Optimal process design of biogas upgrading membrane systems: polymeric vs high performance inorganic membrane materials

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Abstract

Membrane separation is a key technology for biogas purification. Multistaged processes based on either cellulose acetate (CA) or polyimide (PI) materials are classically used for this application. In this study, a systematic process synthesis optimization is performed in order to identify the most cost effective solution for three different membrane materials (CA, PI and zeolite) and three different outlet pressure levels (5, 10 and 15 Bar). It is shown that a costly (i.e. 2000 EUR per square meter vs 50 for CA and PI) but high performance membrane material such a zeolite offers the best cost effective solution compared to commercially available polymeric membranes. Increasing the outlet pressure increases the purification cost. Two stages processes with recycling loops offer the best balance between purity, recovery, complexity and cost, whatever the outlet pressure level. The use of vacuum pumping is shown to improve the process economy, while expander and extra feed compression do not show an interest.

Keywords: Membrane, Process, Synthesis, Biogas, Purification, Cost

1. Introduction

Biogas consists mainly of methane (CH_4) in a range of 50-70% and carbon dioxide (CO_2) at concentrations of 30-50%. Small amounts of other components are also present such as Nitrogen (N_2) at concentrations lower than 3%, water vapor up to saturation at the gas temperature, and oxygen (O_2) at concentrations lower than 1%; hydrogen sulfide (H_2S), ammonia (NH_3) and siloxanes can also be present in trace amounts depending of the biogas origin[1]. Biomethane is the term given to biogas that has been treated to remove all species besides methane and increase its concentration to meet transport and utilization specifications (equivalent to those of natural gas).

Biomethane can thus replace natural gas as a renewable, carbon neutral source since carbon present in biogas comes from sources having fixed that carbon from atmospheric CO_2. Any consumption of fossil fuels replaced by biomethane will lead to a net decrease of CO_2 emissions. Biogas treatment can be divided in a drying stage, where water is removed, a cleaning stage, where harmful or toxic compounds, mainly H_2S but also VOCs, siloxanes, CO and NH_3 are removed, and an upgrading stage where CH_4 concentration is increased mainly by the removal of existing CO_2. Water removal is done by a condenser and a demister or by adsorption technologies. Desulphurisation (H_2S removal) can be done by biological oxidation of the H_2S by aerobic sulphate oxidizing bacteria, by adding doses of iron hydroxide and/or iron salts during biomass digestion, by catalytic oxidation and adsorption with a material such as activated carbon or by caustic treatment with biological regeneration of the washing agent [2].

A number of technologies are available for biogas upgrading, these include: water scrubbing, physical scrubbing by organic solvents, chemical scrubbing by amine solutions, pressure swing adsorption, membrane separation and cryogenic separation [1]. All of these seek to separate the CO_2 in the biogas either by physical of chemical processes. New technologies under development include chemical hydrogenation processes and biological technologies seeking to produce either additional CH_4 from the available CO_2 or additional biomass that could be used for the extraction of high value added products or for biogas production in a circular economy[1].

Each of the available upgrading technologies have different advantages and disadvantages and they all aim to produce the highest CH_4 purity with the lowest CH_4 losses and energy consumption. Several reports exist in the literature reviewing the status and development perspectives of biogas upgrading technologies[1–6]. A summary of process metrics is presented Table 1. There is not an overall better technology, and the best choice will depend on the specific, local conditions [2]. Additionally, total cost of ownership depends on the flowrate of raw biogas to be upgraded. For flowrates of up to around 1000 Nm3/h of biogas, membrane upgrading has been cited as the cheapest technology, and a close alternative to water scrubbing at higher biogas flowrates[4, 7, 8]. Nevertheless confusion still exists as whether membrane upgrading is an overall expensive or inexpensive alternative as it is shown on Table 1. A more detailed information set on process comparison is shown in Appendix A.

Generally speaking, the main cost elements of membrane upgrading are the power consumption originated from the gas compressors/vacuum pumps (OPEX) and the compressors and membranes investment costs (CAPEX) [9]. To reach high CH_4 purities and recoveries, membrane upgrading is systematically based on multistage processes, for which the choice of the right membrane (or membranes), process architecture, and operating parameters are essential to reach the lowest cost possible. A few studies addressed cost analysis and process configuration analysis for biogas upgrading based on Process Systems Engineering approaches. For instance, two stages processes have been recently explored with cellulose acetate and carbon membranes [10], and polyimide two stages systems in another study [11]. A process synthesis study has been also performed with a 3 stages process based on polyimide membranes, in order to achieve the maximal cost efficiency thanks to a process optimization methodology [12]. To our knowledge, no process synthesis study addressed however a rigorous comparison of different membrane materials yet. More specifically, the key question of the potential interest of high performance (but often expensive) membrane materials for biogas (and natural gas) treatment, such as formulated by Baker [13], is thus unsolved.

In this paper we present the application of a global optimization approach based on a NLP formulation of the optimization of membrane upgrading processes by means of a superstructure representation. This global optimization approach has been validated in a previous study [14]. Current upgrading membranes such as cellulose acetate and polyimide will be compared. In a second step, a high performance, inorganic membrane material will be explored. Among the different nanostructured materials which have been reported for biogas purification purpose (e.g. zeolites [15–17], silica [18], Carbon Molecular Sieves [19, 20], ...), we selected a commercially available zeolite membrane which has never never been proposed for biogas applications. The aim is to evaluate from a process and cost perspective the impact of membrane performance. Moreover, the effect of the final pressure of the upgraded gas on the process cost and configuration is also considered since this has never been evaluated by Process Synthesis approaches. Biomethane injection pressure is indeed an important parameter for biogas infrastructure and pressure levels from 5 to 15 bar can be found depending on the location on the grid [10].

Table 1: Comparison between different methods of biogas upgrading

	Pressurized Water Absorption	Chemical absorption	Pressure Swing Adsorption (PSA)	Membrane gas separation
CH_4 purity (%)	$>$ 98 %	>98 %	$>$ 97%	$>$ 98%
CH_4 Recovery (%)	$>$ 98 %	98-99 %	$>$ 92%	98-99%
Removed compounds	$CO_2, VOC's$	$CO_2, VOC's$	$CO_2, VOC's, O_2$ N_2	$CO_2, VOC's, H_2O$ O_2
Energy requirement (kWh/Nm^3 raw biogas)	0.24-0.4	0.6-0.7	0.23-0.4	0.2-0.3
Cost efficiency	++	+/-	+/-	+++

2. Process synthesis methodology

2.1. Optimization method for membrane gas separation

In this study, a membrane process with up to three stages has been considered with the possibility of using a compressor or an expander for the product stream, with 3 different product pressure levels (5, 10 or 15 bar). In order to achieve this target with a minimum process cost, the membrane process should be optimally designed. The optimal design of a membrane process means to determine the best possibility for the number of stages, the membrane material (polymer or inorganic), the elements included in the system (e.g. mixers, splitters, compressors, expandors, vacuum pumps and other necessary equipments;

specially the compressor or expandor on the product stream), their operating conditions and their connections. This requires a rigorous mathematical modeling approach in order to optimize the design of membrane separation systems. Process synthesis methods applied to membrane systems are intensively investigated, following the pioneering analysis of mass exchange networks by El-Hawagi in the 90's [14]. Numerous variants in terms of equipment, connection possibilities, set of constraints and objective function (i.e. overall cost function) can be found. While numerous process synthesis studies addressed the problem of carbon capture, hydrogen purification, Oxygen Enriched Air (OEA) and natural gas treatment, very few publications are reported for biogas purification.The most recent and detailed study has been performed by Scholz et al., with a structural optimization approach making use of GAM's software. A three stages process based on polyimide membranes is investigated, making use of a single compressor for an outlet pressure of 16 Bar. A parametric study shows that increased selectivities significantly improves the economy of the process. A limited set of connections (e.g. no self recycling loop), no vacuum pumping and a single outlet pressure are investigated.

In this study, a general and systematic optimization model for membrane process proposed in [14] is used, which takes into account all the mentioned possibilities as a degrees of freedom in a membrane system (vacuum pumping, self recycling loops). The superstructure and optimization program, named MIND, has been built in house and makes use of KNITRO algorithm. A detailed description of the methodology and characteristics of the program can be found in [21]. Moreover, three different outlet pressure levels are taken as constraints, for three different membrane materials. The overall target is to identify to what extent improved commercially available membrane materials, extended connection possibilities and supplementary equipment options (vacuum pump, expander) impact the biogas purification cost.

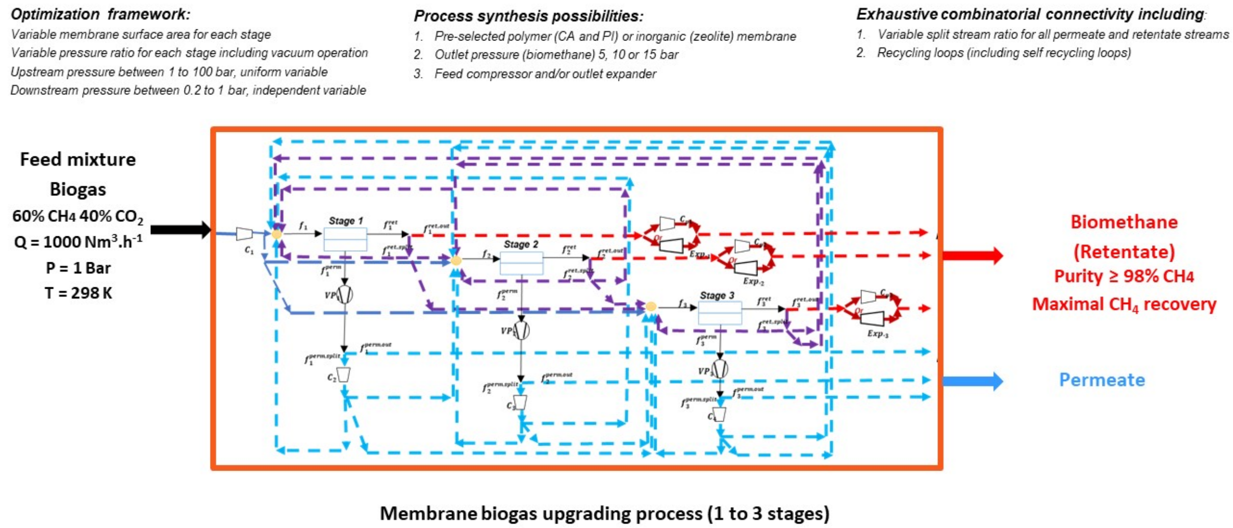


Figure 1: Overall process synthesis framework applied in this study. A membrane separation process including up to 3 stages with compressors and/or vacuum pumps and/or product compressor and/or expander is used. Multiple connection possibilities including recycling loops is applied to achieve biomethane with three levels of product pressures. 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 2 and 3).

More specifically, the overall process cost which is taken as the objective function of the optimization model, is the modification of [14] separation cost and [10] cost parameters. It takes into account the capital expenses (CAPEX) such as membrane area and membrane frame, vacuum pumps, compressors or expanders and the operating costs (OPEX), such as contract and material maintenance cost, local tax and insurance, labor overhead cost, energy requirement, membrane replacement and total operation. The cost function used for biogas upgrading and the parameters used in the objective function are detailed in Table 2 and Table 3 respectively. The energy requirement equations are explained in detail in Appendix B.

Table 2: Cost equations used to determine product gas separation cost

Equipment cost		
$I_{m_s} = A_{m_s} \cdot K_m$	(1)	Membrane cost
$I_{mf_s} = (A_{m_s}/2000)^{0.7} \cdot K_{mf} \cdot (p^{up}/55)^{0.875}$	(2)	Membrane frame cost
$I_{c_s} = C_c \cdot (W_{cp_s}/74.6)^{0.77} \cdot (MPF_c + MF_c - 1) \cdot UF_{1968} \cdot K_{er}$	(3)	Stage compressor cost
$I_{c_f} = C_c \cdot (W_{cp_f}/74.6)^{0.77} \cdot (MPF_c + MF_c - 1) \cdot UF_{1968} \cdot K_{er}$	(4)	Feed compressor cost
$I_{c_{prod}} = C_c \cdot (W_{cp_{prod}}/74.6)^{0.77} \cdot (MPF_c + MF_c - 1) \cdot UF_{1968} \cdot K_{er}$	(5)	Retentate compressor cost
$I_{exp} = C_{exp} \cdot (W_{exp}/0.746)^{0.81} \cdot (MPF_c + MF_c - 1) \cdot UF_{2000} \cdot K_{er}$	(6)	Expander cost
$I_{vp_s} = C_{vp} \cdot (W_{vp_s})$	(7)	Vacuum pump cost
Capital expenditures		
$PFC = I_{c_f} + I_{c_{prod}} \text{or } I_{exp} + \sum_{s \in \mathcal{S}} I_{m_s} + I_{mf_s} + I_{c_s} + I_{vp_s}$	(8)	Process facilities capital
$BPC = 1.12 \cdot PFC$	(9)	Contingency cost
$PC = 0.2 \cdot BPC$	(10)	Base plant cost project
$TFI = BPC + PC$	(11)	Total facility investment
$STC = 0.10 \cdot OPEX$	(12)	Start − up cost
$CAPEX = TFI + STC$	(13)	Total capital cost
Operational expenditures		
$CMC = 0.05 \cdot TFI$	(14)	Contract and material maintenance cost
$LTI = 0.15 \cdot TFI$	(15)	Local taxes and insurance
$DL = 11 \cdot t_{op}$	(16)	Direct labor
$LOC = 1.15 \cdot DL$	(17)	Labor overhead cost
$EC = t_{op} \cdot W_{tot} \cdot K_{el}$	(18)	Energy cost
$MRC = \sum_{s \in \mathcal{S}} A_{m_s} \cdot \nu \cdot K_{mr}$	(19)	Membrane replacement cost
$OPEX = CMC + LTI + DL + LOC + EC + MRC$	(20)	Total operational expeditures
Annual and specific separation costs		
$APL = F^{PERM} \cdot 3600 \cdot 0.0224 \cdot K_{gp} \frac{X_{CH_4}^{PERM}}{X_{CH_4}^{RET}}$	(21)	Annual CH_4 losses
$TAC = CAPEX \cdot \frac{i \cdot (1+i)^{z-1}}{(1+i)^z - 1} + OPEX + APL$	(22)	Total annual costs
$SC_{CH_4} = TAC/(F^{RET} \cdot 3600 \cdot t_{op} \cdot 0.0224)$	(23)	Specific CH_4 separation cost

Table 3: Cost parameters used in Table 1

Capital cost parameters		
C_c	1×23000	USD_{1968}
C_{vp}	1000	EUR/kW
C_{exp}	420	USD_{2000}
K_m(polymer)	50	EUR/m^2
K_m(zeolite)	2000	EUR/m^2
K_{mf}	2.86×10^5	EUR
K_{er}	0.9	EUR/USD
MPF_c	2.9	-
MF_c	5.11	-
UF_{2000}	1.44	-
UF_{1968}	4.99	-
Operational and annual cost parameters		
ν	0.25	-
K_{mr}(polymer)	25	EUR/m^2
K_{mr}(zeolite)	2000	EUR/m^2
t_{op}	8322	h/year
K_{el}	0.08	EUR/kWh
K_{gp}	0.8	EUR/Nm^3
i	0.08	-
z	15	years
η_c	0.85	-
Φ	0.95	-
γ	1.36	-
R	8.314	$J/(K \cdot mol)$
T	293.15	K

The optimal process configuration and the associated operating conditions for the specific target (biomethane under product pressure) are achieved thanks to a a continuous global optimization algorithm presented in [14] to solve the proposed optimization model with the mentioned objective function.

2.2. Biogas purification process: Case study

A biogas with a flowrate of 12.393 mol/s, corresponding to around 1000 Nm^3/h is considered. Inlet gas pressure and temperature are 1 bar and 293.15°K respectively. A classical biogas composition, detailed in Table 4 is used [12]. Product purity is expressed in terms of CH_4 content in the outlet stream with the constraint of at least 98% CH_4, together to minimal methane losses in terms of optimization constraints (Figure 1).

Table 4: Biogas compositions

Gas component	Composition (%mol)
$\mathbf{CH_4}$	60
$\mathbf{CO_2}$	40

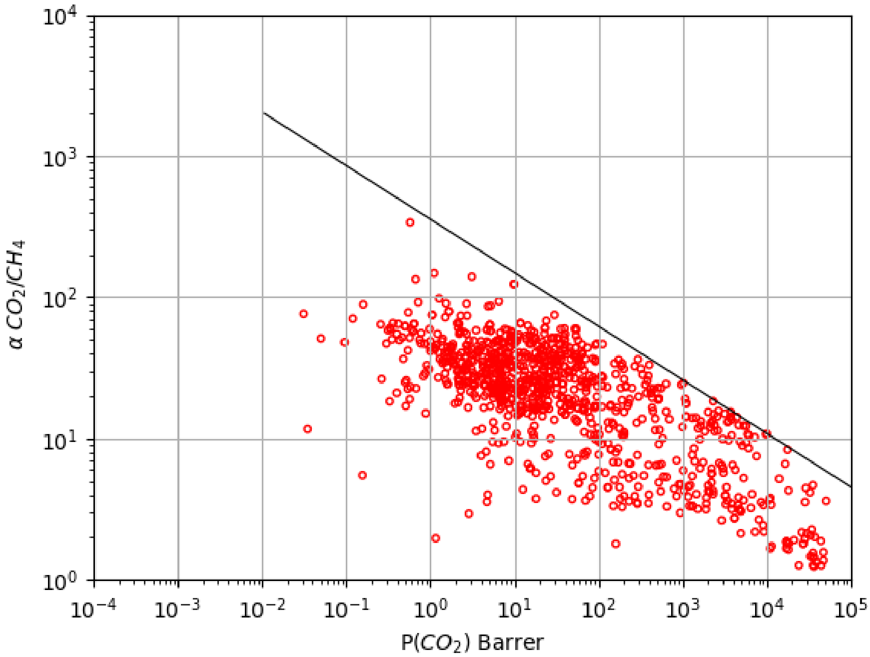
Process configurations up to three membrane stages are studied. The module pressure ratio is variable through a range of downstream and upstream pressure allowed for the optimization. Upstream pressure is the same for all the stages in the system. Technically, by considering vacuum pumping for each permeate stream in the system, the downstream pressure level is allowed to vary between 0.2-1 bar, while upstream pressure vary between 1-100 bar.

The goal of the study is to identify the most effective process structure and operating conditions, which reach the specifications (biomethane with target purity, maximal recovery and outlet pressure level) at the lowest cost. In order to achieve this aim, a system with polymeric membranes (cellulose acetate and polyimide) is first considered and the effects of the three different levels of biomethane pressure on process structure, operating conditions and process cost is studied. In a second step, the same scenario is performed on a process with inorganic (zeolite) membrane performances. Table 5 presents the performances of polymers and inorganic membranes used for the process synthesis study.

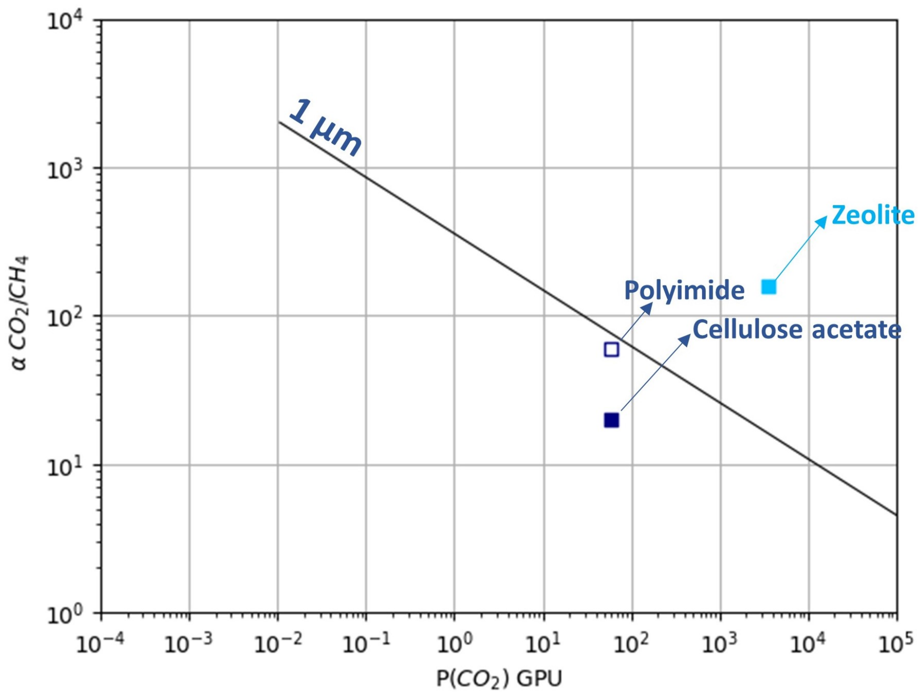
Table 5: Membranes characteristics used for the Process Synthesis study

Membrane material	P_{CO_2}(GPU)	P_{CH_4}(GPU)	Cost (EUR/m^2)	References	Comments
Cellulose Acetate (CA)	60	3	50	[12]	First commercialised membrane material for CO_2/CH_4 separation
Polyimide (PI)	60	1	50	[12]	Second generation polymeric membrane material (improved selectivity, close to trade-off limit)
Zeolite	3500	22	2000	[17]	High performance inorganic membrane material (breakthrough permeance and selectivity)

Figure 2a shows the permeability/selectivity trade-off for CO_2/CH_4 polymeric membrane materials [22]. The performances of the three membranes (CA, PI and Zeolite) investigated in this study are reported in Figure 2b, where a 1 micron active layer thickness is used for the trade-off permeance calculation (a membrane showing a 1 μm thickness and a 1 Barrer permeability corresponds to 1 GPU). The very large selectivity and permeance performances of the zeolite membrane, compared to existing polymeric membrane materials, is highlighted. This is however associated to a very high cost (Table 5). A 2000 EUR/m^2 cost is taken for the inorganic membrane, which is a zeolite CHA type. More generally, typical inorganic membrane costs range between 1000 [23] and 5000 EUR/m^2 [24]. The balance between very high performances membrane material and very high cost will thus be analysed through this study.



(a) CO_2/CH_4 trade-off curve [22]



(b) Selectivity / permeance trade-off curve based on a 1 μm skin layer thickness and performances of two polymers (Polyimide and Cellulose acetate) and one inorganic (Zeolite, CHA type) membrane materials (1 μm thickness with a 1 Barrer permeability corresponds to 1 GPU).

Figure 2: Trade-off curves for CO_2/CH_4 gas pair based on permeability for different polymeric materials (a) and permeance for gas separation membranes (b)

In order to attain biomethane specifications, the possibility of using compressors and/or vacuum pumps and/or an expander on the product stream is investigated. In a first step, the upstream pressure is considered between one bar and the target outlet pressure. Then, the possibility of using/not using a compressor for the product stream is investigated. The product compressor cost (Equ. 5) and the corresponding the PFC (Equ. 8) are included in the objective function for that purpose. In a second step, the same senario is performed with a product stream pressure between the target pressure and 100 bar. The possibility of using/ not using an expander (i.e. an Energy Recovery System) for the product stream is thus explored. The expander cost (Equ. 6) and the associated PFC (Equ. 8) are then included in the objective function. The optimal process structure is finally obtained by comparing the results of these different steps for all cases (up to three stages, different membranes and different biomethane pressure levels).

The general methodology of the study is sketched on Figure 3. The superstructure optimization method used in this study makes use of MIND in house built program (using KNITRO algorithm). The overall cost function is minimized, with fixed retentate purity (98% methane). For the different membranes, outlet pressure levels and stage numbers an optimal design and operating conditions set is generated (such as shown in a series of figures later in the paper). This set of possibilities can be used, in a second step, in order to select the best solution. It is important to stress at this point that the final decision includes additional conditions or criteria, in some cases qualitative. For instance, risk analysis can lead to a rejection of vacuum pump designs, due to explosion hazard resulting from air leaks (oxygen / methane mixtures on the permeate side). Design complexity is also important. For instance, if a three stages design with several compressors only offers a slight cost decrease compared to two stages, it is likely that the two stage process will be favored. Process robustness, which can be evaluated through a parametric sensitivity, is also important. In summary the idea is to provide, through Process Synthesis, a set of optimal solutions to the problem (upper part of the figure), so that the decision maker has an exhaustive view of the different possibilities in the process selection step (lower part of the figure).

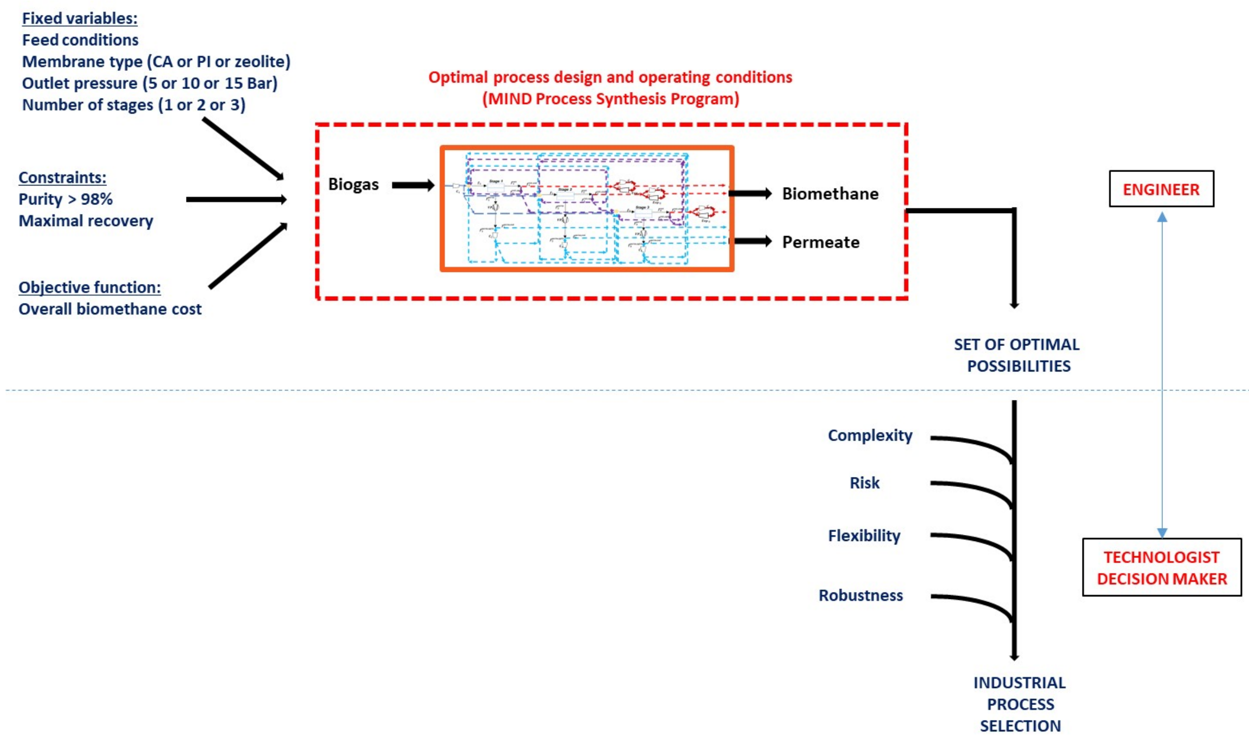


Figure 3: Generic representation of the different steps of a process selection strategy. Process synthesis in a first step proposes a portfolio of optimal solutions for different membranes, number of stages and operating conditions. A decision maker can then use this information set in order to select the best trade-off between cost, complexity, risk and flexibility

3. Results and discussion

3.1. Biogas purification by commercially available polymeric membrane materials

Polymeric membranes are classically used for gas separation applications [25, 26]. Polymers indeed offer low production cost, selective permeability, ease of processing and scaling up characteristics [6, 26, 27]. Cellulose acetate (CA) and Polyimide (PI) are preferred for biogas purification [9].

Figure 4 shows the optimal process configurations for biogas upgrading with three levels of biomethane pressure levels and for up to 3 membrane stages. Interestingly, the optimal process configuration is almost not impacted by the outlet pressure level. For one stage configurations, a recycling loop offers the best cost performances, whatever the outlet pressure. A significant cost decrease is obtained with two stages configuration. Again outlet pressure does not impact optimal configuration. Three stages processes generate a slightly lower purification cost compared to two stages. Two recycling loops are obtained in that case. This suggests two stages processes to be favored in place of three, when complexity is taken into account. This results corroborates classical industrial practice, where two stages processes are most often applied, be it for natural gas or biogas purification applications [9].

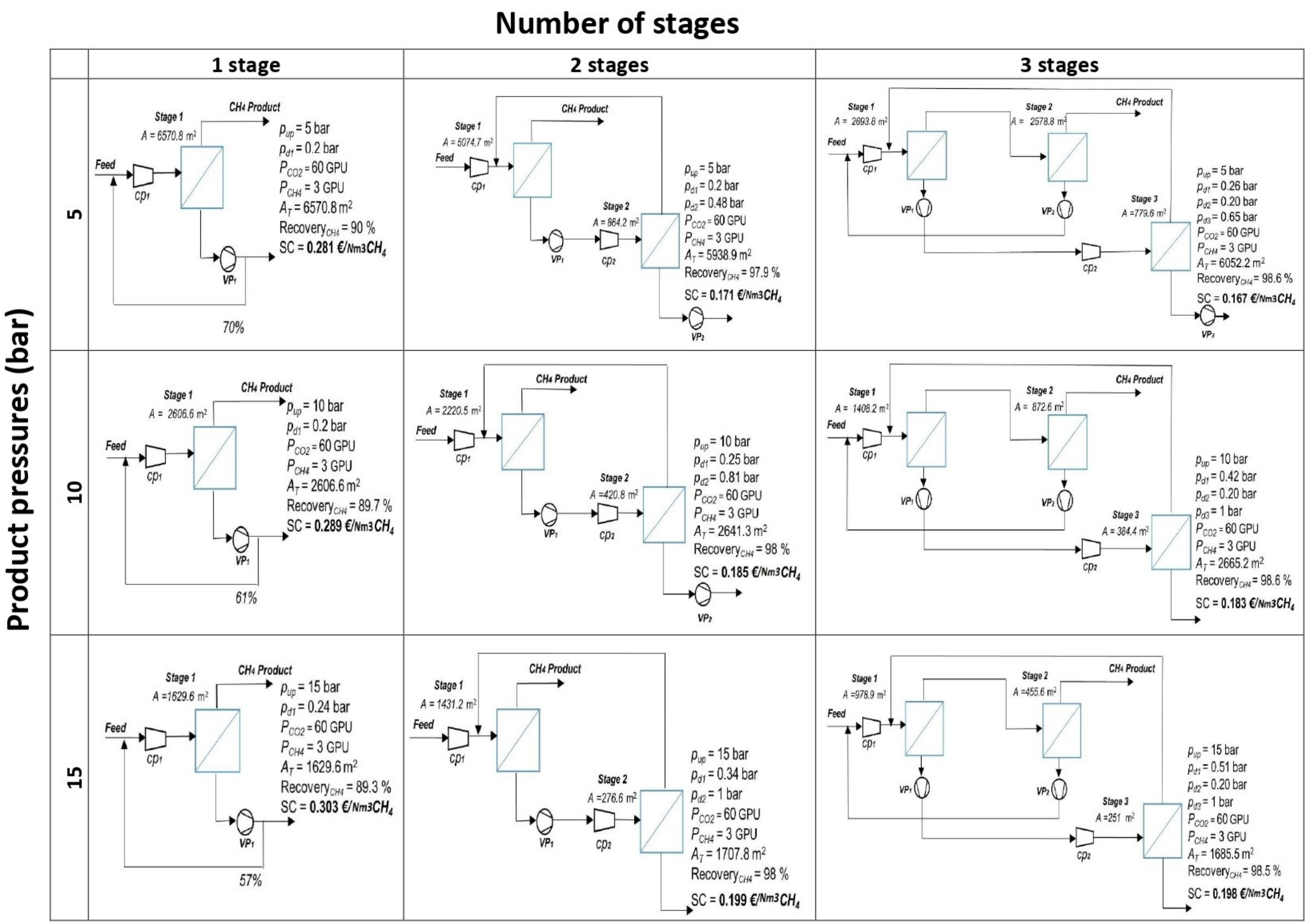


Figure 4: The best process configurations obtained with cellulose acetate membrane for up to three membrane stages and different levels of product pressure

Figure 5 shows the optimal process configurations for a polyimide (PI) membrane based process with up to three membrane stages and different product pressures.

PI is a second generation membrane material, which offers improved selectivity compared to CA (Table 5)[6, 26]. Gloabllay speaking the results obtained with PI are close to those obtained with CA in terms of process structure and characteristics. The major difference comes from the lower purification cost obtained with PI membranes. Costs increase with outlet pressure level, decrease with the number of stages, but again with a very low difference between two and three stages. Expander and extra compression options are not interesting. A single stage process with a recycling loop is obtained for 5 bar pressure level, while a recycling loop is included for 10 and 15 bar. Purification costs vary from 0.194 to 0.142 EUR/ton CH_4 depending on the outlet product pressure. With a single stage process, the separation cost is increased from 26.2% to 11.17% approximately in comparison to a two stage process.

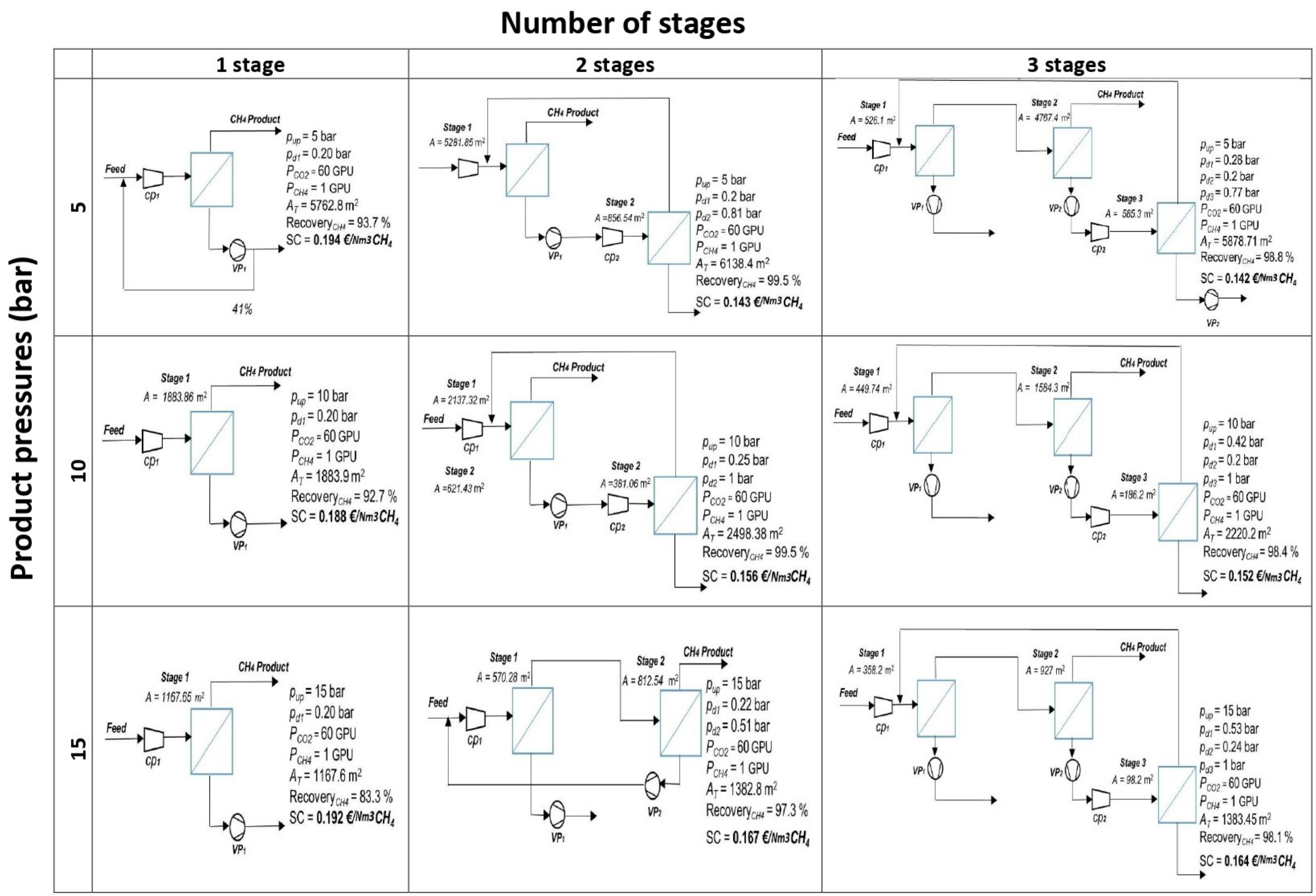


Figure 5: The best process configurations obtained with polyimide membrane for up to three membrane stages and different levels of product pressure

3.2. Biogas purification by high performance inorganic zeolite membrane

In the last part of the study, an inorganic zeolite membrane, showing breakthrough gas separation performances (beyond the Robeson upper bound. Figure 2b) is investigated.

The optimal process configurations with up to three stages and three outlet pressure levels are shown in figure 6.

Globally speaking, the trends obtained with CA and PI are similar: purification costs decrease with the number of stages, a large improvement is obtained between one and two stages, a small cost improvement is obtained with three stages compared to two. Increased outlet pressure levels increase the purification costs. Extra compression and/or expander are not useful. Two stages configurations make use of one recycling loop, while three stages make use of two.

But, the most significant result of the zeolite membrane use is the large decrease in purification cost compared to CA and PI. The key question of the balance between high performances at the expense of a high cost is thus answered. Other aspects and limitations of zeolite membranes obviously have to be taken into account (few suppliers, lower compacity, mechanical resistance, sensitivity to water...). Coming back to the questions indicated in the introductory part, it can be stated that high performance zeolite membranes offer very attractive potentialities for biogas upgrading applications; the optimal process design are similar to PI processes. The very high permeance logically generates impressive decrease of the membrane surface area, while the high selectivity improves the energy efficiency.

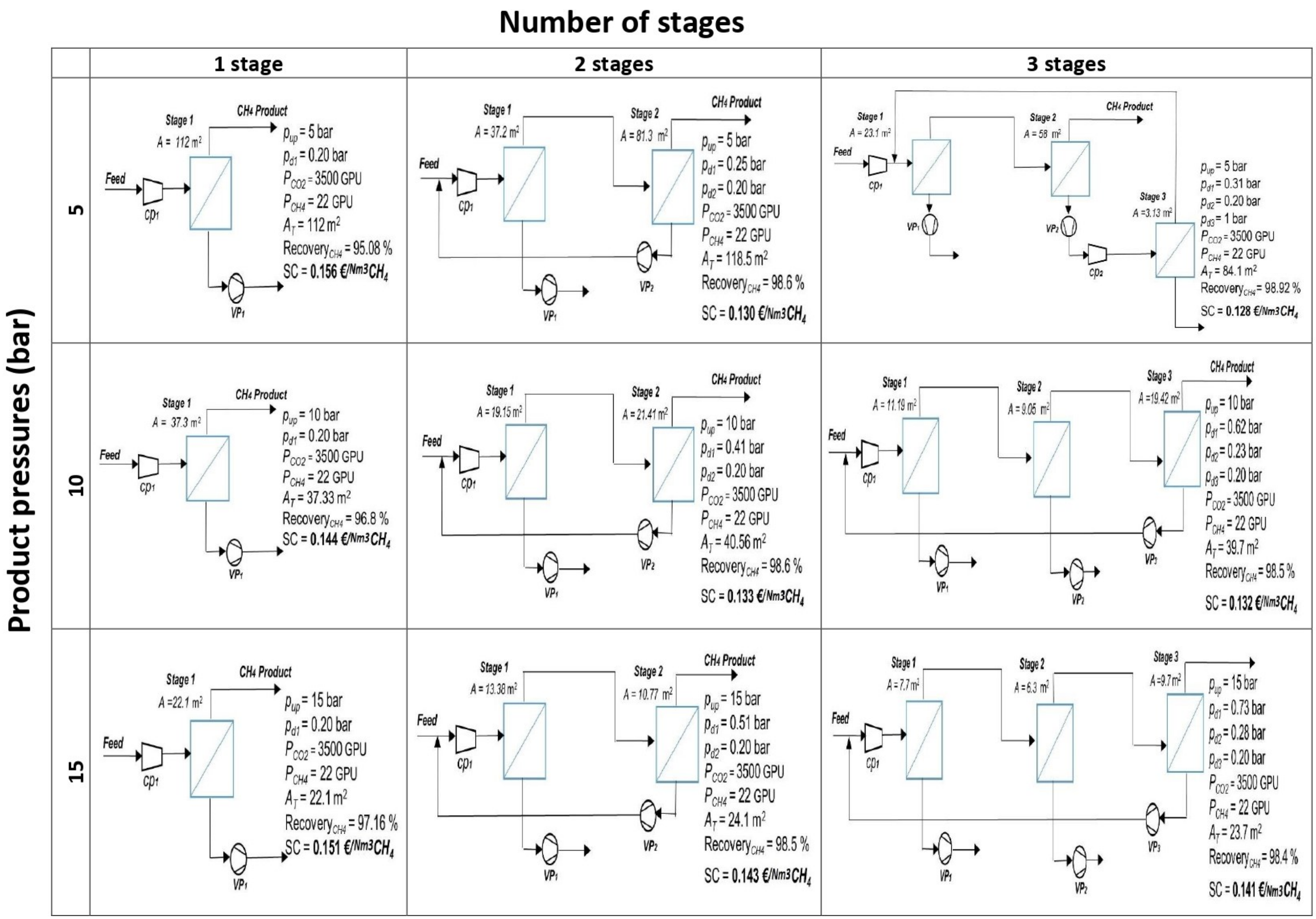


Figure 6: The best process configurations obtained with zeolite membrane for up to three membrane stages and different levels of product pressure

Figure 7 displays the overall separation cost of the optimal process configurations presented in the Figures 5, 4 and 6 regards to the range of the target product pressures for process with one, two and three stages. Figure 7 shows that although the separation cost of a single stage process with all of mentioned membranes is dramatically more than two and three stages process, the separation cost of two and three stages process are quiet close.

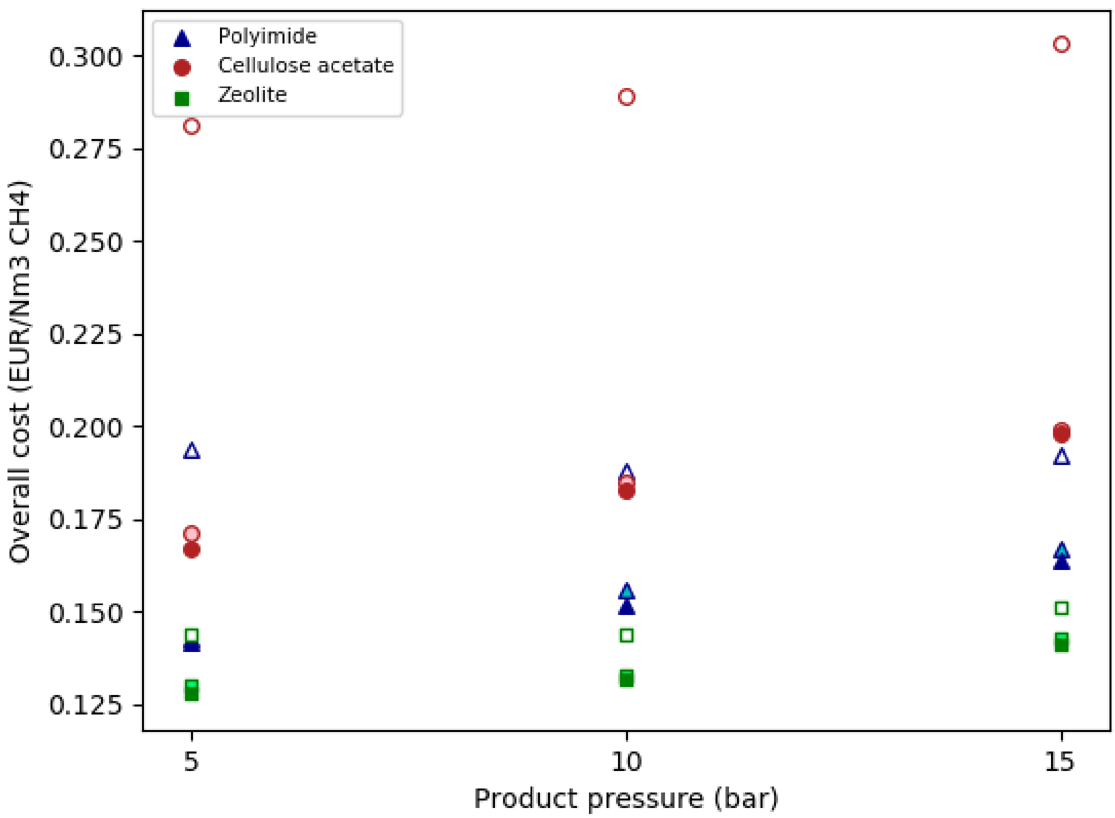


Figure 7: Overall separation cost vs product pressure for the optimal configurations obtained with different membranes. Open, light and dark symbols correspond to one, two and three stages processes respectively.

Minimal biogas purification costs as a function of a target product pressure are presented for the three different membranes and different number of stages in Figure 8. The benefits of PI vs CA and zeolite vs polymeric membrane materials is clear. The very small difference between two and three stages, whatever the membrane type is also noticeable.

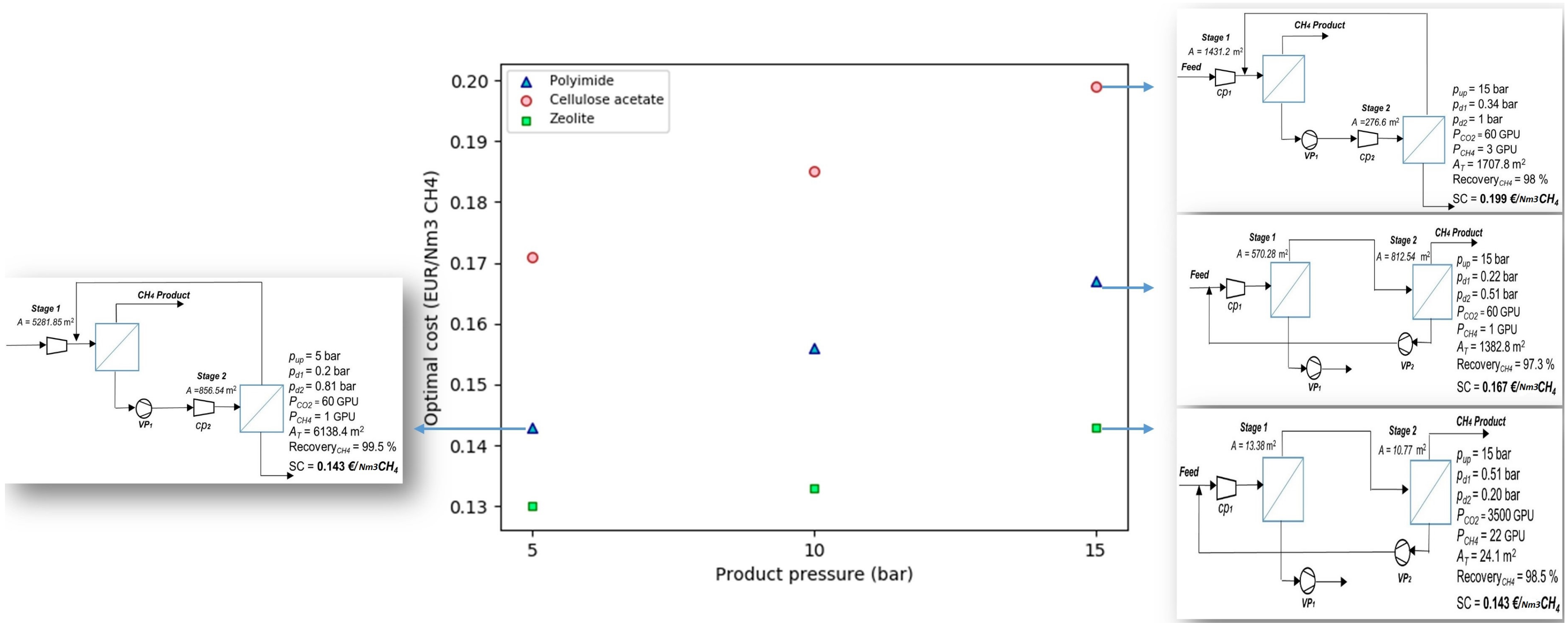


Figure 8: Minimal separation cost vs outlet product pressure for the different optimal two stages configurations obtained with the three different membranes.

3.3. Synopsis

A synopsis of the process configuration results generated through the process synthesis study is shown in Table 6. Taking the 2 stages optimal solution as the best balance between efficiency, cost and complexity, it can be seen that only two types of configurations are finally obtained. Interestingly, these two configurations, namely retentate recycle (left side of Figure 8) and permeate recycle (right side of Figure 8) have been already used by previous authors for biogas purification process studies. The retentate recycle option has been used for technico-economical studies [10] or process design studies [28, 29]. Alternatively, some authors only explore the performances of the permeate recycle configuration, either with 2 stages [11] or 3 stages [12, 30].

A larger outlet pressure generates a larger cost, which is significantly decreased with a zeolite membrane; in that latter case, the very high permeance of the membrane largely decreases the membrane surface area. The OPEX/CAPEX share ratio is roughly the same, whatever the membrane type and outlet pressure. The energy efficiency is in the range reported for membrane biogas upgrading units (Table 1).

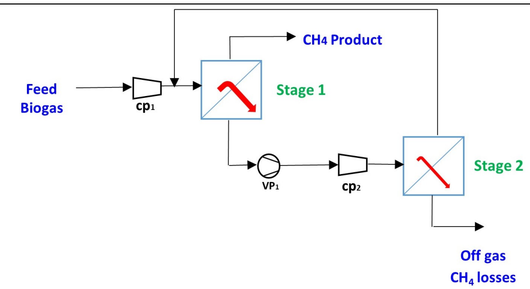
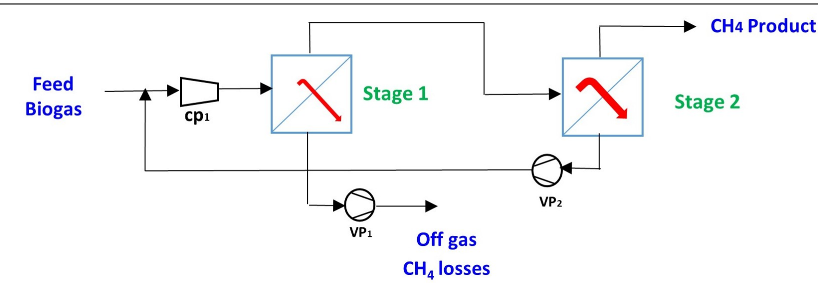
Table 6: Summary of the best process configurations for biogas purification with polymer membrane (PI) and inorganic membrane (Zeolite).

	Plyimide membrane (PI)			Zeolite membrane		
Target product pressure (bar)	5	10	15	5	10	15
Number of stages	2	2	2	2	2	2
Process configuration	Retentate Recycle	Retentate Recycle	Permeate Recycle	Permeate Recycle	Permeate Recycle	Permeate Recycle
Overall cost (EUR/ Nm^3CH_4)	0.143	0.156	0.167	0.130	0.133	0.143
CAPEX(%)	81.7	81.8	82.5	77.9	80.1	81.8
OPEX(%)	18.3	18.2	17.5	22.1	19.9	18.9
Biomethane purity(%)	98	98	98	98	98	98
Biomethane recovery(%)	99.5	99.5	97.3	98.6	98.6	98.5
Overall membrane surface area(m^2)	6138.4	2498.4	1382.8	118.5	40.56	24.1
Stage cut	0.39	0.39	0.40	0.39	0.40	0.40
Energy efficiency (kWh/Nm^3)	0.27	0.29	0.33	0.21	0.26	0.30

The results summarized in Table 6 address a key question concerning the set of conditions which lead to either the retentate or permeate recycle option for a two stage process. To our knowledge, no systematic explanation of the criteria which induce the selection of one or the other of these two possibilities is available. Table 6 suggests that for a highly selective membrane and/or a high pressure, the permeate recycle configuration is the best choice.

We report in Table 7 a qualitative analysis of the conditions which will make one or the other of these two possibilities the best option. The key indicator is the extent of methane losses on the permeate outlet in the first stage. For a low selectivity membrane material, and/or low pressure difference, and/or high stage cut, the methane losses will be important [13]and it is logical to recover the permeate stream of the first stage and recycle the methane from the retentate of the second stage. On the contrary, for a very selective membrane, and/or a high pressure difference, and/or a low stage cut, methane losses in the first stage will be low. In that case, it is more interesting to further increase the methane purity in a second stage, and recover the methane losses from the permeate of the second stage.

Table 7: Analyzing the optimal process results of polymer and zeolite membranes in biogas upgrading. Red arrow corresponds to methane flux. A low selectivity membrane will generate a larger methane flux in the first stage, compared to a high selectivity membrane. This impacts the optimal process design.

Materials: Membrane selectivity	Low	High
Driving force: Transmembrane Pressure	Low	High
Productivity: Stage cut	High	Low
Process type	Low process selectivity of the first stage (Methane permeate flux maximal in first stage)	High process selectivity of the first stage (Methane permeate flux minimal in first stage)
Optimal configuration (2 stages example)	First stage permeate recovery and second stage retentate recycle to feed	Second stage permeate recycle to feed
		
Equipment	2 compressors 1 vacuum pump	1 compressor 2 vacuum pumps
Examples	Low selectivity (e.g. CA) membrane and/or low transmembrane pressure (Biogas)	High selectivity (e.g. PI, zeolite) membrane and/or high transmembrane pressure (natural gas)
References	[10, 28, 29]	[11, 12, 28, 30]

4. Conclusions and perspectives

The objective of this study was to investigate the impact of high performance membrane materials, extended equipment and process connection possibilities and outlet pressure levels on biogas purification costs.

The results can be summarized as follows:

- A high performance, very expensive (e.g. 2000 EUR per square meter) membrane material offers promising perspectives in terms of biogas purification cost. This result confirms the attractively of high performance, costly materials, such as generally suggested by Baker, for the specific case of biogas purification. It can be linked to the fact that for membrane gas separations, capital expenses are by far dominated by compressor costs, while membrane cost have a limited impact. In terms of materials performances, the interest of increased selectivity can be seen from the comparison between cellulose acetate and polyimide; the interest of both improved selectivity and permeance is shown by the zeolite membrane decreased costs.

- Optimal process designs are only slightly affected by membrane performances. Generally speaking, a two stages process with either a retentate or permeate recycling loop is expected to offer the best balance in terms of purity / recovery / process complexity and cost. This conclusion corroborates heuristics in CO_2/CH_4 membrane separation processes, such as classically used for natural gas treatment. It also shows that such a design is robust, whatever the membrane type or outlet pressure level.

- An increased outlet pressure logically generates higher purification costs; extra compression (i.e. feed compression above the outlet pressure level) or an expander do not improve the process economy

- Vacuum pumping is systematically applied for optimal process, whatever the outlet pressure level and number of stages. A moderate vacuum pumping is obtained through optimization (typically 0.2 to 0.5 Bar). This result is noticeable and suggests a more detailed analysis and evaluation for this option. Vacuum pumping is indeed almost systematically discarded for membrane gas separations, because of leaks issues, low energy efficiency and large footprints. Carbon post combustion capture and Oxygen Enriched Air are exceptions for which vacuum pumping is suggested. To our knowledge, vacuum pumping has never been applied for biogas purification, neither investigated for process synthesis studies for this application.

Finally, this study could be extended to more complex systems such as multicomponent feeds (impact of water or nitrogen), multimembrane systems (is there any interest to combine different membranes into multistaged units?) or multitarget applications (e.g. combined biogas purification and carbon capture objective). A parametric sensitivity analysis would also be of interest in order to better evaluate the robustness of the process designs obtained in this study. The impact of feed composition (a different methane content, but also nitrogen content in the feed), of inorganic membrane cost or methane cost would certainly be of importance. It is important to note however that the two stages processes shown on Table 7 are used for a long time for biogas upgrading with polymeric membranes and they have been proven to be robust.

The improvements suggested by this study logically remain to be evaluated within a technological and industrial constrained context. For instance, the use of vacuum pumps cannot be accepted unless breakthrough cost savings are obtained and risk issues (i.e. oxygen in permeate due to leaks) are solved. Process complexity is also a problem and simple designs with minimal compressors, vacuum pumps, and connections will clearly be favored. We think however that the rigorous and exhaustive set of optimal process designs and operating conditions reported in this study will be of interest for decision makers in order to push the economy of biogas purification applications.

Nomenclature

Parameters:

A_T	Total area of the system[m^2]
i	Interest rate [%]
K_{el}	Electricity cost factor [EUR/kWh]
K_{er}	Exchange rate [EUR/USD]
K_{gp}	Upgraded biogas sales price [EUR/Nm^3]
K_m	Unit cost of membrane module [EUR/m^2]
K_{mf}	Base frame cost [EUR]
K_{mr}	Membrane replacement cost [EUR/m^2]
MDF_{exp}	Module factor for expander [$-$]
MF_C	Module factor for compressor [$-$]
MF_{exp}	Material factor for expander[$-$]
MPF_C	Material and pressure factor for compressor[$-$]
P_j	Permeance of component j [GPU]
R	Ideal gas constant [$JK^{-1}mol^{-1}$]
T	Temperature [K]
t_{op}	Operation time per year [h/year]
UF_{1968}	Update factor [Dimensionless]
UF_{2000}	Update factor [Dimensionless]
Z	Project lifetime [years]
γ	Gas expansion coefficient [Dimensionless]
η_c	Isentropic compressor efficiency [Dimensionless]
η_{vp}	Isentropic vacuum pump efficiency [Dimensionless]
θ	Stage cut [Dimensionless]
ν	Membrane annual replacement rate [Dimensionless]
ϕ	Mechanical efficiency [Dimensionless]

Optimization Variables:

A_s	Membrane surface area [m^2]
Feed	Feed gas flow rate [mol/s]
F^{Perm}	Permeate flowrate [mol/s]
F^{Ret}	Retentate flowrate [mol/s]
$f_s^{perm,out}$	Local permeate flowrate of membrane stage [mol/s]
f_s^{perm}	Total permeate flowrate of membrane [mol/s]
f_s^{prod}	Upgraded gas flowrate [mol/s]
P_{in}	Inlet stream pressure [bar]
P^{up}	Upstream pressure of all membrane stages [bar]
P_s^{down}	Downstream pressure of membrane stages [bar]
X_j^{Perm}	Fraction of component j into the system permeate [Dimensionless]
X_j^{Ret}	Fraction of component j into the system retentate [Dimensionless]

Other symbols:

APL	Annual product losses [EUR/year]
BPC	Base plant cost [EUR]
CAPEX	Capital expenditures [EUR]
CMC	Contract and material maintenance cost [EUR/year]
C_c	Compressor base cost [USD_{1968}]
C_{exp}	Expander base cost [EUR_{2000}]
C_{vp}	Vacuum pump cost factor [EUR/kW]
DL	Direct labor [EUR/year]
EC	Energy cost [EUR/year]
I_{c_f}	Feed Compressor investment cost [EUR]
I_{c_s}	Membrane Compressor investment cost [EUR]
I_{exp}	Gas expander investment cost [EUR]
I_{m_s}	Membrane surface investment cost [EUR]
I_{mf_s}	Membrane frame investment cost [EUR]
I_{vp_s}	Vacuum pump investment cost [EUR]
LOC	Labor overhead cost [EUR/year]
LTC	Local taxes and insurance [EUR/year]
MRC	Membrane replacement cost [EUR/year]
OPEX	Operational expenditures [EUR/year]
PC	Project contingency cost [EUR]
PFC	Process facilities capital [EUR]
SC_{CH_4}	Specific CH_4 separation cost [EUR/Nm^3 CH_4]
STC	Start − up cost [EUR]
TFI	Total facility investment [EUR]
TAC	Total annual costs [EUR/year]
W_{c_f}	Feed compressor energy consumption [kW]
$W_{c_{prod}}$	Upgraded gas compressor energy consumption [kW]
W_{cp_s}	Permeate compressor energy consumption of membrane s [kW]
W_{exp}	Expander energy production [kW]
W_{tot}	Total energy consumption [kW]
W_{vp_s}	Vacuum pump energy consumption of membrane s [kW]

Appendix A.

Table A.8: Comparison of commercial biogas upgrading technologies. [1–7]

	Water scrubbing	Physical organic scrubbing	Chemical absorption	Pressure swing adsorption	Cryogenic separation	Membrane separation
CH_4(%) in upgraded gas	95-98[6]; >97[3]; >98[7]; 90-99[2]	>96, <93-98[6]; >97[3]	>98[6, 7]; >99[2, 3]	>96-98[6]; 95-99[3]; 97[7]	99[6]; 98[3]; 99.9[2]	90-92,96[6]; >98[1, 7]
CH_4 recovery (%)	>98[3, 5]; 96-98[1]; 98[7]; 98-99.5[2]	>97[5]; 96-98[1];	>99[5]; 96-99[1]; 98-99[7]	95-98[5]; 96-98[1];	90-98[5]; 97-98[1];	>96[5]; 96-98[1]; 98-99.5[7]
Removed elements	CO_2, H_2S, COV	CO_2, H_2S, NH_3, HCN, H_2O	CO_2, H_2S, COV	CO_2, COV, O_2, N_2	CO_2, H_2S, O_2, N_2	CO_2, H_2S, COV, O_2, H_2O
Energy consumption (kWh/Nm3 upgraded)	0.2-0.5[6]; 0.4-0.5[5]; 0.3-0.9[1]; 0.24-0.4*[7]; 0.2-0.3*[2]	0.10-0.33[6]; 0.21[5]; 0.4[1]; 0.23-0.33*[2]	0.05-0.25[1, 5, 6]; 0.56-0.7*[7]; 0.06-0.17*[2]	0.16-0.43[6]; 0.23-0.30[1]; 0.23-0.4*[7]; 0.15-0.35*[2]	0.2-0.79[6]; 0.76[1];	0.18-0.35[6]; 0.22[5]; 0.18-0.20[1]; 0.2-0.3*[7]; 0.18-0.33*[2]
Upgrading cost	Inexpensive[6]; Expensive[5]; Medium[1]; High[3]; Medium[7]	Expensive[3, 5, 6]; Medium[1];	High[1, 3, 6, 7]; Expensive[5];	Relatively inexpensive[6]; Expensive[5]; Medium[1]; High[3, 7]	Expensive[5, 6]; High[1, 3];	Expensive[6]; High[1]; Low[3, 7]
Main advantages	No chemicals, scalable, easy operation	Co-removal of impurities, low CH_4 losses, smaller footprint	High CH_4 purity, very low CH_4 losses, low power requirement	No chemicals, scalable, compact	High CH_4 purity, very low CH_4 losses, no chemicals	No chemicals, scalable, easy operation
Main drawbacks	Water demand, bacterial clogging, H_2S related corrosion	Difficult operation, heat required, solvent handling	High investment, Heat required for regeneration, solvent handling	High CH_4 losses, valve operation control, fouling by biogas impurities	High investment, high energy consumption, low temperature operation	Energy consumption can be high, membrane fouling

*per Nm^3 raw biogas

Appendix B. Energy consumption calculations:

Equation B.1 implies the power required for compressing the fresh Feed. Note that if the upstream pressure of a membrane is equal to the fresh Feed pressure, $\mathrm{W_{cp_f}}$ equals to zero.

$$\mathrm{W_{cp_f}} = \frac{\mathrm{Feed} \times 10^{-3}}{\eta_\mathrm{c}} \cdot \frac{\gamma \cdot \mathrm{R} \cdot \mathrm{T}}{\gamma - 1} \cdot [(\frac{\mathrm{P^{up}}}{\mathrm{P_{in}}})^{\frac{(\gamma-1)}{\gamma}} - 1] \tag{B.1}$$

Equation B.2 implies the power required for compressing the permeate stream of stage s that does not go out of the system (enters to another stage in the system). It assumed that the compressor is preceded by a vacuum pump so, P_{in} equals to 1 bar.

$$\mathrm{W_{cp_s}} = \frac{(\mathrm{f_s^{perm}} - \mathrm{f_s^{perm,out}}) \times 10^{-3}}{\eta_\mathrm{c}} \cdot \frac{\gamma \cdot \mathrm{R} \cdot \mathrm{T}}{\gamma - 1} \cdot [(\frac{\mathrm{P^{up}}}{\mathrm{P_{in}}})^{\frac{(\gamma-1)}{\gamma}} - 1] \tag{B.2}$$

Equation B.3 implies the vacuum pump energy consumption. Vacuum pump is used for the permeate stream of each stage "s" to increase the driving force in the system. For a membrane s, if the down stream pressure be equal to the atmospheric pressure, then this term equals to zero.

$$\mathrm{W_{vp_s}} = \frac{\mathrm{f_s^{perm}} \times 10^{-3}}{\eta_\mathrm{vp}} \cdot \frac{\gamma \cdot \mathrm{R} \cdot \mathrm{T}}{\gamma - 1} \cdot [(\frac{\mathrm{P_{in}}}{\mathrm{P_s^{down}}})^{\frac{(\gamma-1)}{\gamma}} - 1] \tag{B.3}$$

where equation B.4 presents η_{vp}. Pdown stands for the permeate vacuum level and Pin for the vacuum pump outlet pressure. A decreasing efficiency is thus obtained for a decreasing permeate pressure.

$$\eta_\mathrm{vp} = 0.1058 \cdot \ln(\frac{\mathrm{P_s^{down}}}{\mathrm{P_{in}}}) + 0.8746 \tag{B.4}$$

There is the possibility of using compressor or expander for the product stream to achieve a product with specific pressure. Equations B.5 and B.6 imply compressor and expander energy consumption required for the product stream respectively. If the upstream pressure is greater than the product pressure, we would use expander to obtain the determined target and vice versa. Therefore, the absolute value of the W_{exp} has been considered because the W_{exp} becomes negative based on B.6 equation.

$$\mathrm{W_{cp_{prod}}} = \frac{\mathrm{F^{Ret}} \times 10^{-3}}{\eta_\mathrm{c}} \cdot \frac{\gamma \cdot \mathrm{R} \cdot \mathrm{T}}{\gamma - 1} \cdot [(\frac{\mathrm{P^{prod}}}{\mathrm{P^{up}}})^{\frac{(\gamma-1)}{\gamma}} - 1] \tag{B.5}$$

$$\mathrm{W_{exp}} = \left| \frac{\mathrm{F^{Ret}} \times 10^{-3}}{\eta_\mathrm{c}} \cdot \frac{\gamma \cdot \mathrm{R} \cdot \mathrm{T}}{\gamma - 1} \cdot [(\frac{\mathrm{P^{prod}}}{\mathrm{P^{up}}})^{\frac{(\gamma-1)}{\gamma}} - 1] \right| \tag{B.6}$$

Finally, the total power consumption of the system is the sum of the total compressing power ($\mathrm{W_{cp_s}}$ for each stage and $\mathrm{W_{cpf}}$ for the feed), the total vacuum pump power ($\mathrm{W_{vp_s}}$ for each stage) and product compressing if the product compressor used or subtraction of the expander power if the expander used in the system divided by the mechanical efficiency ϕ:

$$\mathrm{W_{tot}} = \frac{\mathrm{W_{cp_f}} + \mathrm{W_{cp_{prod}}} + \sum_{\mathrm{s} \in \mathcal{S}} (\mathrm{W_{cp_s}} + \mathrm{W_{vp_s}})}{\phi}, \qquad \text{Using compressor for } F^{Prod} \tag{B.7}$$

$$\mathrm{W_{tot}} = \frac{\mathrm{W_{cp_f}} + \sum_{\mathrm{s}\in\mathcal{S}}(\mathrm{W_{cp_s}} + \mathrm{W_{vp_s}})}{\phi} - \phi \cdot \mathrm{W_{exp}}, \qquad \text{Using expander for } F^{Prod} \tag{B.8}$$

References:

[1] I. Angelidaki, L. Treu, P. Tsapekos, G. Luo, S. Campanaro, H. Wenzel, P. G. Kougias, Biogas upgrading and utilization: Current status and perspectives, Biotechnology Advances 36 (2018) 452–466.

[2] D. Wilken, F. Strippel, H. F., et al., Biogas to biomethane. Biogas Know-how 3, Fachverband Biogas e.V., 2017.

[3] I. Ullah Khan, M. H. D. Othman, H. Hashim, T. Matsuura, A. F. Ismail, M. Rezaei-DashtArzhandi, I. Wan Azeele, Biogas as a renewable energy fuel- a review of biogas upgrading, utilisation and storage, Energy Conversion and Management 150 (2017) 277–294.

[4] M. Miltner, A. Makaruk, M. Harasek, Review on available biogas upgrading technologies and innovations towards advanced solutions, Journal of Cleaner Production 161 (2017) 1329–1337.

[5] O. W. Awe, Y. Zhao, A. Nzihou, D. P. Minh, N. Lyczko, A review of biogas utilisation, purification and upgrading technologies, Waste and Biomass Valorization 8 (2017) 267–283.

[6] R. Kapoor, P. Ghosh, M. Kumar, V. K. Vijay, Evaluation of biogas upgrading technologies and future perspectives: a review, Environmental Science and Pollution Research 26 (2019) 11631–11661.

[7] Y. Rouaud, From biogas to biomethane. air liquide sales presentation for biogas upgrading solutions. sassenage, 11/04/2013., 2013.

[8] F. Bauer, C. Hulteberg, T. Persson, D. Tamm, Biogas upgrading-review of commercial technologies. sgc rapport 2013:270., 2013.

[9] R. W. Baker, Membrane technology and applications, John Wiley & Sons, 2012.

[10] S. Haider, A. Lindbråthen, M.-B. Hägg, Techno-economical evaluation of membrane based biogas upgrading system: A comparison between polymeric membrane and carbon membrane technology, Green Energy & Enviroment 1 (2016) 222–234.

[11] D. Havas, L. Haiqing, Optimal membranes for biogas upgrade by removing CO_2: High permeance or high selectivity?, Separation science and Technology 52 (2017) 186–196.

[12] M. Scholz, M. Alders, T. Lohaus, M. Wessling, Structural optimization of membrane-based biogas upgrading processes, Journal of Membrane Science 474 (2015) 1–10.

[13] R. W. Baker, B. T. Low, Gas separation membrane materials: a perspective, Macromolecules 47 (2014) 6999–7013.

[14] A. A. Ramirez-Santos, M. Bozorg, B. Addis, V. Piccialli, C. Castel, E. Favre, Optimization of multistage membrane gas separation processes.Example of application to CO_2 capture from blast furnace gas, Journal of Membrane Science 566 (2018) 346–366.

[15] J. Gascon, F. Kapteijn, B. Zornoza, V. Sebastian, C. Casado, J. Coronas, Practical approach to zeolitic membranes and coatings: state of the art, opportunities, barriers, and future perspectives, Chemistry of Materials 24 (2012) 2829–2844.

[16] Y. Chen, Y. Zhang, C. Zhang, J. Jiang, X. Gu, Fabrication of high-flux SAPO-34 membrane on -al 2 o 3 four-channel hollow fibers for CO_2 capture from CH_4, Journal of CO_2 Utilization 18 (2017) 30–40.

[17] K. Kida, Y. Maeta, K. Yogo, Pure silica CHA-type zeolite membranes for dry and humidified CO_2/CH_4 mixtures separation, Separation and Purification Technology 197 (2018) 116–121.

[18] N. Kosinov, C. Auffret, C. Gücüyener, B. M. Szyja, J. Gascon, F. Kapteijn, E. J. Hensen, High flux high-silica ssz-13 membrane for co 2 separation, Journal of Materials Chemistry A 2 (2014) 13083–13092.

[19] C. Zhang, W. J. Koros, Ultraselective carbon molecular sieve membranes with tailored synergistic sorption selective properties, Advanced Materials 29 (2017) 1701631.

[20] W. J. Koros, C. Zhang, Materials for next-generation molecularly selective synthetic membranes, Nature materials 16 (2017) 289.

[21] Bozorg, M., Polymeric membrane materials for nitrogen production from air: A process synthesis study, Chemical Engineering Science 207 (2019) 1196–1213.

[22] L. M. Robeson, The upper bound revisited, Journal of Membrane Science 320 (2008) 390–400.

[23] J.A. Medrano, M.A. Llosa-Tanco, Upgrading biogas with novel composite carbon molecular sieve (ccms) membranes: Experimental and techno-economic assessment, CHEMICALoo Engineering Journal 394 (2020) 124957.

[24] A. Julbe, Studies in surface science and catalysis, in: INTRODUCTION TO ZEOLITE SCIENCE AND PRACTICE, 3rd edition, volume 168, Elsevier, 2007.

[25] S. Basu, A. L. Khan, A. Cano-Odena, C. Liu, I. F. Vankelecom, Membrane-based technologies for biogas separations, Chemical Society Reviews 39 (2010) 750–768.

[26] X. Y. Chen, H. Vinh-Thang, A. A. Ramirez, D. Rodrigue, S. Kaliaguine, Membrane gas separation technologies for biogas upgrading, Rsc Advances 5 (2015) 24399–24448.

[27] D. D. Iarikov, S. T. Oyama, Review of CO_2/CH_4 separation membranes, in: Membrane Science and Technology, volume 14, Elsevier, 2011, pp. 91–115.

[28] Y. Alcheikhhamdon, M. Hoorfar, Natural gas purification from acid gases using membranes: A review of the history, features, techno-commercial challenges, and process intensification of commercial membranes, Chemical Engineering and Processing-Process Intensification 120 (2017) 105–113.

[29] R. W. Baker, Future directions of membrane gas separation technology, Industrial & engineering chemistry research 41 (2002) 1393–1411.

[30] M. Ungerank, B. Goetz, M. Priske, H. Roegl, Processs for separation of gases, 2013.