

# 1 **Model validation and dynamic simulation of post-combustion carbon** 2 **dioxide separation with membranes**

3 Antonio Tripodi, Renato La Pietra, Matteo Tommasi, Ilenia Rossetti\*

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5 Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano,  
6 CNR-SCITEC and INSTM Unit Milano-Università, via C. Golgi 19, 20133 Milano, Italy

## 7 8 9 **Abstract**

10 This work presents a finite-element numerical model for N<sub>2</sub>-O<sub>2</sub>-CO<sub>2</sub> separation by hollow fiber  
11 membranes, scaled-up to treat the combustion gases coming from a medium-size coal-based power  
12 unit. The equation set has been expanded to include, beyond the membranes, also compressors and  
13 condensers. Two process layouts have been evaluated: one open loop allowing for high purification  
14 level, and a recirculating scheme yielding superior enrichments. The resulting simulation, valid from  
15 pilot to full-plant scale, takes then into account the interplay of both active and passive process units  
16 besides the active membranes, and is fully dynamic in definition and scope.

17 The results show that the degree of purification is mainly affected by the enrichment-side pressure,  
18 while the CO<sub>2</sub> concentration depends largely on the CO<sub>2</sub>:N<sub>2</sub> selectivity. Even when this latter value  
19 is relatively low, a proper scale-up of series/parallel modules can overcome the limitation without  
20 exceeding 7 – 8 bar pressurisation. Simulating the impact of pressure and flow transients on the plant  
21 outflows, the recovery procedure and timescales are identified.

22  
23 *Keywords:* Carbon Capture; CO<sub>2</sub> sequestration; CO<sub>2</sub> separation; Membrane separation; Dynamic  
24 simulation.

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\* Corresponding author: fax +39-02-50314300, email [ilenia.rossetti@unimi.it](mailto:ilenia.rossetti@unimi.it)

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## 26 **1 - Introduction**

27 As carbon capture has gained importance, both within an environmental impact and atom-economy  
28 perspectives, waste-gases produced by power plants can be treated by pre-combustion, oxy-  
29 combustion, or post-combustion strategies [1]. Oxy-combustion is limited by the need of pure  
30 oxygen, which in turn can be energy-demanding (if obtained by distillation) or requires additional  
31 separation plants; the second issue belongs also to the pre-combustion approach. Post-combustion  
32 approach, on the other hand, foresees simpler plant layouts, but on the other hand yields lower  
33 concentrations of CO<sub>2</sub> in the effluents. It is nonetheless considered a very promising technology  
34 because it can be easily retrofitted to existing power plants [1–3].

35 The separation of carbon dioxide via membranes is very attractive as it needs virtually no thermal  
36 inputs. It is preferentially applied to gases with a CO<sub>2</sub> content of 10 – 20% vol [4], because very  
37 diluted mixtures would require a high specific compression power [5], while for already pre-  
38 concentrated streams cryogenic processes become viable [6]. A first section usually purifies the plant  
39 effluents, while a second one enriches the carbon dioxide stream [7]. This technology does not require  
40 other chemicals (amines, salts, physical solvents) to be purchased and stored. Membranes packages  
41 can also be easily adapted to a wide range of process scales [8], and do not need the regeneration  
42 cycles typical of solid adsorbents (which imply larger capital expenses and the extra equipment  
43 needed by coupling batch with continuous processes). The main disadvantages of the membrane-  
44 based capture are the relatively low purity of the captured CO<sub>2</sub>, and the need to remove water [9] and  
45 other species potentially non-compatible with the membranes material [10,11].

46 Ongoing research has made available a variety of materials and shapes with ever increasing selectivity  
47 and packing efficiency [12]. Fiber membranes folded in hollow cylinders, in turn arranged into  
48 modules composed of 10<sup>3</sup> – 10<sup>5</sup> stems, feature a very high active surface per element, 10 to 100 times  
49 larger than other membranes types [13,14] and can be well represented by mono-dimensional models  
50 using the cylinder axis as the only spatial coordinate, thanks to their small radius. The very high

51 thickness-to-radius ratio, on the other hand, decreases their permeability and makes them sensitive to  
52 water condensation (unless they are used as contactors to enhance the transport coefficient of gas-  
53 liquid applications [13,15,16]), so a reliable simulation for the gas-gas technology must consider  
54 separating devices.

55 Simulation works related to the whole separation process usually account for plants steady states  
56 [17,18], while more accurate dynamic calculations are often employed to treat a membrane's inner  
57 behavior [19] or pilot-scale single elements [20].

58 To fill this gap, in this work, a fully dynamic simulation is extended to a whole separation plant,  
59 except for the CO<sub>2</sub> enrichment part, after validating and scaling-up a model built to represent a single  
60 bench-scale module. This allows to foresee the off-design plant conditions that are the outcomes of  
61 transient behaviors. The strategy is the adoption, as basic process units, of membrane stacks made of  
62 parallel modules. The conservative permeance values (under 100 GPU for CO<sub>2</sub>, in the low-  
63 performance range of the materials reviewed in [5,21,22]) of a polymeric hollow fiber have been  
64 selected, nonetheless coupled to very large available surfaces and an average CO<sub>2</sub>:N<sub>2</sub> selectivity of  
65 30 [21,23].

66 The treated gas is a stream coming from the combustion of coal. A power plant of 607 MW<sub>el</sub> (Neurath  
67 Unit 4 [24]) is taken as reference and the gas flow and composition have been estimated by the plant  
68 fuel consumption and lignite composition analysis [10].

69

## 70 **2 – Methods**

71 The simulation of the membrane adsorption has been carried out with an equation-oriented approach,  
72 using Aspen Custom Modeler v8 by Aspen Tech [25]. This software allows defining and solving a  
73 linear system of first-order (with respect to time) differential equations, plus algebraic equations and  
74 boundary conditions. Moreover, the steady state solutions (equivalent to the convergence points of a  
75 steady-state process simulation) can be sought independently by setting to zero all the time

76 derivatives, without waiting for the variables to complete their dynamic from a non-stable initial  
77 point. The algebraic and differential equations are solved by separate sub-calculators.

78 In the model developed for this work, a finite-element approach has been used to represent the  
79 membrane modules, rather than resorting to partial differential equations. The integration method  
80 selected – already provided by the software – is the one by Gear [26], preferred to the default choice  
81 (implicit-Euler).

82 The process simulation has been carried out through the following steps:

- 83 a. choice of a dynamic model for the membranes and its translation into the Aspen Custom  
84 Modeler proprietary programming language, defining an independent “membrane module”  
85 subsystem;
- 86 b. validation of the model translation, checking the results when using the same process  
87 conditions defined by the original models;
- 88 c. choice of a model for the flue gas compressor and reimplementation of the equations;
- 89 d. steady-state solution of the compressor model for a reference performance curve (see “scale-  
90 up” paragraph) and comparison of the gas flow with the rated hydraulic conditions of a  
91 membrane;
- 92 e. scale-up of the membrane model active surface by two orders of magnitude, to align it with  
93 the gas flow calculated by the compressor model;
- 94 f. further modelling of mixers, splitter (they distribute the gas between two-three parallel  
95 membrane trains), and water condenser;
- 96 g. process design by connection of the appropriate number of blocks, modifying at need the  
97 compressors curves and the condenser geometries and duties.

98 The compressor is modeled after the work of Venturini [27], that uses two polynomial interpolation  
99 of the characteristic and efficiency curves and deals with mass accumulation and shock-waves across  
100 the unit. The condenser model accounts for three phenomena: 1) liquid and vapor separation  
101 according to the thermodynamic equilibrium (at fixed volume and mixture composition), 2) heat

102 exchange via an overall heat transfer coefficient (at fixed imposed outer temperature) and 3) influence  
103 of the vessel geometry on the vapor velocity (which has to be low enough to minimize the liquid  
104 entrainment). The only simplifying assumption is that the transport at the vapor-liquid interface is  
105 instantaneous.

106 The mixer and splitter models are meant to be used always together, to represent a fluid header with  
107 multiples inlet/outlets, so only the mixing part is assigned a non-zero volume with ensuing dynamic  
108 behavior, while the mixing part acts just as a routing for the outlets. Other details are in Table 2.

109

### 110 **3 - Membrane model validation**

111 The developed model is based on the approach by Coker [23], that adopts the following further  
112 assumptions:

- 113 • the membranes are treated with mean transport coefficients depending only on the chemical  
114 species, hiding the detailed dependences on thickness, pore sizes and diffusion coefficients;
- 115 • the process is isothermal;
- 116 • the transport driving force depends on the partial pressures, that are in turn calculated by the  
117 perfect gas law without non-ideality effects;
- 118 • a membrane module is represented by ten sub-modules placed in series (and connected with  
119 retentate and permeate either in counter-current or co-current arrangements): each sub-module  
120 is considered in mixed-flow conditions; in this way the spatial domain is discretized, and not  
121 considered as a variable in the differential equations solution.

122 According to the above-mentioned reference work, the model has been set-up and validated for a case  
123 of air purification, nevertheless the cited authors give a set of transport coefficients valid also for the  
124 other chemical species involved in flue gas purification (see

125 Table 1). We tested the model with an air-separation case, not with CO<sub>2</sub> separation case of study,  
126 because the original finite-element formulas were not fully disclosed in the cited reference and were  
127 solved with a different software and a different mathematical technique. Through this preliminary

128 validation we ensured that the same finite-element approach and the same permeability values yielded  
 129 the same results, ruling out pure mathematical differences.  
 130 The same mathematical model has been used also by other authors [28], who reported also  
 131 comparable ranges for gases permeability and selectivity. An implementation with the Aspen Custom  
 132 Modeler software has also been carried out by Scholz et al. [29] for a CO<sub>2</sub>-CH<sub>4</sub> case study. The  
 133 geometrical details regarding a membrane module can be found in the referenced paper, while the  
 134 comparison of the original model (lines) and the test calculation of the present work (points) are found  
 135 in Figure 1.

136

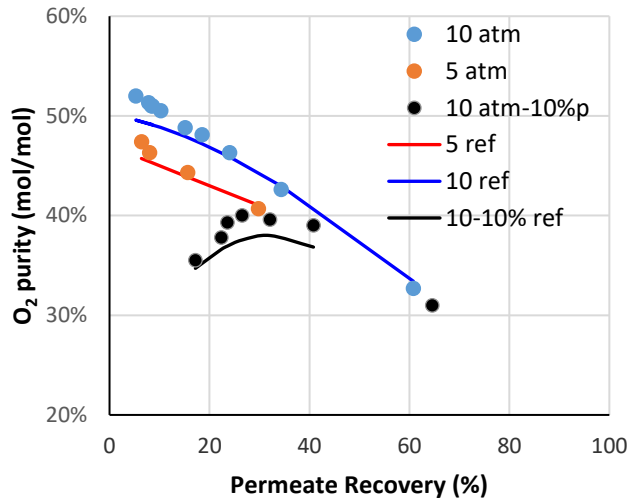
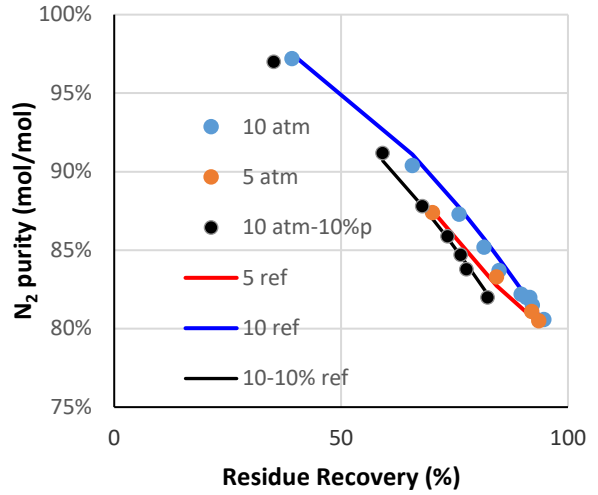
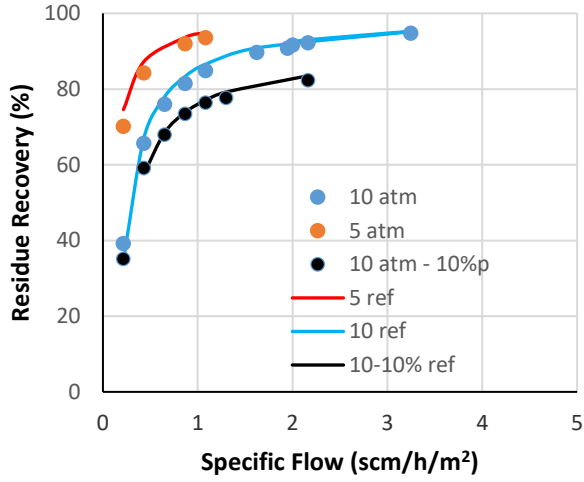
<b>Main membrane parameters [23]</b>	
Pressure	0 – 10 bar
Membrane type	Hollow fiber
CO <sub>2</sub> Permeability	10 – 100 GPU
CO <sub>2</sub> :N <sub>2</sub> selectivity	30 GPU/GPU
O <sub>2</sub> :N <sub>2</sub> selectivity	5.6 GPU/GPU
Specific surface	1500 m <sup>2</sup> /m <sup>3</sup>

137

138 Table 1: Main membrane parameters from the reference work [23]. 1 GPU =  $10^{-6}$  std-cm<sup>3</sup> cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup> =  $7.501 \times 10^{-12}$

139

$$\text{std-m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} = 3.346 \times 10^{-13} \text{ kmol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}.$$



140

141

142 Figure 1: Evaluation of the model re-implementation behavior with respect to the original formulas for the case of air  
 143 separation: the lines represent the results of Coker et al. [23], the circles are from this work calculations.

144

145 The variation of membranes permeability and selectivity according to temperature [30,31] will be  
 146 considered in further works. The differential and algebraic equations used to set-up this simulation  
 147 are listed in Table 2.

n	block	equation
1		$\frac{dn_{i,Ret}}{dt} = RET_{IN}z_{i,Ret,IN} - RET_{OUT}z_{i,Ret} - J_i$
2	membrane	$\frac{dn_{i,Per}}{dt} = PER_{IN}z_{i,Per,IN} - PER_{OUT}z_{i,Per} + J_i$
3		$J_i = S v_{Ret} G_i (p_R z_{i,Ret} - p_P z_{i,Per})$

---

4		$\frac{1}{f} = 4 \log_{10} \left( \frac{\varepsilon}{3.7D_{Ret}} + \frac{2.51}{Re_{Ret} f^{1/2}} \right)$
5		$(p_{Ret,IN} - p_{Ret}) = 0.433 f \frac{v_{Ret}}{A_{Ret}^{3/2}} \rho_{Ret} u_{Ret}^2$
<hr/>		
6		$\frac{dn_i}{dt} = Fz_i - Lx_i - Vy_i$
7		$\frac{dH}{dt} = Fh - Lh_L - Vh_V + Q$
8		$Q = -UA(T - T_{amb})$
9		$F = CV_{IN}(P_{IN} - P)$
10	Water separator	$V = CV_V(P - P_{amb})$
11		$L = CV_L(P - P_{amb})$
12		$\varphi = \frac{L \times PM_L}{V \times PM_V} \left( \frac{\rho_V \times PM_V}{\rho_L \times PM_L} \right)^2$
13		$k = 0.01 + \frac{0.3\varphi^{0.7}}{0.03 + \varphi} e^{-0.6\varphi}$
14		$u_{max} = k \sqrt{\frac{\rho_L \times PM_L}{\rho_V \times PM_V}}$
<hr/>		
15		$W = \frac{F_{out}}{3600} \frac{\gamma}{\gamma - 1} RT_{in} \left[ \left( \frac{P_{out}}{P_{in}} \right)^{\frac{\gamma-1}{\eta\gamma}} - 1 \right]$
16		$\eta = \eta_1 + \frac{\eta_3}{\left[ \frac{F_{out}}{PM} \times \frac{RT_{in}}{P_{in}} - \eta_2 \right]^{\eta_4}}$
17	compressor	$T_{out} = T_{in} \left( \frac{P_{out}}{P_{in}} \right)^{\frac{\gamma-1}{\eta\gamma}}$
18		$\frac{P_{out}}{P_{in}} = p_1 + \frac{p_3}{\left[ \frac{F_{out}}{PM} \times \frac{RT_{in}}{P_{in}} - p_2 \right]^{p_4}}$
19		$\frac{dF_{in}}{dt} = \frac{A_{suc}}{L_{suc}} (P_{suc} - P_{in})$
20		$\frac{dP_{in}}{dt} = \gamma RT_{in} \frac{F_{in} - F_{out}}{PM \times v_{cmpr}}$

---



148 Table 2: List of the equations used in the model. See the list of symbols. The membrane friction factor is calculated with  
149 the Coolebrok formula. The compressor efficiency and pressure ratio are fitted with rational functions, while its  
150 momentum balance is calculated after [27]. The vapor velocity correction factor is interpolated after [32].  
151

## 152 **4 - Process layout and scale-up**

153 Due to the fact that the compressor model is rigorous, its reliability depends on the use of actual  
154 performance curves, so its size has to be chosen as the maximum one for which such details are  
155 available in the open literature or undisclosed industry reports. A further constrain is the choice of  
156 data for the simulated range of pressures only. This has brought to model a unit [33] that can treat  
157 roughly one tenth of the above mentioned gas flow, implying that the cost of the simulated process  
158 should be rescaled. Though larger machines are available on the market, we could not obtain detailed  
159 performance curves.

160 The membrane model is scaled-up placing only ten sub-modules in series, but supposing to handle  
161 larger stacks of 100 modules in parallel, with the retentate (and permeate) side in perfect radial mixing  
162 conditions: this means that, for the same sub-module length, the active surface, the sides hydraulic  
163 sections and volumes are multiplied by 100. This size has been chosen judging that the resulting  
164 scale-up of the shells-side (retentate) hydraulic radius would be not so important as to impose to  
165 reconsider the model. Then other stacks are placed in series to achieve the desired separation level.

166 As a result, the gas flow handled by a scaled-up stack accounts for about a half of the selected  
167 operating point in the used performance curve (Figure 4) for a high pressure level of 6 – 7 bar, which  
168 in turn is well within the membrane model validation range. The details are found in

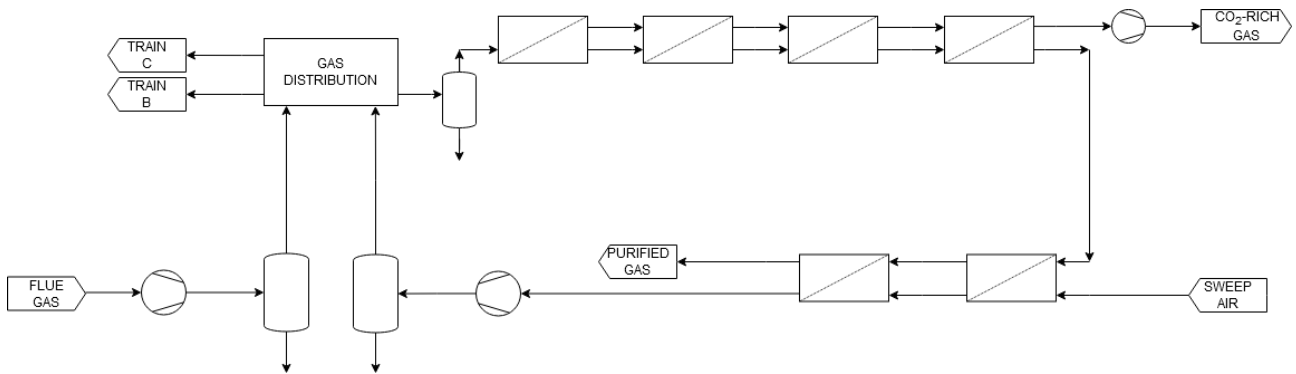
169 Table 4 for the nominal working point.

170 The separation layout follows two designs: a simple once-through scheme (Figure 2) and one where  
171 the combustion gases are re-diluted with recirculating air (resembling the schemes where the  
172 combustion chamber is fed with air from the membranes [34,35], or the ones where undiluted  
173 permeate is recycled [36]; see also Figure 3): this latter configuration requires additional membrane  
174 surface to accommodate the larger flow ensuing. The direct sweep gas (almost all nitrogen) mixing

175 to the flues allows to simulate the furnace feeding by air used for CO<sub>2</sub> purification, but without  
176 modeling also the combustion section and also varying the gas flows without the need to respect the  
177 N<sub>2</sub>:O<sub>2</sub>:C proportion imposed by the stoichiometry.

178 Since this work is focused on the model development and dynamic behavior, other possible  
179 configurations will be considered in further works. Alternative possible designs are exemplified in  
180 references [31–33,35].

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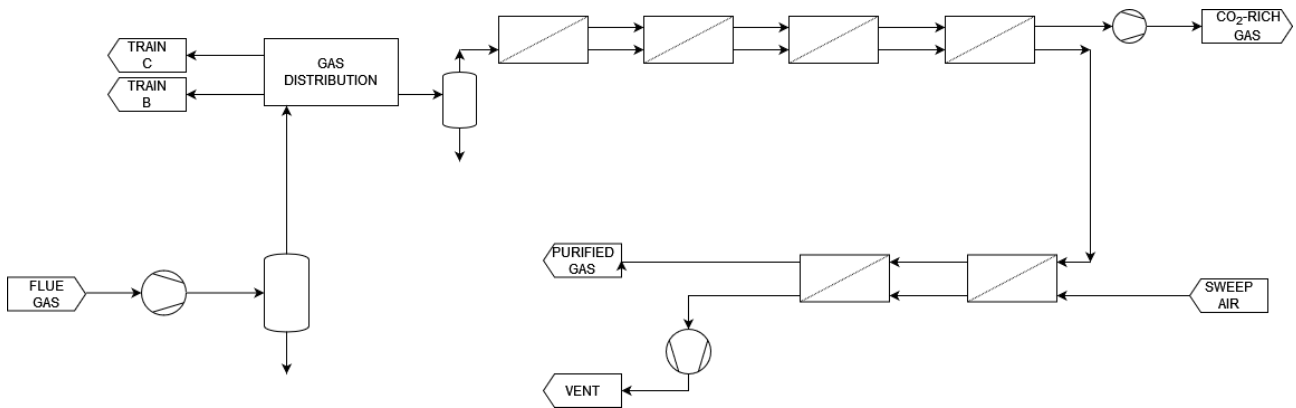


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Figure 2: Layout with recycle.

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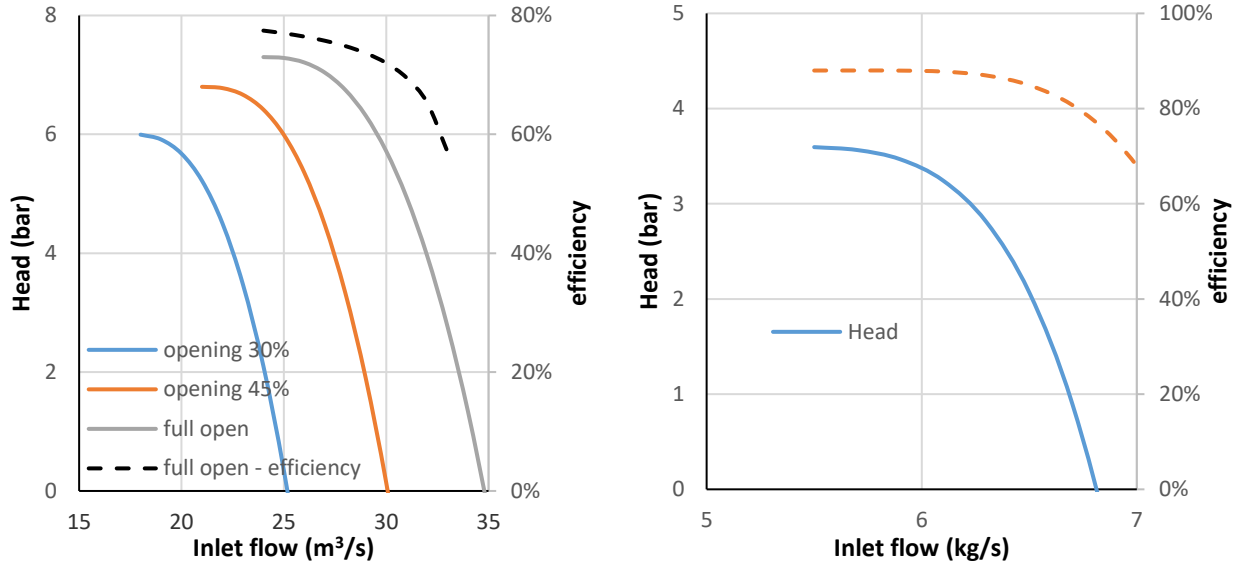
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Figure 3: Layout without recycle.

187

188 The sweep air compressor is modeled in the same way as the flue unit, and in this case the  
189 performance curve used has been taken from the literature [37], the needed pressure level is reached  
190 in two stages.



191

192

Figure 4: (left) large and (right) small compressors curves.

193

194 The scale-up of the process has brought to define the input data and main parameters values reported  
 195 in

196

Table 3

197 Table 3 and

198 Table 4. With the permeate side kept at sub-atmospheric pressure, the waste gas can be compressed  
 199 to mild levels (below 10 bar) to ensure a good operation [31]. A very interesting comparison about  
 200 process layouts and mixtures compositions has also been done by Merkel et al. [38].

	Flues	Sweep gas
CO <sub>2</sub>	0.201	0.01
N <sub>2</sub>	0.741	0.98
H <sub>2</sub> O	0.058	0.01

201

202

Table 3: Simulation input streams composition (mass fractions).

203

204

205

		Membrane module	Module stack	Flue compressor	Air compressor	Plant Unit	Compressor per unit	Stacks per compressor
<b>Configuration with recycle (Figure 2)</b>								
<b>Flue gas</b>	<b>scm/s</b>	0.0784	7.84	28.5	0.00	418	15	4
<b>Sweep gas</b>	<b>kg/h</b>	200	20000	0.00	20000	300000	15	2
<b>Recycle</b>	<b>scm/s</b>	0.0556	5.55	0.00	0.00	296		
<b>Total flow</b>	<b>scm/s</b>	0.134	13.4	28.5	20000	714	30	6
<b>Reference flow</b>	<b>scm/s</b>	0.140	14.0	24.0 – 34.0	-	746	-	-
<b>Configuration without recycle (Figure 3)</b>								
<b>Flue gas</b>	<b>scm/s</b>	0.0784	7.84	28.5	0.00	418	15	4
<b>Sweep gas</b>	<b>kg/h</b>	200	20000	0.00	20000	300000	15	2
<b>Total flow</b>	<b>scm/s</b>	0.0784	7.84	28.5	20000	418	30	6
<b>Reference flow</b>	<b>scm/s</b>	0.140	14.0	24.0 – 34.0	-	418		

206

207 Table 4: Reference design points for the configurations of Figure 2 and Figure 3. scm = m<sup>3</sup> measured in standard  
208 conditions (i.e. 298 K, 1 atm).

209

## 210 **5 - Simulation results**

211 The results presented are relative to six different dynamic scenarios, all starting and ending with a  
212 steady state. The variations of the tested process variables are listed in Table 5, while several rated  
213 plant working points belonging to each run are listed in Table 6.

214

<b>Dynamic 1</b>				<b>Dynamic 2</b>			
Hours	Variable	Action	Final state	Hours	Variable	Action	Final state
0-2	-	wait	1	0-2	-	wait	1
2-3	flow	Ramp to 110%	-	2-3	flow	Ramp to 110%	-

3-10	-	wait	2	2.5-3.5	Sweep air	Ramp to 90%	-
10-11	Sweep air	Ramp to 105%	-	3-3.5	Vacuum	Ramp to 90%	-
11-21	-	Wait	3	3.5-24	-	Wait	11
21-22	Sweep air	Ramp to 95%	-				
22-40	-	Wait	4				
40-41	Vacuum	Ramp to 90%	-				
41-60	-	Wait	5				
<b>Dynamic 3</b>				<b>Dynamic 4</b>			
Hours	Variable	Action	Final state	Hours	Variable	Action	Final state
0	-	-	11	0-1	-	Wait	1
0-2	Compression	Ramp to 107%	-	1-5	Condenser outlet Cv	Ramp to 33%	20
2-12	-	wait	12	5-6	Vacuum	Ramp to 90%	-
12-12.5	Vacuum	Ramp to 75%	-	6-11	-	Wait	21
12.5-24	-	Wait	13				
<b>Dynamic 5</b>				<b>Dynamic 6</b>			
Hours	Variable	Action	Final state	Hours	Variable	Action	Final state
0-2	-	Wait	50	0-2	-	Wait	50
2-3	flow	Ramp to 120%	51	2-3	Vacuum	Ramp to 350%	-

3-3.5	Vacuum	Ramp to 75%	-	3-4	-	Wait	61
3.5-6	-	WAIT	52	4-6	flow	Ramp to 75%	62
6-8	Condenser inlet Cv	Ramp to 5000	-	6-12	-	wait	63
8-24	-	Wait	53				

Table 5: Dynamic simulation schedules.

215

216

Case	Scheme	sequence	Purified flow kmol/h	CO <sub>2</sub>		Pressure		Compr Duty kWe
				Purity Mol/mol	recovery (%)	Retentate	Permeate bar	
1	recycle	1	1395.5	0.009270	94.087	6.5957	0.25	14253
2	recycle	1	1475.8	0.01040	90.757	6.5763	0.25	14255
3	recycle	1	1512.2	0.01083	92.531	6.569	0.25	14335
4	recycle	1	1439.6	0.01017	93.009	6.5836	0.25	14176
5	recycle	1	1437.8	0.009530	93.972	6.584	0.22	14172
11	recycle	2-3	1400.5	0.008768	96.33	6.5916	0.2	14086
12	recycle	3	1378.7	0.007224	93.98	7.0901	0.2	14315
13	recycle	3	1381.2	0.008123	96.33	7.0894	0.25	14322
20	recycle	4	1685.6	0.01615	93.39	5.6487	0.25	14747
21	recycle	4	1429.1	0.01143	84.438	5.7873	0.2	14216
50	open	5	561.9	0.002883	93.852	6.7713	0.25	14240
51	open	5	745.42	0.003691	93.101	6.7275	0.25	14306
52	open	5	742.54	0.003593	84.928	6.7275	0.2	14239
53	open	5	757.68	0.004197	91.256	6.4787	0.2	14230
61	open	6	567.83	0.006415	81.952	6.7771	0.95	14293
62	open	6	394.81	0.006513	72.625	6.8184	0.95	14243
63	open	6	395.54	0.005818	94.039	6.8183	0.95	14271

Table 6: Simulation results for rated working points

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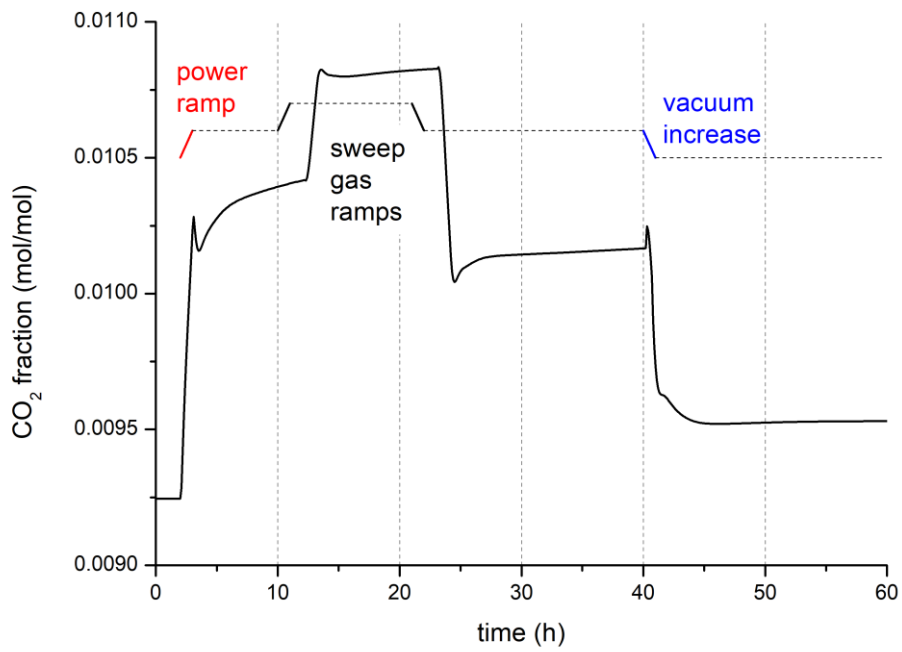
219 As expected, the open-cycle cases grant CO<sub>2</sub> fractions always below 1%, but with poorer recoveries.

220 The compressor duties are instead similar because the layout difference impacts only on the enriched

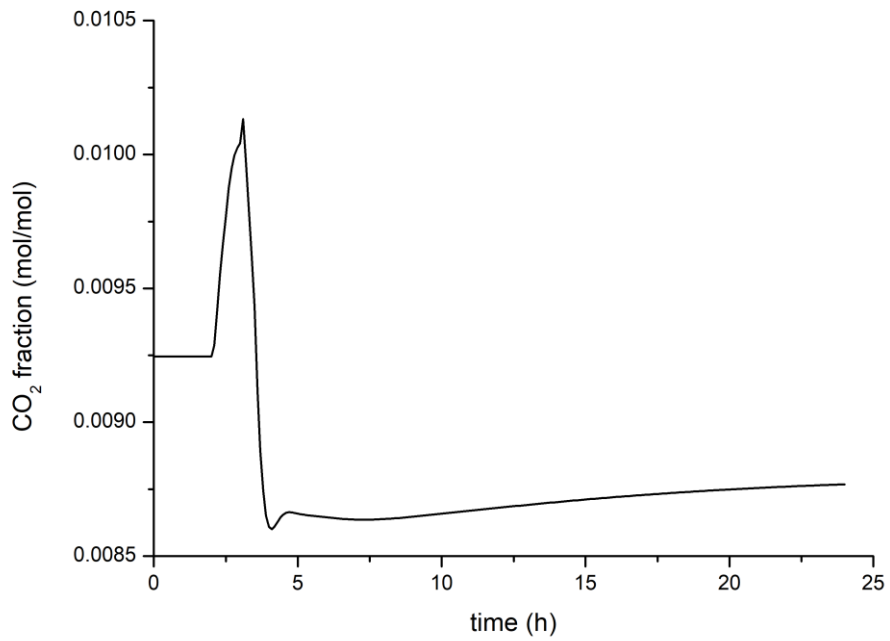
221 gas compressor. In general, closed configurations (with recycle) might be preferred because the

222 carbon content of the flues is still small and higher recoveries make a better option for possible

223 downstream CO<sub>2</sub> reuse.



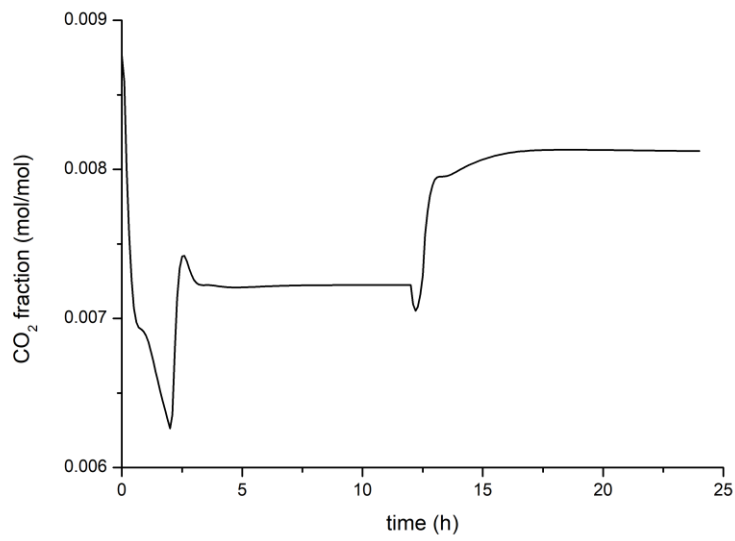
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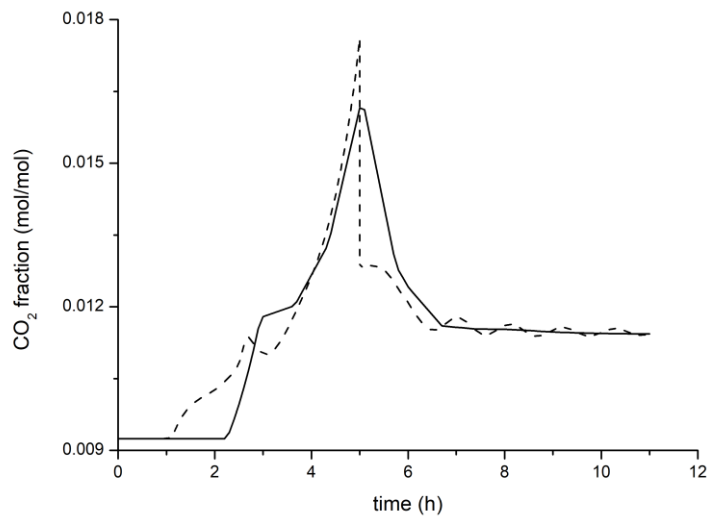
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226 Figure 5: CO<sub>2</sub> fractions in the purified flues for the simulation schedules 1-2. The top graph shows also the occurrence  
 227 of the process parameters variations along the timeline.



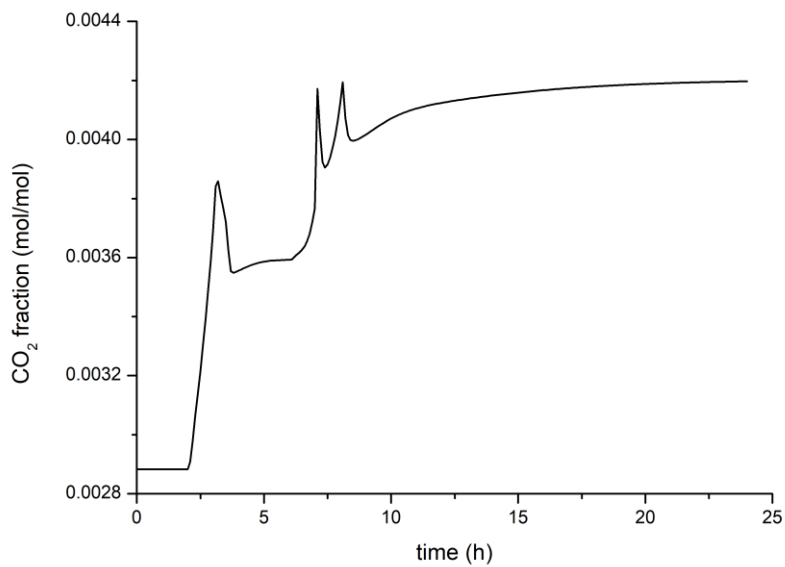


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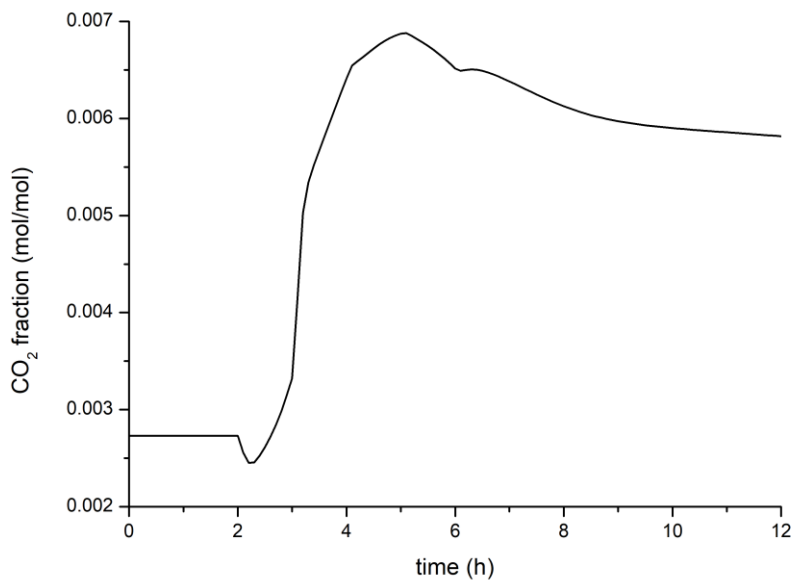


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230 Figure 6: CO<sub>2</sub> fractions in the purified flues for the simulation schedules 3-4. For the fourth run, the dotted line  
 231 represents the numerical solution with the default integration options, that had to be obtained breaking the time-flow  
 232 and accumulating a series of steady-state solutions in several critical passages; the continuous line represents a smooth-  
 233 running solutions obtained introducing a lowpass numerical filter in the form of fixed expanded integration steps.



234



235

236 Figure 7: CO<sub>2</sub> fractions in the purified flues for the simulation schedules 5-6. The sixth run was run with the same  
 237 noise-damping strategies adopted for the fourth.

238

239 The trend obtained for the dynamic 1 simulation (Fig. 5) shows that an increase in plant power (e.g.  
 240 in flues emission), can be compensated by a reduced recycle flow, and not an increase, because we  
 241 consider the purge gas as containing a fraction of CO<sub>2</sub>. Variations of a 10% in the permeate vacuum  
 242 level (last part of dynamic 1 and dynamic 2) have, instead, a minor effect.

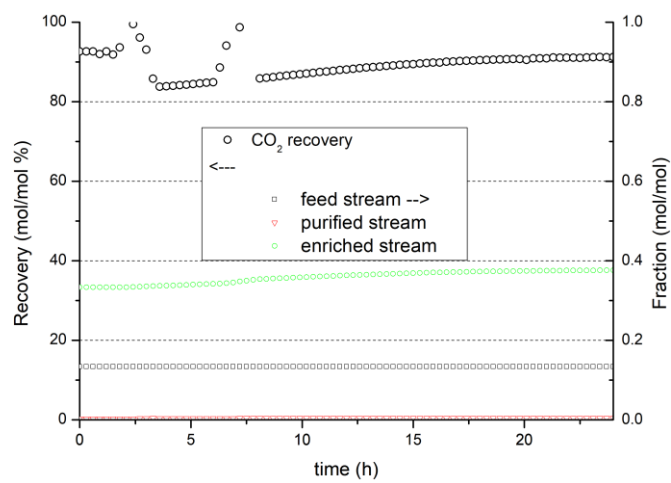
243 The third schedule shows the effect of an increase in the membrane operating pressure: the interesting  
244 feature is the relatively high difference in the transient and steady state purification levels achieved,  
245 0.66% and 0.73% vol. respectively (with respect to the rated 0.88%), which can be appreciated only  
246 having set up a full dynamic calculation for compressors and separators beside membranes. In this  
247 case, the relative effect of a moderate vacuum loss is appreciable.

248 On the other hand (dynamic 4) a reduced working pressure can even double the nominal CO<sub>2</sub> content:  
249 this dynamic run has highlighted several model criticalities that depends strictly on the mathematical  
250 problem, and can remain hidden according to the boundary conditions and variations tested. In this  
251 case, the step-change imposed to the system pressure first derivative (at the end of the ramp), results  
252 in a too big numerical oscillation for the flow in the sweep-air compression modules. This problem  
253 is numerical, because steady solutions are always promptly calculated (as any tested pressure value  
254 still belongs to the compressor operating range). The approach used by the default integration package  
255 is to reduce dynamically the integration step size when discontinuities are encountered, in order to  
256 proceed gradually from one state to the other, but in this case the enhanced resolution in the time  
257 domain results in further numerical oscillations. The issue has been solved in two ways: a) stop the  
258 pressure ramp just before the step-change of the pressure derivative, then solve the steady state and  
259 resume the dynamic; b) impose a fixed integration time large enough to damp the numerical  
260 oscillation.

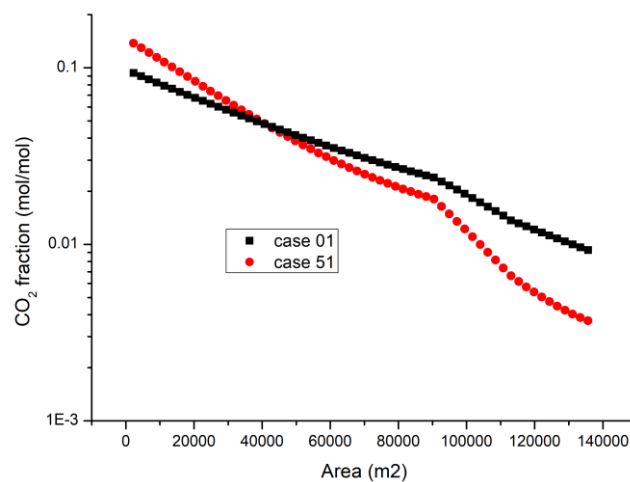
261 Dynamic 5 highlights again the differences between transient and stabilized value following power  
262 surges and vacuum losses (but without recycles), and dynamic 6 simulates a total vacuum loss, which  
263 can be taken as a design accident (stemming from a power loss or line big leak) for the permeate side  
264 of the separation plant.

265 The process layout with recycled air yields systematically higher CO<sub>2</sub> fractions in the treated gas,  
266 because the membranes have to treat a larger quantity of N<sub>2</sub>, on the other hand this value is less  
267 sensitive (on relative terms) to variations in the process parameters. Both the co-current and counter-  
268 current membrane arrangements separate the larger part of the CO<sub>2</sub> flow in their inlet zone.

269 Also the sixth dynamic run presented numerical problems similar to those of the fourth schedule, and  
 270 has been run at fixed integration steps. These limitations could come from the fact that the adopted  
 271 models mix a “flow driven” approach (the membranes, that inherit a fixed flow and yield the resulting  
 272 pressure) with a “pressure driven” one (the compressors and the condensers, that require fixed outlet  
 273 pressures). Moreover, there is not a unique combination of boundary conditions (fixed pressure and  
 274 flows) yielding, in principle, a solvable system, but it has been found heuristically that certain choices  
 275 cannot be handled.



276

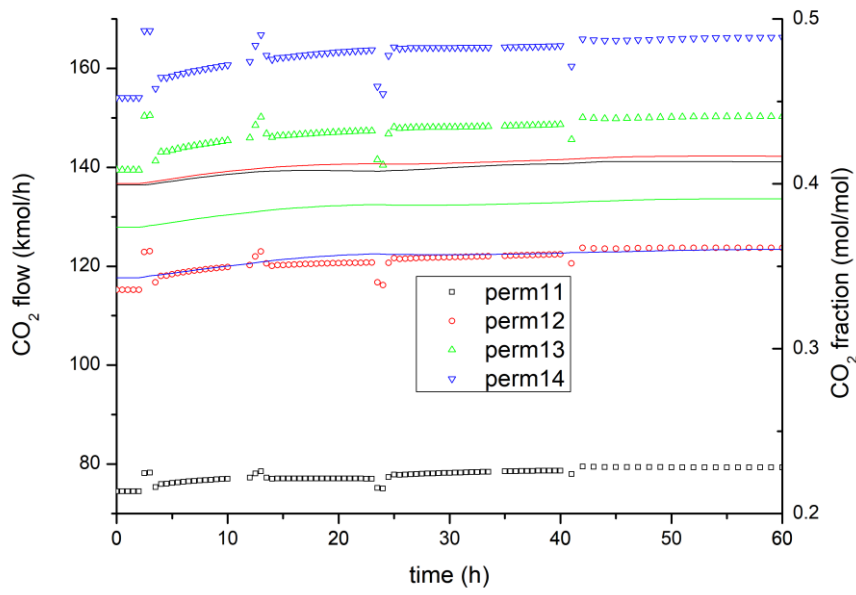


277

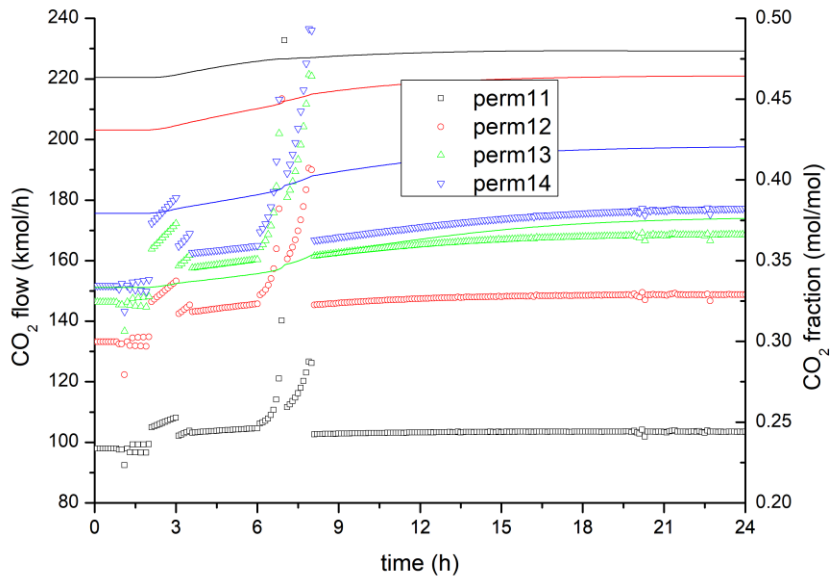
278 Figure 8: CO<sub>2</sub> recovery and mole fraction for dynamic 5. Comparison between the retentate-side CO<sub>2</sub> fractions with  
 279 (case 01) and without (case 51) air recycle.

280

281 Figure 8 represents the CO<sub>2</sub> recovery for the fifth and sixth dynamic run, together with the  
282 concentration level achievable in the carbon-enriched stream. Though the final CO<sub>2</sub> concentration for  
283 these simulations is relatively low, the results are aligned with what reported in the literature at similar  
284 permeate vacuum levels [30], also considering that the flue gas purification predicted by the present  
285 calculus is, on the other hand, very good (CO<sub>2</sub> < 2% wt). Also the qualitative correlation between  
286 permeate pressure and stream flow is in agreement with published pilot-plant data [39]. Working  
287 pressures of 5 – 6 bars for the feed section have been tested also by Wu et al. [40], who used  
288 membranes with a higher permeability but a similar selectivity with respect to the values obtained in  
289 this work, keeping the permeate side at atmospheric level. Their findings for a single membrane stack  
290 are in line with the recovery/purity outcomes of the 1<sup>st</sup> co-current block without sweep air-injections  
291 simulated in this work (Figure 9). Single-pass enrichments below 40% and 50%, at very high recovery  
292 values, have also been calculated by Franz et al. [41] and by Brinkman et al. [42], respectively.  
293 On the other hand, the tested case with sweep air recirculation yields lower CO<sub>2</sub> concentration after  
294 each co-current stage. The greatest difference, with respect to other cited simulation works, is the  
295 CO<sub>2</sub> dilution foreseen by the present calculation as the waste gas purification proceeds, due to the  
296 ever-increasing transport of N<sub>2</sub> through the membrane. This is due essentially to two factors: the  
297 relatively high pressure ratio adopted (which determines an appreciable driving force for all species),  
298 and the arrangement between the first and second membrane sections, which is designed to achieve  
299 a low CO<sub>2</sub> fraction in the wastes rather than a high CO<sub>2</sub> purity in the permeate.  
300



301



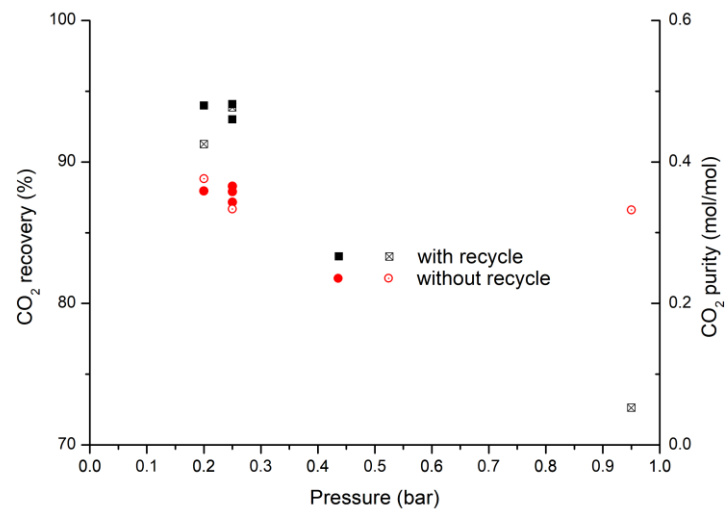
302

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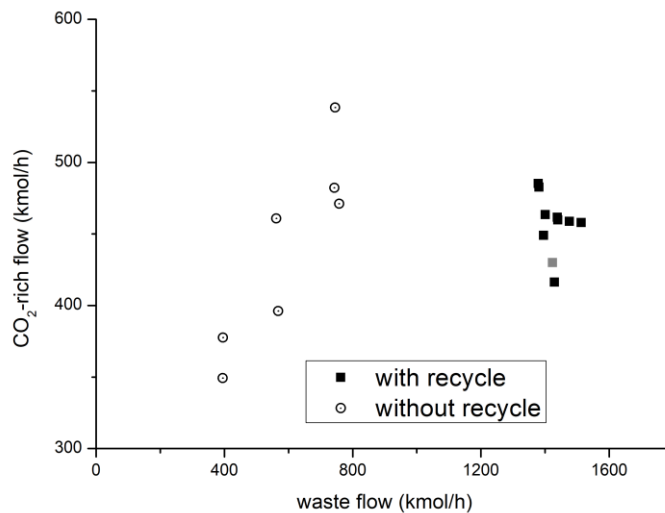
Figure 9: CO<sub>2</sub> flows (symbols, left axis) and fractions (lines, right axis) for the co-current cascade in dynamic simulations no. 1(top) and 5 (bottom).

304

305



306



307

308 Figure 10: (top) CO<sub>2</sub> recovery (filled markers) and purity (empty markers) as a functions of pressure; (down) CO<sub>2</sub> flow  
 309 as function of waste flow (the grey square is a doubtful output).

310

311 Considering a selection of quasi-steady states (from Table 6), it is found that the carbon recovery is  
 312 sensitive to the permeate vacuum (i.e. to the pressure ratio, Figure 10), but is stabilized if the recycle  
 313 air is added: in this case the CO<sub>2</sub>-rich flow becomes independent by the purified flues flow (Figure  
 314 10), while otherwise the two streams are proportional to one another. The achieved purity is not  
 315 affected appreciably by the tested process variables, because it is linked to the selectivity.

316

## 317 **Conclusions**

318 A dynamic model to describe the operation of a hollow-fiber membrane has been validated for the  
319 case of N<sub>2</sub>-O<sub>2</sub> separation, and extended to the N<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O mixture. In order to simulate dynamically  
320 the whole process of combustion gases purification, equations for compressors and condensers have  
321 been added, and all the blocks linked into process flowsheets, obtaining a scaled-up simulation for  
322 the whole fuel purification. The treated gas quantity and the total membranes that are needed have  
323 been increased adopting the largest compressor characteristic curve available in detail as constraint:  
324 this grants the best compromise between the needed units (14 compressors) and the model reliability.  
325 The dynamic calculation helps to foresee undesired oscillations in the main process outcome (CO<sub>2</sub>  
326 residue in the purified stream), and the delays caused by the blocks volume. The steady state results  
327 are comparable with other simulation and plant data available: the proposed design, anyway, is not  
328 aimed to CO<sub>2</sub> purification, so the membrane layout has been optimized to grant <1% mol in the exit  
329 flues, despite the low concentration < 40% mol in the carbon-rich stream.

330 A layout featuring air recycle can stabilize the system dynamics, keeping the CO<sub>2</sub> content variation  
331 within 30% and its oscillation within 150% (dynamic 4), a once-through layout yields variations as  
332 high as 200-300%, but it needs roughly half the membrane area to achieve the same purification  
333 targets. This poses the basis to evaluate the compromise between additional installation costs and  
334 possible transient off-target performance of the plant.

335

## 336 **Acronyms and Symbols**

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f	Friction factor	A	Hydraulic Area
k	Vapor velocity correction	Cv	Valve coefficient
i	Species index	D	Hydraulic diameter
n	Moles	F	Feed mass flow
p	Partial pressure	J	Molar flux

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u	Velocity	L	Liquid mass flow
v	Volume	P	Total pressure
x	Liquid mole fraction	Q	Thermal power
y	Gas mole fraction	R	Gas constant
z	Molar fraction	S	Permeation surface
$\varepsilon$	Rugosity	T	Temperature
$\varphi$	Flow factor	U	Heat exchange coefficient
$\gamma$	Heat capacities ratio	V	Vapor mass flow
$\eta$	Efficiency	W	Work
$\rho$	Mass density	GPU	Gas-Permeation Unit
		Re	Reynold number
		RET	Retentate
		PER	Permeate
		PM	Molar weight

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337

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354

### 355 **Dedication**

356 This paper is dedicated to the memory of Prof. Lucio Forni, formerly professor at Università degli  
357 Studi di Milano, passed away at the end of December 2022. I. Rossetti, as former student and  
358 colleague, gratefully remembers all the teachings and the moments spent together.

359

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