8 %	92.7 %	221	46.7
30 %	N	64.4 %	95.2 %	32.8	1	94.7 %	94.6 %	9.7	94.7 %	90.0 %	204	42.4

S12. Optimization results – alternative material

Table S14 illustrates the optimal results obtained by the VPSA-membrane hybrid process using European average values for price and footprint of electricity and IISERP MOF2 as adsorbent material. The large industrial scale (i.e., 2000 t/h of flue gas) is considered. A breakdown for the two hybrid steps is included.

Table S14. Optimal results for the VPSA-hybrid process in base case (i.e., EU location) and for the larger industrial scale (i.e., 2000 t/h of flue gas), using IISERP MOF2 as adsorbent material.

		VPSA			Membrane				Hybrid			
CO_2 conc.	Recycle	CO_2 purity	CO_2 recovery	CAC (€/t)	no. stages	CO_2 purity	CO_2 recovery	CAC (€/t)	CO_2 purity	CO_2 recovery	SEC (kWh/kg)	CAC (€/t)
3.5 %	Y	65.6 %	97.5 %	54.5	1	95.2 %	77.5 %	4.7	95.2 %	97.5 %	213	55.9
10 %	Y	80.8 %	96.2 %	38.2	1	95.1 %	93.2 %	3.7	95.1 %	96.2 %	225	39.7
12.5 %	Y	82.4 %	97.3 %	36.9	1	96.0 %	90.3 %	3.2	96.0 %	97.3 %	229	38.4
15 %	Y	82.1 %	94.4 %	35.8	1	95.3 %	92.0 %	3.3	95.3 %	94.4 %	222	37.1
18 %	Y	85.1 %	96.0 %	34.7	1	95.1 %	94.1 %	3.0	95.1 %	96.0 %	200	35.3
22 %	Y	84.7 %	96.6 %	34.0	1	95.0 %	94.7 %	3.1	95.0 %	96.6 %	201	34.7
30 %	N	94.7 %	91.6 %	32.8	1	97.9 %	98.2 %	2.2	97.9 %	90.0 %	187	33.6

Table S15 illustrates the optimal results obtained by the VPSA-membrane hybrid process using European values for price and footprint of electricity and an activated carbon as adsorbent material. The large industrial scale (i.e., 2000 t/h of flue gas) is considered. A breakdown for the two hybrid steps is included.

Table S15. Optimal results for the VPSA-hybrid process in base case (i.e., EU location) and for the larger industrial scale (i.e., 2000 t/h of flue gas), using an activated carbon as adsorbent material.

		VPSA			Membrane				Hybrid			
CO_2 conc.	Recycle	CO_2 purity	CO_2 recovery	CAC (€/t)	no. stages	CO_2 purity	CO_2 recovery	CAC (€/t)	CO_2 purity	CO_2 recovery	SEC (kWh/kg)	CAC (€/t)
3.5 %	Y	27.5 %	98.6 %	68.3	2	95.0 %	74.3 %	20.9	95.0 %	98.6 %	401	89.2
10 %	N	39.2 %	97.9 %	46.3	2	94.9 %	91.9 %	17.7	94.9 %	90.0 %	357	64.0
12.5 %	N	39.6 %	97.8 %	40.9	2	95.1 %	92.0 %	17.8	95.1 %	90.0 %	325	58.7
15 %	N	41.5 %	96.4 %	37.7	2	95.0 %	93.4 %	17.1	95.0 %	90.0 %	309	54.8
18 %	N	45.6 %	97.1 %	37.8	2	94.9 %	92.7 %	14.7	94.9 %	90.0 %	293	52.6
22 %	N	59.1 %	95.8 %	41.4	1	94.4 %	94.0 %	9.6	94.4 %	90.0 %	275	51.0
30 %	N	39.9 %	97.6 %	30.3	2	95.2 %	92.2 %	17.2	95.2 %	90.0 %	269	47.5

References

[1] Jeon J-K, Ihm S-K, Park Y-K, Kim JS, Dong J-I, Kim S, et al. Membrane/PSA Hybrid Process for Carbon Dioxide Recovery at Low Concentration. Stud. Surf. Sci. Catal., vol. 153, 2004, p. 543–6. https://doi.org/10.1016/S0167-2991(04)80311-2.

[2] Warmuzinski K, Tanczyk M, Jaschik M, Janusz-Cygan A. A hybrid separation process for the recovery of carbon dioxide from flue gases. Energy Procedia, vol. 37, 2013. https://doi.org/10.1016/j.egypro.2013.06.094.

[3] Warmuzinski K, Tanczyk M, Jaschik M. Experimental study on the capture of CO2 from flue gas using adsorption combined with membrane separation. Int J Greenh Gas Control 2015;37:182–90. https://doi.org/10.1016/j.ijggc.2015.03.009.

[4] Jaschik M, Tanczyk M, Jaschik J, Janusz-Cygan A. The performance of a hybrid VSA-membrane process for the capture of CO2 from flue gas. Int J Greenh Gas Control 2020. https://doi.org/10.1016/j.ijggc.2020.103037.

[5] Janusz-Cygan A, Jaschik J, Wojdyła A, Tańczyk M. The separative performance of modules with polymeric membranes for a hybrid adsorptive/membrane process of CO2 capture from flue gas. Membranes (Basel) 2020;10. https://doi.org/10.3390/membranes10110309.

[6] Haghpanah R, Majumder A, Nilam R, Rajendran A, Farooq S, Karimi IA, et al. Multiobjective Optimization of a Four-Step Adsorption Process for Postcombustion CO $_2$ Capture Via Finite Volume Simulation. Ind Eng Chem Res 2013;52:4249–65. https://doi.org/10.1021/ie302658y.

[7] Subraveti SG, Roussanaly S, Anantharaman R, Riboldi L, Rajendran A. Techno-economic assessment of optimised vacuum swing adsorption for post-combustion CO2 capture from steam-methane reformer flue gas. Sep Purif Technol 2021. https://doi.org/10.1016/j.seppur.2020.117832.

[8] Farmahini AH, Krishnamurthy S, Friedrich D, Brandani S, Sarkisov L. Performance-Based Screening of Porous Materials for Carbon Capture. Chem Rev 2021. https://doi.org/10.1021/acs.chemrev.0c01266.

[9] Krishnamurthy S, Rao VR, Guntuka S, Sharratt P, Haghpanah R, Rajendran A, et al. CO2 capture from dry flue gas by vacuum swing adsorption: A pilot plant study. AIChE J 2014;60:1830–42. https://doi.org/10.1002/aic.14435.

[10] Estupiñan Perez L, Sarkar P, Rajendran A. Experimental validation of multi-objective optimization techniques for design of vacuum swing adsorption processes. Sep Purif Technol 2019. https://doi.org/10.1016/j.seppur.2019.05.039.

[11] Maring BJ, Webley PA. A new simplified pressure/vacuum swing adsorption model for rapid adsorbent screening for CO2 capture applications. Int J Greenh Gas Control 2013. https://doi.org/10.1016/j.ijggc.2013.01.009.