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Polymeric membrane materials for nitrogen production from air: a process synthesis study

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Abstract

Nitrogen production from air by membrane gas separation processes is a mature technology which is applied in numerous industrial sectors (chemical, food, aeronautics, space..). Depending on the nitrogen purity requirements (typically between 90 and 99.9%), single stage or multistage membrane process configurations are used. A very large number of advanced membrane materials have been recently reported, showing increasing permeability and/or selectivity for air separation applications (i.e. trade-off limits of dense polymeric materials for the O_2/N_2 gas pair) compared to the commercially available membranes. The interest of these new materials in terms of nitrogen production cost and their impact in terms of process configuration are reported through a process synthesis study. Based on a tailor made optimization methodology and program, the production cost and associated optimal process configuration are first identified for two standard O_2/N_2 separation membranes at four different levels of N_2 purity (90, 95, 99, 99.9%). The same strategy is then performed with advanced trade-off membrane materials, with the possibility to combine different materials in multistaged systems. The impact in terms of nitrogen production cost for the different purities and the corresponding optimal membrane materials and process configurations are discussed. Surprisingly, a medium membrane selectivity combined to a high permeability is shown to systematically offer the best set of performances, for mono or multistaged systems. Vacuum operation and recycling loops are shown to generate lower N_2 production costs.

Keywords: Nitrogen, Membrane, Process, Synthesis, Optimization, Materials, Cost

1. Introduction

Membrane processes are one of the key technologies for gas separation applications [1, 2]. Hydrogen purification, natural gas treatment, Volatile Organic Compounds recovery, gas drying are increasingly applied into different industrial sectors thanks to membrane units [3], but the number one market of membrane gas separations remains nitrogen production from air (Nitrogen Enriched Air, NEA) [4]. Starting from a nitrogen content in air of approximately 79%, a membrane gas separation unit indeed enables purity levels of 90% or more to be easily obtained. A membrane process is continuous (no regeneration step), it does not involve chemicals, does not generate waste, offers intensification possibilities, it is modular (ease of scale up) and does not imply complex operations (such as cycles) [5]. These arguments are of major interest for on board systems (e.g. boats, planes, space applications). But membrane units are also used for large capacity industrial applications, such as blanketing for explosive environments (hydrocarbons and solvent storage), or generation of inert atmospheres (e.g. non oxidizing) for chemicals or materials production, among others [1]. Nitrogen production by membranes is also favorable because the target compound is less permeable than the air compounds to be eliminated (O_2, H_2O, CO_2). As a consequence, a purified stream of nitrogen can be continuously produced on the retentate (i.e. high pressure) side. In a large number of situations, no additional purification or recompression step are needed.

Generally speaking, membrane processes are more interesting for moderate purity, and low to moderate capacity N_2 applications [6]. Cryogeny is the best available technology for high purity (e.g. > 99.99%) high capacity (e.g. > 200 ton per day) units. Adsorption processes are favored for intermediate purity and capacity [7]. The improvements in membrane materials and process designs have enlarged the domain of application of membranes through the years. Commercial membrane materials remain almost exclusively based on dense polymers, which should ideally combine a high selectivity and high permeability [8]. Hundreds of structures have been investigated in order to maximize these two characteristics [9–11] but a trade-off limit, based on a concept suggested by Robeson [12], exists between the two. Few membrane materials for nitrogen production applications are commercially available today (i.e. polysulfones, polyimides, polyphenylene oxide)[4]. The level of performances of these materials is below the trade-off limits and the interest of advanced materials, with performances close to the trade-off limit, in terms of N_2 production cost, is logically a key question. To our knowledge however, no study addressed so far the rigorous analysis of the impact of advanced membrane materials for nitrogen production. Such a piece of work should ideally combine a large choice of membrane materials together with modern process design tools, in order to identify the most promising production strategies.

In this study, the production cost of NEA for four different levels of purity is analyzed (90, 95, 99 and 99.9%). In a first step, the minimal cost and optimal process configuration with currently commercially available membrane materials is identified thanks to a tailor made process synthesis package, recently developed for carbon capture applications [13]. The optimal structure (number of stages, compression or vacuum operation, multistage configuration) and the associated nitrogen production costs are thus obtained and will correspond to the reference case. In a second step, the possibilities of advanced trade-off materials are explored thanks to a novel, generic approach: the minimal production cost for a given nitrogen purity is identified based on systematic screening of trade-off membrane performances and process

45 configurations (including compression, vacuum pumping and recycling loops), with two op-
46 tions: same optimal trade-off membrane used for all membrane stages or possibility to use a
47 different trade-off membrane material in each membrane stage.

48 The objectives of the study are to provide an answer to the following questions:

- 49 • How does nitrogen purity impact process configuration and cost with currently com-
50 mercially available membranes?
- 51 • What are the best process configurations and the associated costs with advanced mem-
52 brane materials (i.e. trade-off limit performances)?
- 53 • What is the best membrane material for each nitrogen purity level within the trade-off
54 limits (i.e. high selectivity or high permeability)?
- 55 • Is there an interest to combine different membrane materials into multistaged units for
56 nitrogen production?

57 This set of results is expected to provide clear guidelines for air separation membrane de-
58 velopments and also help to better evaluate the interplay between materials performances,
59 process design and production cost.

60 **2. PROCESS SYNTHESIS METHODOLOGY APPLIED TO MEMBRANE GAS** 61 **SEPARATIONS AND NEA PRODUCTION**

62 *2.1. Process synthesis and membrane gas separations: overall methodology*

63 The optimal process designs detailed hereafter are obtained by means of a tailor made com-
64 puter program specifically designed for membrane gas separations. Starting from separation
65 specifications (feed composition, permeate and/or retentate composition), the optimal pro-
66 cess flow-sheet and the associated operating conditions are identified thanks to a global
67 optimization algorithm with an objective cost function. The overall process synthesis frame-
68 work is summarized in Figure 1 .

Process synthesis possibilities:

1. Fixed pre-selected membrane permeances for all stages
2. Uniform optimal membrane limited by Robeson's upper bound for all stages
3. Independent optimal membrane limited by Robeson's upper bound for each stage

Optimization framework:

Variable membrane surface area for each stage
Variable pressure ratio for each stage including vacuum operation
Upstream pressure 1 to 100 bar
Downstream pressure 0.2 to 1 bar

Exhaustive combinatorial connectivity including:
Variable split ratio for each stream node
Self recycling loops

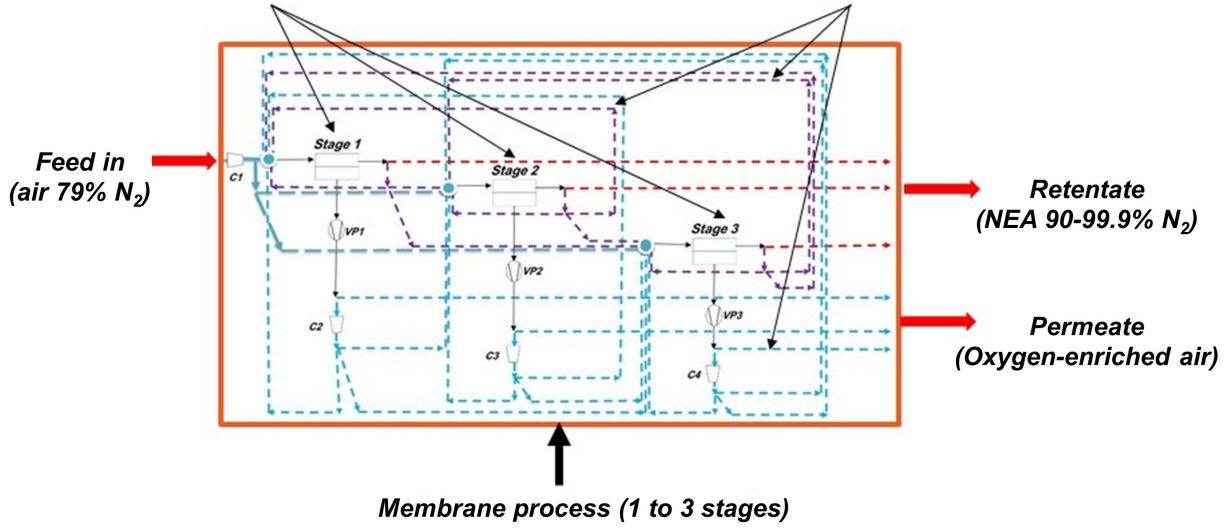


Figure 1: Overall process synthesis framework used for this study. A membrane separation process including up to 3 stages with compressors and/or vacuum pumps and multiple connection possibilities including recycling loops is applied to nitrogen production from air with four different target purities. The different configuration possibilities and operating variables are taken into account in order to achieve the lowest production cost (i.e. objective function, detailed in Tables 1 and 2).

69 The program makes use of a rigorous set of equations for membrane module simulation,
70 extendable to multi-component mixtures [14]. All the possibilities of connections are explored
71 for a system with one, two or three stages, including recycling loops from one stage to another
72 or self recycling loops. One specificity of the program, compared to most of the approaches
73 in this domain, is to allow a variable pressure ratio in each stage with vacuum pumping
74 as one possibility. A given range is applied to the operating conditions, in order to take
75 into account technological limitations (typically upstream pressure is limited to 100 bar and
76 vacuum limited to 0.2 bar). Compressors or vacuum pumps are included in the recycling
77 loops when pressure changes exist at the boundaries of the connection. The overall cost
78 function, taken as the objective function, takes into account capital expenses (CAPEX)
79 such as compressors, vacuum pumps, membrane modules and operating costs (OPEX), such
80 as energy requirement, membrane replacement and operation and maintenance cost. The
81 cost function used for NEA production is detailed in Table 1. The detailed mathematical
82 framework and associated optimization strategy can be found in [13].

Table 1: Cost equations used to determine product gas separation cost

Equipment cost		
$I_{m_s} = A_{m_s} \cdot K_m$	(1)	Membrane cost
$I_{m_{fs}} = (A_{m_s}/2000)^{0.7} \cdot K_{mf} \cdot (p^{up}/55)^{0.875}$	(2)	Membrane frame cost
$I_{cc_s} = C_{cc} \cdot (W_{cp_s}/10^6)^{0.7} \cdot MF_{cc} \cdot MDF_{cc} \cdot UF_{2000}$	(3)	Stage compressor cost
$I_{cc_f} = C_{cc} \cdot (W_{cp_f}/10^6)^{0.7} \cdot MF_{cc} \cdot MDF_{cc} \cdot UF_{2000}$	(4)	Feed compressor cost
$I_{vp_s} = C_{vp} \cdot (W_{vp_s}/10^3)$	(5)	Vacuum pump cost
Capital expenditures		
$CAPEX = (I_{cc_f} + \sum_{s \in \mathcal{S}} (I_{m_s} + I_{m_{fs}} + I_{cc_s} + I_{vp_s})) \cdot ICF$	(6)	Total capital cost
Operational expenditures		
$C_{O\&M} = \sum_{s \in \mathcal{S}} A_{m_s} \cdot \nu \cdot K_{mr} + 0.03 \cdot CAPEX$	(7)	Operation and maintenance cost
$C_{en} = t_{op} \cdot W_{tot} \cdot K_{el}$	(8)	Energy cost
$OPEX = C_{en} + C_{O\&M}$	(9)	Total operational expenditures
Annual and specific separation costs		
$C_{cap} = CAPEX \cdot a$	(10)	Annual capital costs
$C_{tot} = C_{cap} + OPEX$	(11)	Total annual costs
$M_{N_2 \text{ per year}} = F^{Ret} \cdot X_{N_2}^{Ret} \cdot M_{N_2} \cdot 10^{-6} \cdot 3600 \cdot t_{op}$	(12)	Annual separated N_2
$SC_{N_2} = C_{tot}/M_{N_2 \text{ per year}}$	(13)	Specific N_2 separation cost

Table 2: Cost parameters used in Table 1

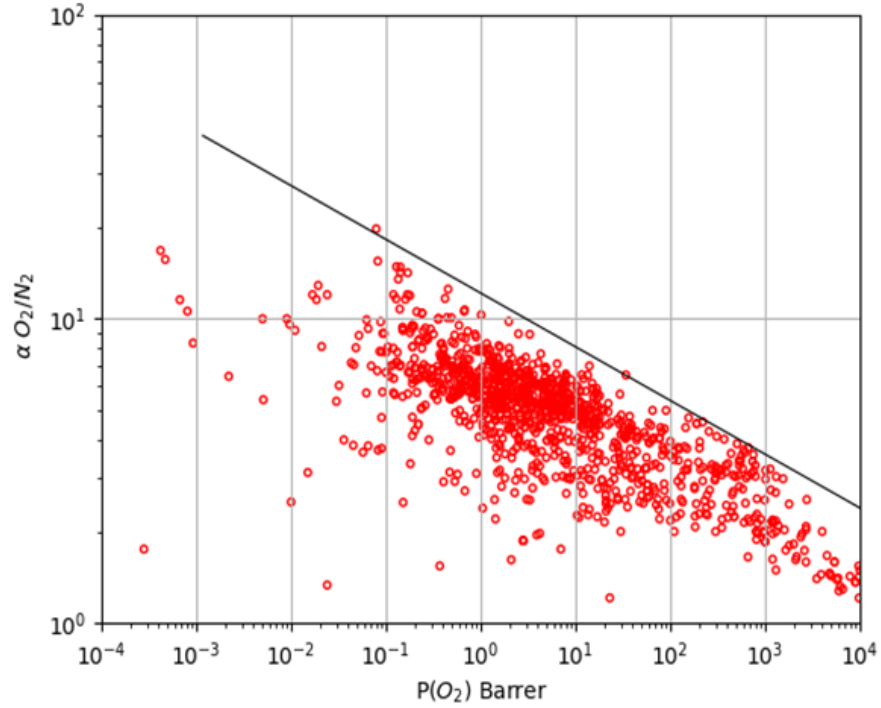
Capital cost parameters		
C_{cc}	1×10^6	EUR ₂₀₀₀
C_{vp}	1500	EUR/kW
K_m	40	EUR/m ²
K_{mf}	286×10^3	EUR
MDF_{cc}	2.72	-
MF_{cc}	1.4	-
UF_{2000}	1.42	-
ICF	1.8	-
T	308.15	K
R	8.314	$JK^{-1}mol^{-1}$
η	0.85	-
ϕ	0.95	-
γ	1.36	-
λ	0.85	-
Annual cost parameters		
ν	0.2	-
K_{mr}	25	EUR/m ²
t_{op}	8322	h/year
K_{el}	0.044	EUR/kWh
a	0.0854	-
M_{N_2}	28.01	g/mol

83 Three different strategies have been used in the study:

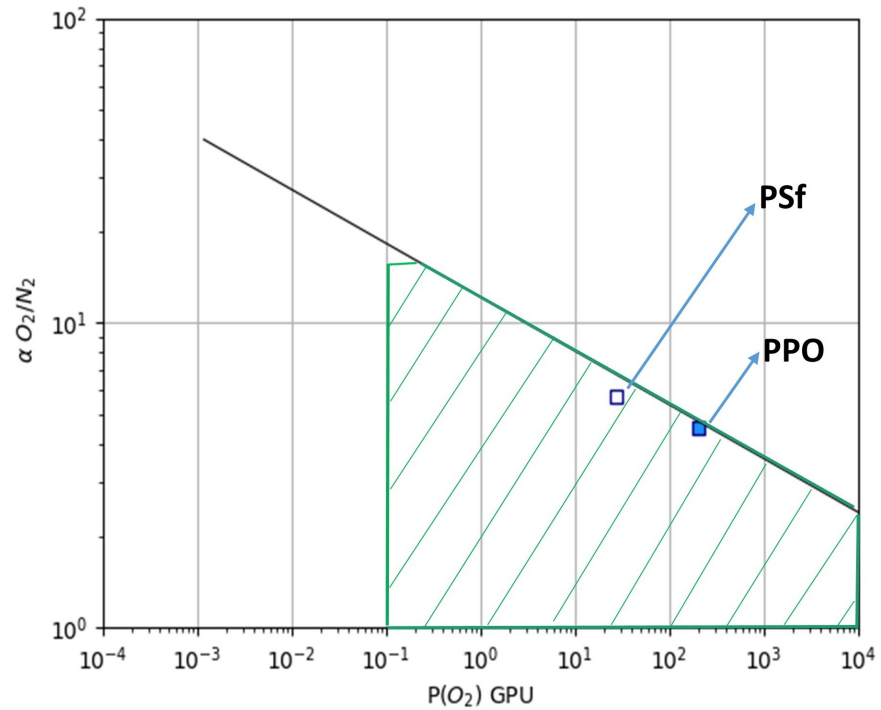
- 84 • As a first step, membrane separation characteristics are fixed (i.e. membrane oxygen
85 and nitrogen permeance), and the optimal process design and operating conditions is
86 obtained for one, two and three membrane stages, for the four levels of target nitrogen
87 purity (90, 95, 99 and 99.9%). Benchmark gas permeances for commercially available
88 membranes are used.
- 89 • As a second step, the membrane characteristics are allowed to vary within a defined
90 domain, limited by trade-off performances represented by Robeson’s upper bound re-
91 lationship and a single set of membrane permeances is allowed. As a consequence, the
92 solutions obtained in that case necessarily make use of the same, optimal membrane,
93 for all the stages of the system.
- 94 • As a final step, membrane permeances for each individual stage are allowed to vary
95 within the same domain as in the previous step. This allows a different optimal mem-
96 brane to be selected for each stage, when a multistage solution is investigated.

97 Nitrogen ranks among the top ten chemicals in terms of production capacity (ca 100 mil-
98 lion tons per year), with a large portfolio of applications (inerting in chemical industries,
99 food protection, steel manufacturing, light bulbs, cryopreservation) [14]. Production tech-
100 nologies systematically use air as a feedstock (i.e. 0.79 volume fraction nitrogen content).
101 Depending on the nitrogen purity and unit capacity, cryogeny, adsorption based processes
102 (PSA, Pressure Swing Adsorption) or membranes are used [15]. Membrane separations for

103 NEA (Nitrogen Enriched Air) production correspond to the most recent production tech-
104 nology and compete with cryogeny and PSA when a moderate purity (typically below 99)
105 and moderate capacity are required [16]. As already explained, Nitrogen production from
106 air is today the biggest market of membrane gas separation processes, with more than 100
107 000 units installed through the world [4]. From a membrane material point of view, dense
108 polymers are exclusively used [17]. Oxygen, water and carbon dioxide are faster permeants
109 than nitrogen into polymers. As a consequence, NEA is recovered dry and purified on the
110 retentate (i.e. high pressure) outlet of the membrane modules. Different polymers have been
111 developed for industrial scale application, with a classical selectivity / productivity trade-off
112 to be tackled. Polysulfone (PSf), Polyimides (PI) and Poly-phenylene-oxide (PPO) dense
113 skin membranes are commercially available [2]. The two major performance characteris-
114 tics of a given dense skin membrane are the separation performance, expressed through the
115 O_2/N_2 selectivity(α^*), and the effective membrane productivity, usually expressed in GPU
116 (Gas Permeation Unit). The selectivity / permeability trade-off curve for different polymers
117 for the O_2/N_2 gas pair is shown on Figure 2a. It can be noticed that oxygen is systematically
118 faster than nitrogen ($\alpha > 1$). In order to translate the intrinsic polymer permeability into a
119 process productivity variable (i.e. permeance, in GPU), a dense skin of 1 μm thickness is of-
120 ten assumed [18]. The corresponding graph is shown on Figure 2b(1 Barrer corresponds to 1
121 GPU in that case). The current level of performances of two classical commercially available
122 air separation membranes (PSf and PPO), which will be used in this study, is indicated.



(a) O_2/N_2 polymeric materials trade-off curve [12]



(b) Selectivity / permeance trade-off curve based on a $1 \mu m$ skin layer thickness and performances of two commercially available membrane materials (PSf and PPO). Dashed area corresponds to the domain used for optimal membrane identification when performances are not fixed

Figure 2

123 Besides the membrane material selection question, a process design analysis has also to
 124 be performed. The goal is to identify the most effective process structure and operating
 125 conditions, which reaches the specifications (nitrogen purity and production capacity) with
 126 the lowest cost. Surprisingly, this point is poorly documented in the open literature, despite
 127 the important market of nitrogen membrane production units. Figure 3 summarizes three
 128 main configurations reported from industrial practice, which correspond to increasing levels
 129 of nitrogen purity [16]. An increasing number of membrane stages is needed when increasing
 130 the target nitrogen purity. The maximum number of stages is however limited to three,
 131 because of the strong impact of multiple compressors in the overall cost [1, 2, 4]. The
 132 increasing complexity of the process when a larger purity is aimed is noticeable (multiple
 133 stages with recycling loops).

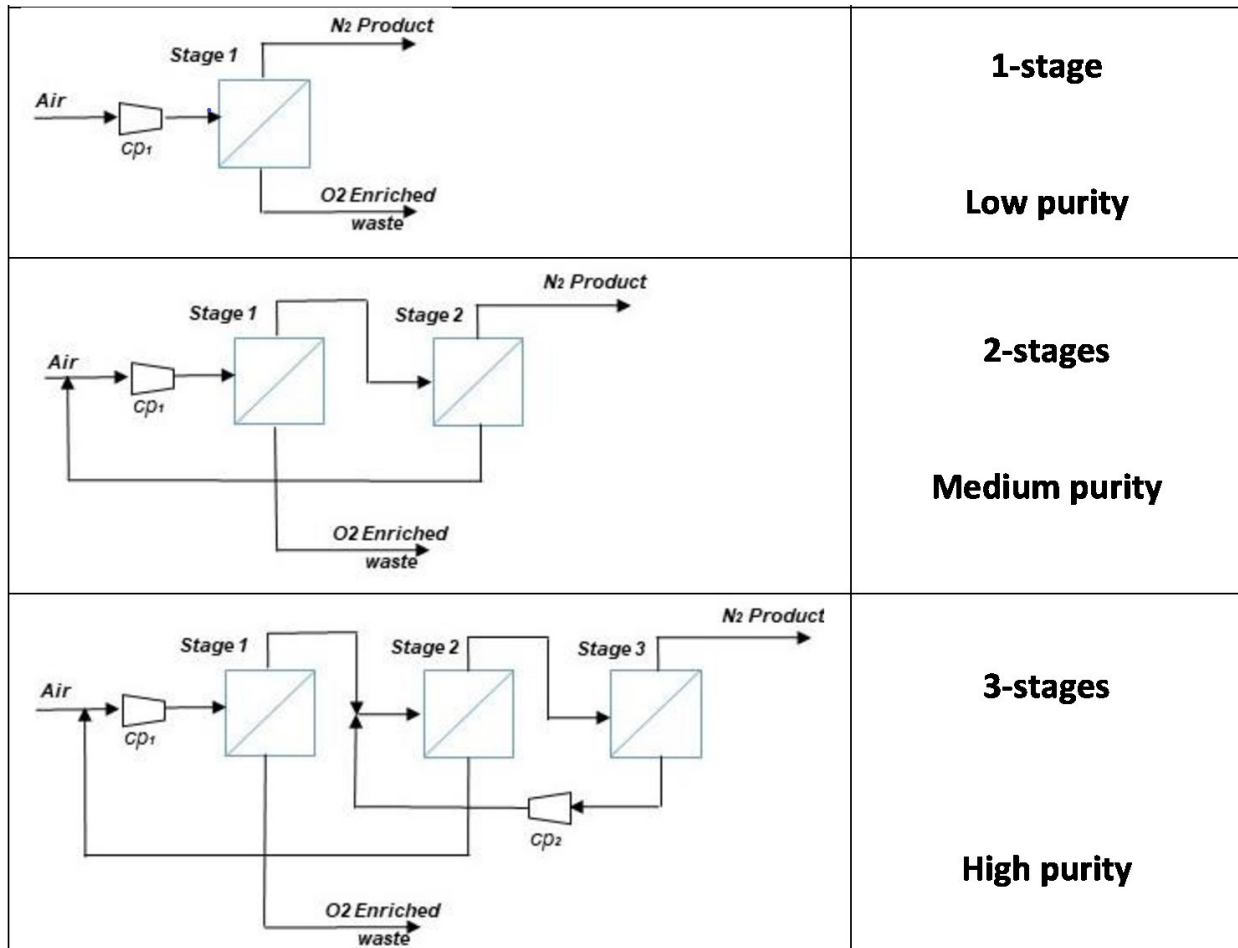


Figure 3: Membrane process configurations for three different levels of nitrogen purity, adapted from [16]

134 The process configurations reported on Figure 3 correspond to the current state of the art of
 135 the most effective structures obtained with commercially available polymeric air separation
 136 membrane materials. Nevertheless, due to the very large nitrogen market, tremendous efforts
 137 have been made the last decades in order to push the limits of polymer performances. It
 138 is thus important to explore the impact of high performances membrane materials both in

139 terms of nitrogen production costs and optimal process configurations.

140 *2.2. NEA production: high performance materials*

A series of high performance membrane materials covering a broad range of selectivity / permeability trade-off is detailed in Table 3. The different possibilities can be expressed through a generic trade-off equation, such as suggested by [12]. For the specific oxygen / nitrogen pair gas, the trade-off limit can be expressed as:

$$P_{O_2} = k\alpha^n \tag{14}$$

141 where $k = 1396000$ Barrer and $n = -5.666$.

142 This generic equation will be used to evaluate the interest of different high performance
143 materials in the process synthesis study reported hereafter.

Table 3: Examples of advanced membrane materials (not commercially available today), close to the Robeson trade-off limit, for air separation applications (from [12]).

Polymer	Permeability O_2 (Barrer)	α O_2/N_2
Polyimide (BPDA-ODA)	0.079	19.8
Polyimide (BTDA-ODA)	0.170	14.2
Polyetherimide	0.90	11.2
Polypyrrolone (6FDA/PMDA(25/75)-TAB)	1.01	10.03
PPO sulfonated (32.9 %) and brominated (60 %)	12.6	7.4
PPO sulfonated (20.2 %) and brominated (60 %)	14.0	7.0
Polyimide (BADBSBF-BTDA)	18.0	9.0
Poly[1-phenyl-2-p-(trimethylsilyl)phenylacetylene]	1550	2.98
PIM-1	370	4.0
PIM-7	190	4.5

144 **3. Results and discussion**

145 *3.1. Nitrogen production by commercially available membrane materials*

146 In a first step, the minimal nitrogen production cost with current commercial membrane
147 materials is explored. Two different membranes, summarized in Table 4, have been selected
148 and the corresponding minimal production cost and optimal process configuration were eval-
149 uated. The two materials detailed in Table 4 correspond to two major families of polymers
150 used for air separation applications. Polysulfone shows an increased selectivity, at the ex-
151 pense of a lower permeance. PPO shows the highest oxygen permeance, with a slightly lower
152 selectivity. The objective of this first part of the study is to define the reference production

153 costs and process configurations for these two membranes. The sensitivity of selectivity ver-
 154 sus permeance, in terms of production cost and possible process configuration differences is
 155 also of interest.

Table 4: Characteristics of the two commercially available membranes used for NEA production in this work

Polymer	O_2 permeance (GPU)	N_2 permeance (GPU)	$\alpha O_2/N_2$ (-)	Reference
Polysulfone (PSF) ¹	27	4.7	5.7	[19]
Polyphenyleneoxide (PPO) ²	200	44	4.5	[20]

156 The results obtained for PSF and PPO membranes are summarized figures 4 and 5 respec-
 157 tively.

Number of stages

N ₂ Purity	1 stage	2 stages	3 stages
90%	<p style="text-align: center;"> $p_{up} = 2.68 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 4964 \text{ m}^2$ $SC = 39.8 \text{ €/ton } N_2$ </p>	<p style="text-align: center;"> $p_{up} = 4.1 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 4992 \text{ m}^2$ $SC = 59.81 \text{ €/ton } N_2$ </p>	<p style="text-align: center;"> $p_{up} = 5.85 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $p_{d2} = 0.20 \text{ bar}$ $p_{d3} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 6715 \text{ m}^2$ $SC = 107.5 \text{ €/ton } N_2$ </p>
95%	<p style="text-align: center;"> $p_{up} = 6.9 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 4667 \text{ m}^2$ $SC = 117.2 \text{ €/ton } N_2$ </p>	<p style="text-align: center;"> $p_{up} = 6.0 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 7040 \text{ m}^2$ $SC = 109.8 \text{ €/ton } N_2$ </p>	<p style="text-align: center;"> $p_{up} = 8.21 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $p_{d2} = 0.20 \text{ bar}$ $p_{d3} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 8056 \text{ m}^2$ $SC = 179.2 \text{ €/ton } N_2$ </p>
99%	<p style="text-align: center;"> $p_{up} = 11.1 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 3886 \text{ m}^2$ $SC = 280.5 \text{ €/ton } N_2$ </p>	<p style="text-align: center;"> $p_{up} = 9.3 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 9039 \text{ m}^2$ $SC = 200.4 \text{ €/ton } N_2$ </p>	<p style="text-align: center;"> $p_{up} = 8.21 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $p_{d2} = 0.20 \text{ bar}$ $p_{d3} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 8056 \text{ m}^2$ $SC = 179.2 \text{ €/ton } N_2$ </p>
99.9%	<p style="text-align: center;"> $p_{up} = 11.1 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 3886 \text{ m}^2$ $SC = 280.5 \text{ €/ton } N_2$ </p>	<p style="text-align: center;"> $p_{up} = 9.3 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 9039 \text{ m}^2$ $SC = 200.4 \text{ €/ton } N_2$ </p>	<p style="text-align: center;"> $p_{up} = 8.21 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $p_{d2} = 0.20 \text{ bar}$ $p_{d3} = 0.20 \text{ bar}$ $P_{O_2} = 27 \text{ GPU}$ $P_{N_2} = 4.7 \text{ GPU}$ $A_T = 8056 \text{ m}^2$ $SC = 179.2 \text{ €/ton } N_2$ </p>

Figure 4: Summary of the best NEA process configurations obtained with PSF membrane for up to three membrane stages and different nitrogen purity levels.

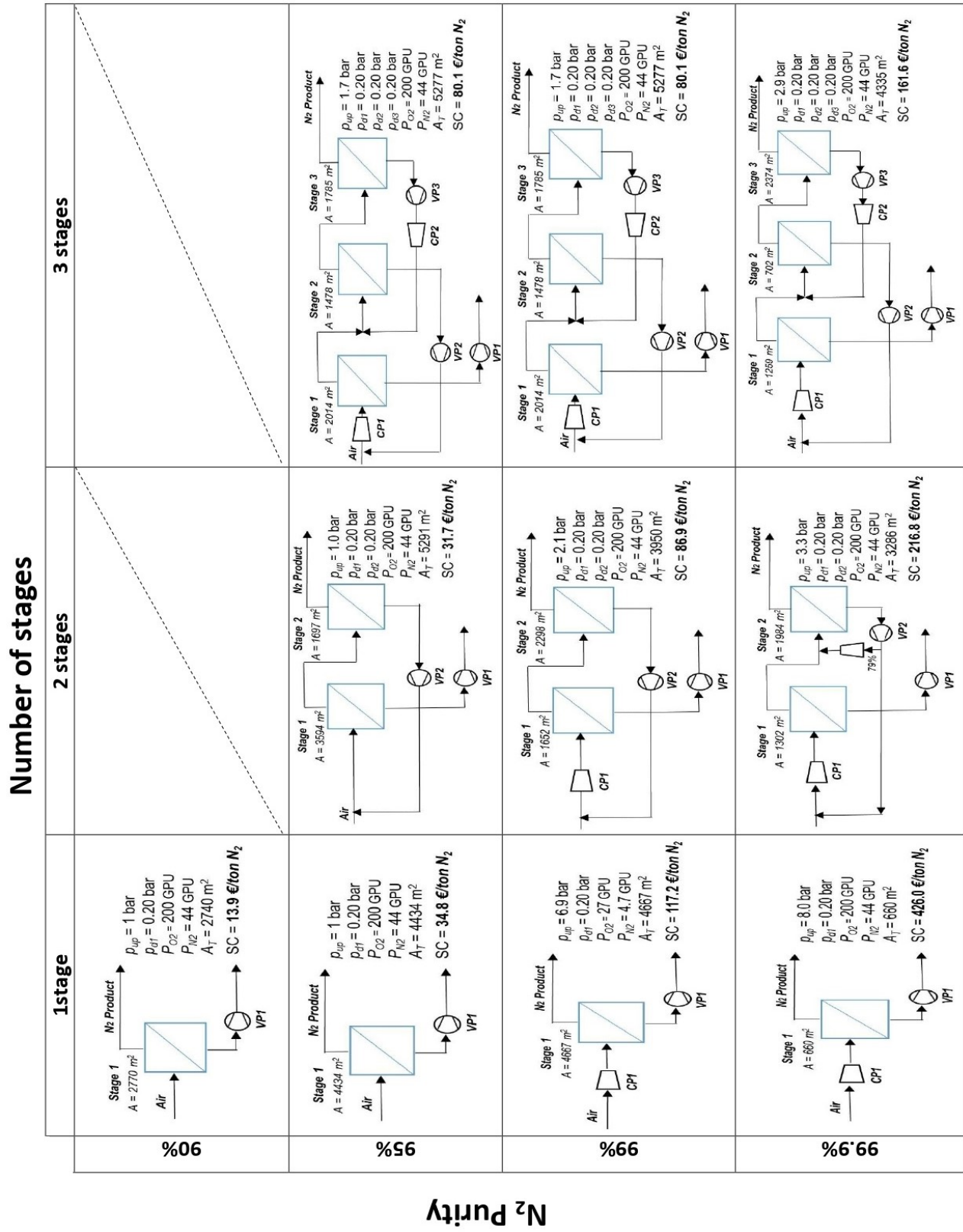


Figure 5: Summary of the best NEA process configurations obtained with PPO membrane for up to three membrane stages and different nitrogen purity levels.

158 Generally speaking, figures 4 and 5 confirm general statements and guidelines of membrane
159 gas separation processes presented figure 3:

- 160 • An increased target purity increases the nitrogen production cost through a non linear,
161 quasi exponential dependence
- 162 • An increased nitrogen purity translates into an increasing number of stages and in-
163 creasing process complexity (e.g. multiple recycling loops, combined compression and
164 vacuum operation...).

165 A single stage process with no recycling loop systematically offers the best performances
166 for 90 percent purity. Interestingly, no solution with 2 or 3 stages can be obtained by the
167 computer program for this purity level. A series of 2 or 3 modules is generated, without re-
168 cycling loop, without any recompression step; this is then equivalent to a single, segmented
169 module. A two stage configuration with recycling loop is the best process for moderate (95
170 percent) nitrogen purity. Three stages, including two recycling loops, are needed for larger
171 purity levels (99 and 99.9 percent). It is likely that nitrogen production cost is not compet-
172 itive at this purity level. The competitive window for nitrogen production by membranes is
173 effectively often mentioned to range from 90 to 99 percent [16].

174 The general structures obtained through the process synthesis study perfectly fit the struc-
175 tures reported up to now (figure 3). The number of stages for the different purity levels,
176 the number and location of the recycling loops for multistage processes are exactly the same
177 as the one detailed in figure 3. This point is remarkable and provides a good proof of the
178 efficiency and relevance of the simulation/optimization program when applied to existing
179 membrane materials. Moreover, a nitrogen production cost around 30 Euros per ton is ob-
180 tained for a 95 percent purity, which matches the cost reported in a recent study [21]

181 Furthermore, besides the confirmation of the three different process flow-sheets detailed in
182 Figures 4 and 5, the optimal structures and operating conditions obtained with commercial
183 PSF and PPO membranes lead to additional insights, which are of interest:

- 184 • Vacuum operation is of major interest in order to generate the lowest production cost.
185 This option is rarely taken into account by membrane process synthesis softwares.
186 This operation possibility is included in our tailor made program and seems to be
187 important for cost minimization. It has to be stressed however that vacuum operation
188 is most often discarded for industrial units, because of the large footprint of vacuum
189 pumps, low energy efficiency and problems generated by leaks. Vacuum operation
190 in membrane gas separations is effectively limited to VOC recovery, oxygen enriched
191 air or carbon capture [4]. These serious limitations have to be taken into account
192 for NEA production. The optimal flow-sheets reported in Figures 4 and 5 suggest
193 however that the use of vacuum in place of or complementary to feed compression
194 should be investigated. Feed compression is operated only for high purity levels, when
195 too large membrane surface areas are needed. Vacuum pumping seems however to offer
196 a very useful solution when membrane surface area and energy requirement have to be
197 balanced.
- 198 • Nitrogen production costs with PPO are systematically lower than with PSF. This
199 suggests that a larger permeance such as offered by PPO is more interesting than a

200 higher selectivity (offered by PSf).

201 The reference case obtained through this first process synthesis study confirms the rules
202 and guidelines reported for nitrogen production by membranes. The impact of novel, high
203 performance materials, such as those detailed in Table 3 and corresponding to trade-off
204 limits, on these guidelines and conclusion are analyzed in the next section.

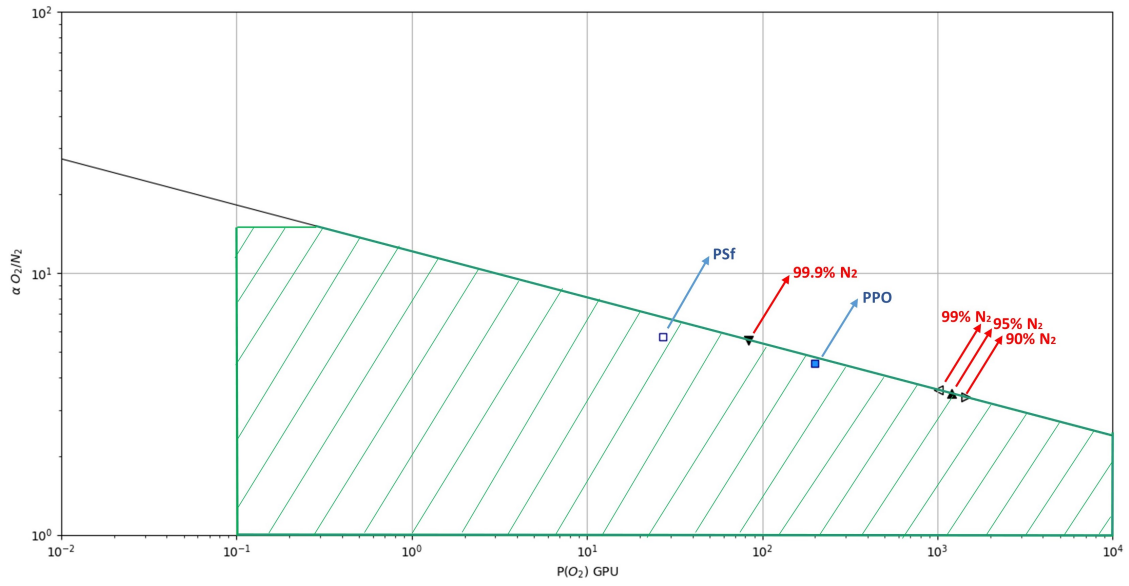
205 *3.2. Nitrogen production by high performance membrane materials*

206 In the second part of this study, the minimal nitrogen production cost with high performances
207 membrane materials, within the trade-off limits, is explored. In that case, membrane perfor-
208 mances (i.e. oxygen and nitrogen permeances) are not fixed (such as in the previous step)
209 but these two variables are free within the trade-off limits shown on Figure 2b (dashed area).
210 Two different strategies have been compared:

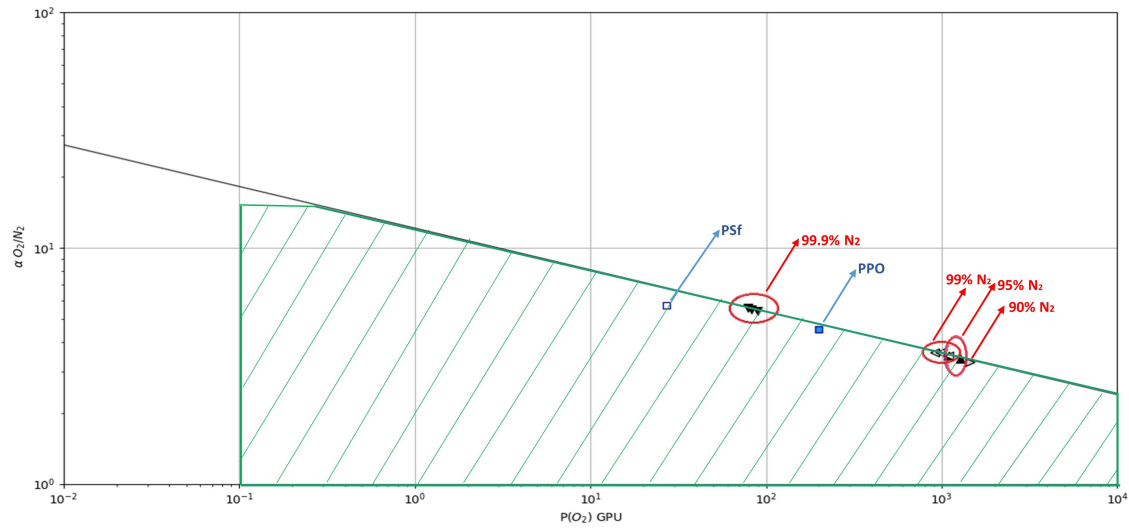
- 211 • Membrane permeances are allowed to vary within the trade-off limits but the same
212 membrane is used for all stages. One set of permeances is considered as in the previous
213 section, but instead of being input values, the optimal pair of gas permeances are
214 determined along with process configuration and operation parameters for each level
215 of nitrogen purity by the optimization program.
- 216 • Membrane performances are allowed to vary within the trade-off limits but a different
217 membrane can be selected for each stage. A set of optimal membrane permeances
218 will be determined for each stage and nitrogen purity level. To our knowledge, this
219 possibility has never been explored up to now for NEA production. The results of the
220 optimization (process synthesis) are expected to generate useful guidelines for mem-
221 brane material development: is it better to push selectivity or permeance in order to
222 decrease NEA production cost? Is it interesting to combine different membranes in a
223 multistaged unit, in order to achieve lower production costs?

224 The results of the two strategies (optimal membrane for all stages and optimal membrane
225 for each stage) for NEA production study for the four levels of nitrogen purity and for 1,
226 2 and 3 stages units are detailed in the appendix A.10 and A.11. The optimal selectivity
227 / permeance for fixed and variable strategies are summarized Figure 6. Except for the
228 99.9 percent purity case, most optimal membrane performances are very close together. An
229 increased permeance is favored, at the expense of a slight decrease in selectivity. Surprisingly,
230 the variable permeability option (figure 6b) does not offer interesting performances. The
231 different membrane performances for the optimal membranes per stage case are indeed very
232 close and located in the same place as the optimal membrane for all stages case. This result
233 is somewhat unexpected and it is of interest for NEA production.

234 The optimal flowsheets and operating conditions are summarized in Figure 7 for both strate-
235 gies.



(a) Optimal membrane performances for the different nitrogen purity levels when the same membrane is used in all stages.



(b) Optimal membrane performances for the different nitrogen purity levels when a different membrane is used in each stage. PSf and PPO membranes are included for reference.

Figure 6

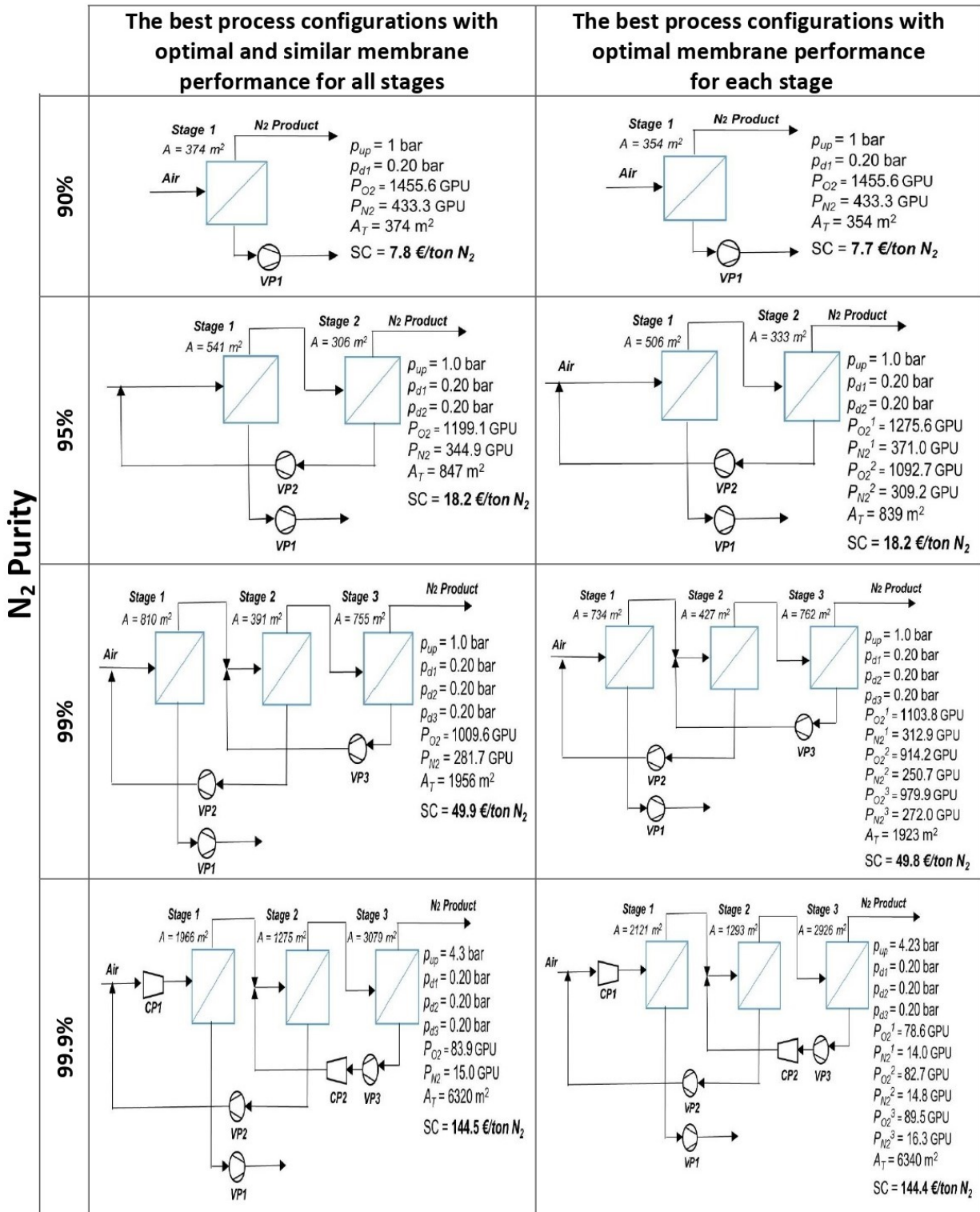


Figure 7: Overall best process configurations with up to three membrane stages at different nitrogen purity levels including optimal membrane permeances when the same membrane is used in all stages (left) and when a different membrane is used in each stage (right).

236 From a production cost point of view, the high performance materials generate a significant
237 decrease. A comparison between Figure 4-5 and Figure 7 shows the the impact of improved
238 membrane materials for the minimization of NEA production costs. The cost difference
239 between having an overall optimal membrane or having different optimal membranes for
240 each stage is negligible. This clearly results from the fact that the latter approach ends
241 up to similar membrane performances than those generated by just considering one optimal
242 membrane performance for all stages.

243 Since the results presented above highligh the interest of permeance over selectivity for NEA
244 production, it is tempting to explore the incidence of thinner layers (i.e. larger permeance).
245 Thin dense layers down to 50 nm are effectively achievable for some gas separation membranes
246 [3]. A 0.1 μm thickness could thus be possibly obtained with the trade-off materials listed
247 in Table 3. This point is analysed in the next section.

248 *3.3. Nitrogen production by high performance membrane materials and ultra thin dense layer* 249 *membranes*

250 An optimization study of trade-off membrane materials showing a ten fold increase in per-
251 meance has been undertaken. This new case study corresponds to 0.1 μm thick layer mem-
252 branes, in place of the standard 1 μm assumption taken in the previous sections. The best
253 configurations, operating conditions and membrane performances for the four nitrogen purity
254 levels are summarized figure 8.

255 The optimal membrane pemfomances for the one membrane for all stages and one membrane
256 for each stage strategies are shown on the trade off curves presented figure 9.

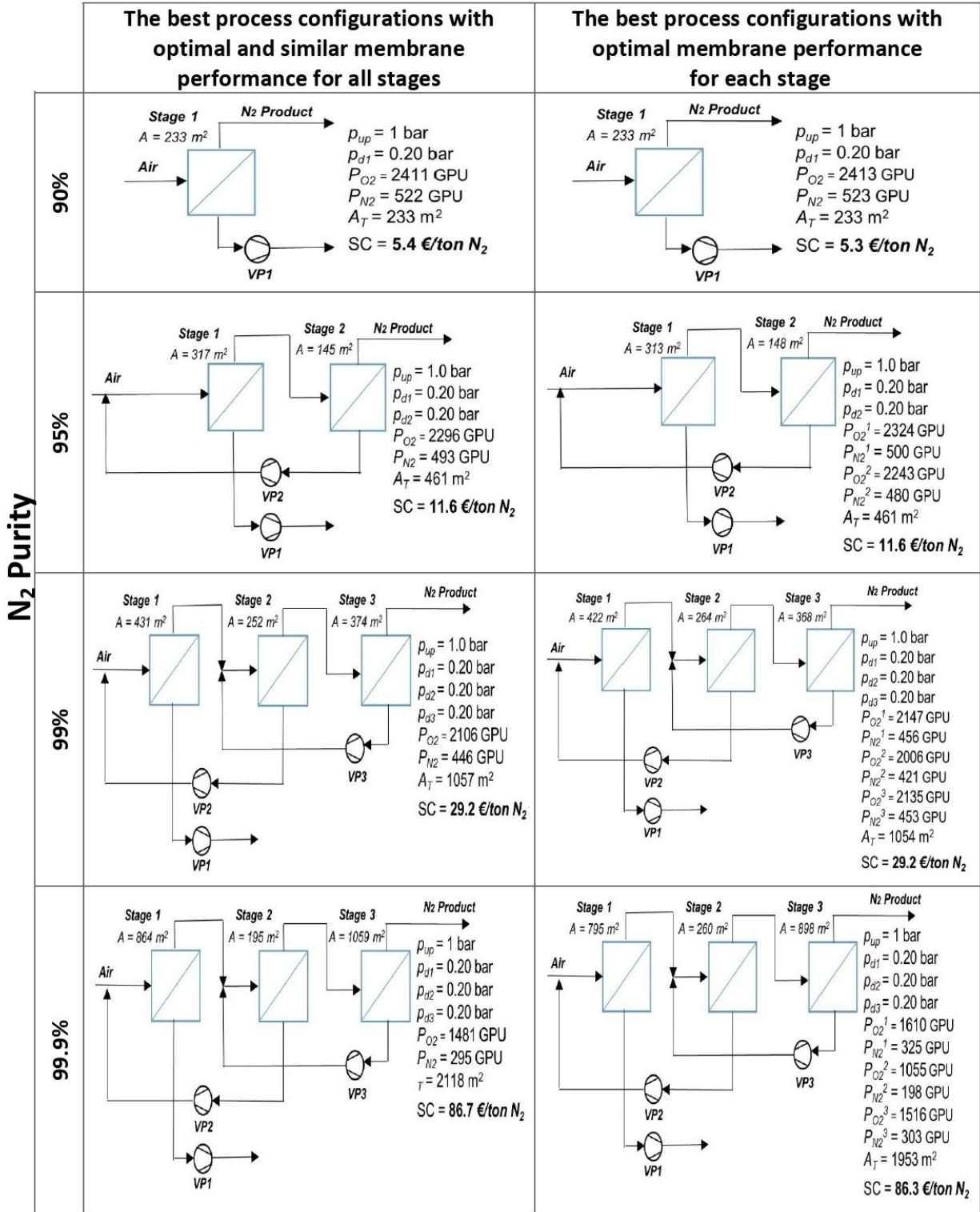
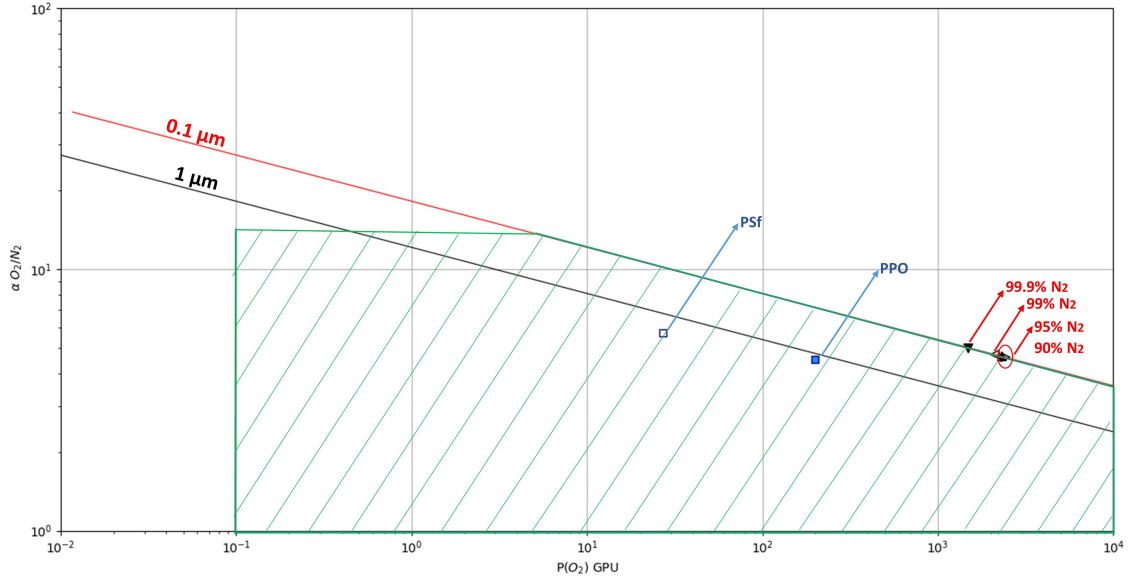
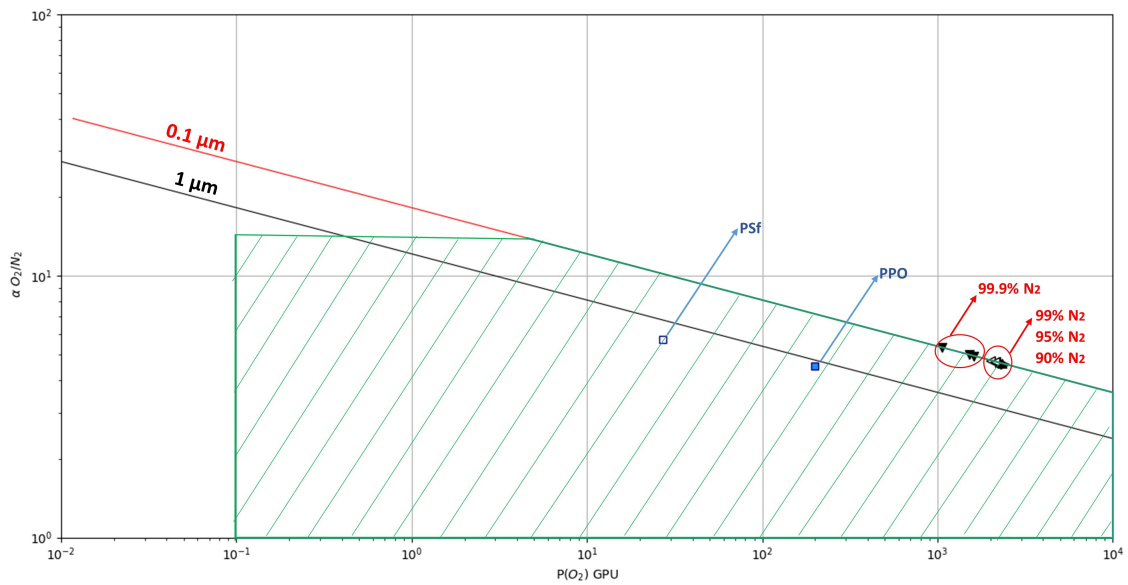


Figure 8: Overall best process configurations with up to three membrane stages at different nitrogen purity levels including optimal membrane permeances when the same membrane is used in all stages (left) and when a different membrane is used in each stage (right). Membrane thickness used to calculate membrane permeance from permeability values is taken as $0.1 \mu\text{m}$.



(a) Optimal membrane performances for the different nitrogen purity levels when the same membrane is used in all stages



(b) Optimal membrane performances for the different nitrogen purity levels when a different membrane is used in each stage. PSf and PPO membranes are included for reference.

Figure 9

257 The two strategies show, again, very close results. This confirms that for NEA production,
 258 the association of different membranes into multistage units is of low interest. A very narrow
 259 domain is obtained for optimal membrane performances for the different nitrogen purity
 260 levels. This result is surprising and also interesting because it suggests that a single optimal
 261 membrane development could possibly fit the requirements for a broad range of nitrogen
 262 purities. In terms of selectivity / permeance trade-off, the optimal membrane characteristics
 263 clearly shift towards larger permeances, without large increase in selectivity. This unexpected

264 result corresponds to a generic guideline for membrane materials development for NEA
 265 production: permeance has to be favored. The performances of recently reported materials
 266 such as PIM, with ultra-high permeabilities [10], are of major interest in that perspective.
 267 It is worth to note that with high permeance membranes, the process configurations remain
 268 unchanged for each purity level, but the specific cost is largely decreased (typically around
 269 40 percent). This highlights the potential of thin, highly permeable membrane materials for
 270 nitrogen production.

271 *3.4. Synopsis*

272 In the last part of this study, the different case studies are summarized in Table 5, in order
 273 to enable an overview of the key results. The optimal conditions for the four purity levels
 274 are presented for the current membrane materials (represented by PPO results), trade-off
 275 materials and ultra-high permeance materials (limited to the one optimal membrane for all
 276 stages case, the differences with the optimal membrane for each stage case being very small).

Table 5: Summary of the best process configurations for NEA production with commercial membrane (PPO) and trade-off membrane materials with uniform permeability and 1 and 0.1 μm membrane layer thickness.

	N_2 purity	Cost(EUR/ton N_2)	Number of stages	α	P_{O_2} (GPU)	V_p / C_p	θ	Energy(kWh/Nm ³)
Commercial membrane (PPO)	90%	13.9	1	4.54	200	V_p	0.44	0.07
	95%	31.7	2	4.54	200	V_p	0.57	0.16
	99%	80.1	3	4.54	200	V_p & C_p	0.59	0.36
	99.9%	161.6	3	4.54	200	V_p & C_p	0.67	0.79
Optimal membrane performance with 1 μm dense layer for all stages	90%	7.8	1	3.4	1455.6	V_p	0.54	0.1
	95%	18.2	2	3.5	1199.1	V_p	0.64	0.22
	99%	49.9	3	3.6	1009.6	V_p	0.76	0.56
	99.9%	144.5	3	5.6	83.9	V_p & C_p	0.57	0.59
Optimal membrane performance with 0.1 μm dense layer for all stages	90%	5.4	1	4.6	2411	V_p	0.45	0.07
	95%	11.6	2	4.6	2296	V_p	0.57	0.15
	99%	29.2	3	4.7	2106	V_p	0.68	0.37
	99.9%	86.7	3	5	1481	V_p	0.85	0.98

277 The overall set of results which are detailed in Table 5 can be summarized as follows:

- 278 • A higher nitrogen purity logically generates higher (non linear) production costs. This
 279 logical statement applies to both the current commercially available membranes and
 280 advanced prospective materials.
- 281 • Trade-off membrane materials offer promising performances in terms of production
 282 cost, with a two to three fold decrease compared to the current production cost. It is
 283 important to note that the average cost of 30 Euros per ton, obtained with commercial
 284 PPO gas separation membranes for 95 percent purity, is in excellent agreement with a
 285 recent study [21].
- 286 • A single stage process is the most economical for the lowest purity level (90% N_2),
 287 whatever the membrane type. Similarly, two and three stages processes with recycling
 288 loops offer better performances for higher nitrogen purity specifications, independently
 289 of the membrane characteristics. This shows the robustness of the process flowsheets,
 290 generated through engineering studies in the 80's. The three types of configurations,

291 selected as target nitrogen purity only (Figure 3) for decades, are indeed confirmed
292 throughout the different case studies explored in this paper.

- 293 • In contrast to current practice, the optimal configurations obtained with high perfor-
294 mance membrane materials make use of vacuum operation. Except for the high purity
295 target, compression is not the best retained technology for the optimal configuration.
296 This result shows the interest to combine materials and engineering for process design
297 studies, and also the interest to systematically explore the vacuum option in membrane
298 process synthesis studies. It has to be stressed however that vacuum operation is often
299 rejected for industrial applications due to the drawbacks of vacuum pumps (risk of
300 leaks, large footprint, low energy efficiency, higher capital costs). The optimal results
301 shown on figures 7 and 8 thus address a key question in terms of process selection.
- 302 • The overall stage cut (i.e. ratio of the total permeate over total feed flowrate) ranges
303 between 0.4 and 0.85. This is typical of industrial membrane units [3]. Thus, the fact
304 that air is considered as free for NEA production does not generate very low stage
305 cut values. Generally speaking, a larger stage cut is obtained when nitrogen purity
306 increases, in order to achieve a much intense oxygen removal (oxygen being faster than
307 nitrogen).
- 308 • The energy requirement has been also calculated and it is detailed in the last column of
309 Table 5. Interestingly, the overall energy requirement (classically expressed in kWh per
310 unit feed flowrate [1]) is comparable to previously reported data for NEA production
311 (typically 0.26 to 0.45 kWh per standard cubic meter nitrogen at 98 to 99 percent [1]).
312 Energy requirement for the optimal configuration seems to depend on nitrogen purity
313 only, with a ten fold increase from 90 to 99.9 percent.
- 314 • One of the most striking and unexpected result of the study concerns however the op-
315 timal membrane performances. First, a moderate selectivity is systematically obtained
316 as the optimal one, whatever the nitrogen purity level. This point is counterintuitive.
317 It is often stated that for high purity, a larger selectivity helps. The subtle inter-
318 play between permeance (surface area) and selectivity (separation performances) in
319 multistage configurations including recycling loops suggests however, according to the
320 results shown in figures 7 and 8 that a moderate selectivity associated to a trade-off
321 permeance (i.e a much larger permeance compared to commercial membranes) is the
322 best solution. To some extent, this conclusion is of great interest for the recent genera-
323 tion of high permeability polymers (TRP, PIM, superglassy) [9–11]. Thus, it could be
324 suggested to materials developers to promote permeability increase, rather than trying
325 to develop super selective materials.
- 326 • Finally, the most puzzling results comes from the possibility to combine different mem-
327 brane materials into multistage units. This option is almost unexplored in membrane
328 science and has never been investigated for NEA production. The possibility to com-
329 bine nitrogen selective and carbon dioxide selective membrane has been shown to offer
330 very attractive performances for carbon capture applications [22]. It might be expected
331 that for NEA production, the same conclusion could be drawn. Our study shows that
332 the situation is completely different. The optimal multistaged processes shown on

333 Figure A.11 make use of approximately the same membrane (a moderate selectivity
334 around 3.6 to 4.6, a permeance level at the trade-off limit). It is obvious that this
335 statement does not systematically hold and should be reconsidered from case to case
336 depending on the separation targets and feed mixture. For the set of parameters tested
337 in our NEA study, it seems however that the use of different membranes in a multistage
338 system does not offer attractive improvement possibilities.

339 4. Conclusions and perspectives

340 Nitrogen Enriched Air (NEA) is the main application of membrane gas separations to-
341 day. Nevertheless, few studies have been reported on either process [16, 23, 24] or techno-
342 economical analyses for this important application [25, 26]. The situation is quite different
343 for Oxygen Enriched Air (OEA), which has been more extensively investigated [27–30]. Nu-
344 merous innovative NEA concepts have been explored, including adsorption, hybrid systems
345 or membrane column processes [31–33]. This study intended to achieve a rigorous optimiza-
346 tion study of membrane gas separations units with up to three stages.

347 For the specific case of polymeric membranes, it has been shown that a large progress is
348 achievable for the production cost point of view for low purity NEA (i.e. 90 and 95%),
349 compared to the existing commercially available membrane materials. A very large cost
350 decrease is also in principle possible for higher purities (i.e. > 95%), but the comparison to
351 alternative technologies, such as PSA, is needed in that case.

352 More specifically, the process synthesis study performed on air separation has shown that :

- 353 • Process synthesis converges to the same process configurations as the ones developed
354 by gas producers for a long time (same number of stages and recycling loops as a
355 function of N_2 purity),
- 356 • Trade-off limit membrane materials do not impact the process configuration
- 357 • From a membrane materials point of view, a high permeance, combined to a moderate
358 selectivity, offers the best performances, whatever the N_2 purity target . This result is
359 of great importance for membrane material development because it suggests to promote
360 highly permeable structures rather than very selective materials.
- 361 • The possibility to use different membranes into multistage units does not provide a
362 significant improvement for NEA.
- 363 • Vacuum operation is a major interest (even though the practical use of vacuum pumps
364 is not favored in industry due to large footprint and leaks complications).

365 It has to be stressed that the above conclusions are by no means generic, but limited to the
366 NEA application with polymeric membranes. Future work on high performance materials,
367 showing performances far beyond the trade-off limits [34] is currently in progress, in order
368 to better understand the interplay between materials performances and process engineering.
369 It might be that the conclusions obtained for polymeric membrane materials are completely
370 different when ultrapermeable and/or ultraselective materials are used. Finally, the exten-
371 sion of the methodology to other gas separations applications (e.g. natural gas treatment,
372 hydrogen purification) is obviously also of interest.

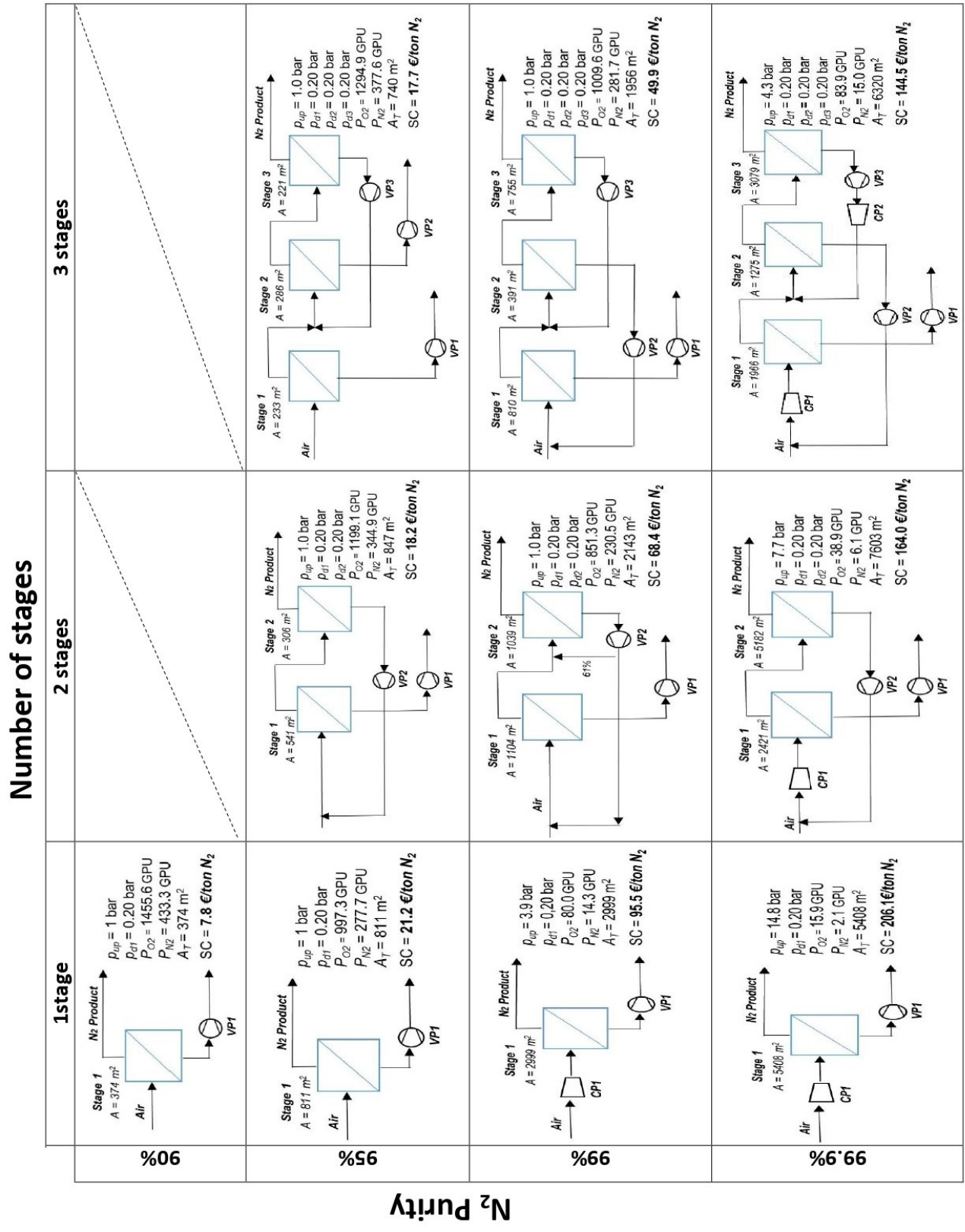


Figure A.10: Summary of the best process configurations obtained when the optimal membrane is used in all stages. A membrane process with up to three stages and different nitrogen purity levels has been considered.

Number of stages

	1stage	2 stages	3 stages
90%	<p> $p_{up} = 1 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 1455.6 \text{ GPU}$ $P_{N_2} = 433.3 \text{ GPU}$ $A_T = 354 \text{ m}^2$ $SC = 7.7 \text{ €/ton } N_2$ </p>	<p> $p_{up} = 1.0 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $p_{d2} = 0.20 \text{ bar}$ $P_{O_2}^1 = 1275.6 \text{ GPU}$ $P_{N_2}^1 = 371.0 \text{ GPU}$ $P_{O_2}^2 = 1092.7 \text{ GPU}$ $P_{N_2}^2 = 309.2 \text{ GPU}$ $A_T = 839 \text{ m}^2$ $SC = 18.2 \text{ €/ton } N_2$ </p>	<p> $p_{up} = 1.0 \text{ bar}$ $p_{d1} = 0.25 \text{ bar}$ $p_{d2} = 0.20 \text{ bar}$ $p_{d3} = 0.20 \text{ bar}$ $P_{O_2}^1 = 1932.1 \text{ GPU}$ $P_{N_2}^1 = 604.6 \text{ GPU}$ $P_{O_2}^2 = 1137.7 \text{ GPU}$ $P_{N_2}^2 = 324.3 \text{ GPU}$ $P_{O_2}^3 = 1253.1 \text{ GPU}$ $P_{N_2}^3 = 363.3 \text{ GPU}$ $A_T = 710 \text{ m}^2$ $SC = 17.6 \text{ €/ton } N_2$ </p>
95%	<p> $p_{up} = 1 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 995.8 \text{ GPU}$ $P_{N_2} = 277.2 \text{ GPU}$ $A_T = 812 \text{ m}^2$ $SC = 21.2 \text{ €/ton } N_2$ </p>	<p> $p_{up} = 1.0 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $p_{d2} = 0.20 \text{ bar}$ $P_{O_2}^1 = 963.7 \text{ GPU}$ $P_{N_2}^1 = 266.7 \text{ GPU}$ $P_{O_2}^2 = 757.3 \text{ GPU}$ $P_{N_2}^2 = 200.9 \text{ GPU}$ $A_T = 2091 \text{ m}^2$ $SC = 68.2 \text{ €/ton } N_2$ </p>	<p> $p_{up} = 1.0 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $p_{d2} = 0.20 \text{ bar}$ $p_{d3} = 0.20 \text{ bar}$ $P_{O_2}^1 = 1103.8 \text{ GPU}$ $P_{N_2}^1 = 312.9 \text{ GPU}$ $P_{O_2}^2 = 914.2 \text{ GPU}$ $P_{N_2}^2 = 250.7 \text{ GPU}$ $P_{O_2}^3 = 979.9 \text{ GPU}$ $P_{N_2}^3 = 272.0 \text{ GPU}$ $A_T = 1923 \text{ m}^2$ $SC = 49.8 \text{ €/ton } N_2$ </p>
99.9%	<p> $p_{up} = 14.8 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $P_{O_2} = 15.9 \text{ GPU}$ $P_{N_2} = 2.1 \text{ GPU}$ $A_T = 5408 \text{ m}^2$ $SC = 206.1 \text{ €/ton } N_2$ </p>	<p> $p_{up} = 7.7 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $p_{d2} = 0.20 \text{ bar}$ $P_{O_2}^1 = 41.0 \text{ GPU}$ $P_{N_2}^1 = 6.5 \text{ GPU}$ $P_{O_2}^2 = 38.2 \text{ GPU}$ $P_{N_2}^2 = 6.0 \text{ GPU}$ $A_T = 7536 \text{ m}^2$ $SC = 164.0 \text{ €/ton } N_2$ </p>	<p> $p_{up} = 4.23 \text{ bar}$ $p_{d1} = 0.20 \text{ bar}$ $p_{d2} = 0.20 \text{ bar}$ $p_{d3} = 0.20 \text{ bar}$ $P_{O_2}^1 = 78.6 \text{ GPU}$ $P_{N_2}^1 = 14.0 \text{ GPU}$ $P_{O_2}^2 = 82.7 \text{ GPU}$ $P_{N_2}^2 = 14.8 \text{ GPU}$ $P_{O_2}^3 = 89.5 \text{ GPU}$ $P_{N_2}^3 = 16.3 \text{ GPU}$ $A_T = 6340 \text{ m}^2$ $SC = 144.4 \text{ €/ton } N_2$ </p>

N₂ Purity

Figure A.11: Summary of the best process configurations obtained with optimal membrane performance when a different optimal membrane is considered in each stage. A membrane process with up to three stages and different nitrogen purity levels has been considered.

374 **Acknowledgements**

375

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378 **Nomenclature**

379 **Parameters:**

a	Annuity coefficient for equipment [Dimensionless]
ICF	Indirect cost factor [Dimensionless]
k	Front factor of the log – log plot of the Robeson bound [Dimensionless]
K_{el}	Electricity cost factor [EUR/kWh]
K_m	Unit cost of membrane module [EUR/m ²]
K_{mf}	Base frame cost [EUR]
K_{mr}	Membrane replacement cost [EUR/m ²]
M_{N_2}	N ₂ Molar mass [kg/mol]
MDF_{cc}	Compressor module factor [Dimensionless]
MF_{cc}	Compressor material factor [Dimensionless]
n	Slop of the log – log plot of the Robeson bound [Dimensionless]
R	Ideal gas constant [JK ⁻¹ mol ⁻¹]
T	Temperature [K]
t_{op}	Operation time per year [h/year]
UF_{2000}	Update factor [Dimensionless]
γ	Gas expansion coefficient [Dimensionless]
δ	Thickness of the membrane layer [μ m]
η	Isentropic compressor efficiency [Dimensionless]
θ	Stage cut of membrane separation [Dimensionless]
λ	Isentropic vacuum pump efficiency [Dimensionless]
ν	Membrane annual replacement rate [Dimensionless]
ϕ	Mechanical efficiency [Dimensionless]

380 **Variables:**

A_{m_s}	Area of membrane s [m^2]
A_T	Total area of the membrane system [m^2]
CAPEX	Capital expenditures [EUR]
C_{cap}	Annual capital costs [EUR/year]
C_{en}	Annual electricity cost [EUR/year]
C_{cc}	Compressor cost [EUR]
$C_{O\&M}$	Annual operation and maintenance investment cost [EUR/year]
C_{tot}	Total annual costs [EUR/year]
C_{vp}	Vacuum pump cost factor [EUR/kW]
F^{Ret}	System Retentate flowrate [mol/s]
I_{ccf}	Feed Compressor investment cost [EUR]
I_{ccs}	Membrane Compressor investment cost [EUR]
I_{ms}	Membrane surface investment cost [EUR]
I_{mfs}	Membrane permanentframe investment cost [EUR]
I_{vps}	Vacuum pump investment cost [EUR]
$M_{N_2 \text{ per year}}$	Annual separated N_2 [Tons/year]
OPEX	Operational expenditures [EUR/year]
p_{ds}	Down stream pressure of membrane s [bar]
p_{up}	Up stream pressure of all membranes [bar]
P_j	Permeance of component j [GPU]
SC_{N_2}	Specific N_2 production cost [EUR/Ton N_2]
X_j^{Ret}	Fraction of component j into the system retentate [Dimensionless]
W_{cpf}	Feed compression power consumption of membrane s [kW]
W_{cps}	Permeate compression power consumption of membrane s into s_1 [kW]
W_{tot}	Total energy consumption [kW]
W_{vps}	Vacuum power consumption of membrane s [kW]
α	Selectivity [Dimensionless]

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