Analysis of the techno-economic competitiveness of a three-stage membrane separation process for biogas upgrading using a biopolymer based mixed matrix membrane

Ricardo Abejón[1*], Andrea Torre-Celeizabal[2], Clara Casado-Coterillo[2], Aurora Garea[2]

[1]*Departamento de Ingeniería Química y Bioprocesos, Universidad de Santiago de Chile, Av. Libertador Bernardo O'Higgins 3363, Estación Central, Santiago 9170019, Chile*

[2]*Department of Chemical and Biomolecular Engineering, Universidad de Cantabria, Avda, Los Castros, s/n, 39005 Santander, Spain*

(*) Corresponding author: Ricardo Abejón (ricardo.abejon@usach.cl)

Abstract

Considering the transition to cleaner energy sources, the use of renewable energies and alternative fuels to replace fossil fuels is a goal for reducing greenhouse gas emissions. Biogas is a promising option to substitute natural gas, but adequate purification of the produced biogas is necessary (the CO_2 content of the raw biogas must be reduced). Membrane technologies have proven its technical viability to purify biogas until the defined requirements. Moreover, membranes based on biopolymers could reduce the environmental footprint of these purification processes. Nevertheless, due to the trade-off between purity and recovery, single-stage processes are not able to attain desired targets, so multiple stages are required to reach the desired high purities and recoveries at the outlet of the biogas purification system. The aim of this study is to advance in the use of biopolymer-based membranes for the separation of CO_2/CH_4 and evaluate the economic competitiveness of the designed multistage purification process. For this purpose, a chitosan composite membrane with organic (ionic liquid) and inorganic (titanosilicate) fillers in the selective layer was used to study the multistage configuration, considering CO_2 and CH_4 as both target products. The process configuration is based on three membrane units operating in series to enrich CO_2 in the product stream from the permeate line, while the retentates are collected from each stage and mixed to obtain a CH_4-rich stream in the retentate. The target objectives were purities and recoveries of ≥95% of CO_2 in the permeate outlet, and ≥97% of CH_4 in the retentate outlet stream of the multistage process. The stage-cut was the main decision variable. The economic evaluation of the proposed three-stage separation process was performed for different process scales, from small installations to large plants (100-1000 Nm^3 h^{-1} feed flowrate basis), operated with two different pressure ratios (8 and 16). Total specific costs and contributions of the different cost terms to fixed and operation costs were estimated. Operating costs were the largest contributor to total costs in all the scenarios studied. To highlight the total specific costs for the installations of 1000 Nm^3 h^{-1} capacity, the obtained total costs were 0.33 and 0.20 US \$ Nm^{-3} for the 8 and 16 pressure ratio values respectively. This latter cost was competitive when compared to the cost published in literature. Moreover, a sensitivity analysis was performed to evaluate the effects of increased specific costs of materials (membrane cost) and energy (electricity cost) on the total specific costs of the three-stage separation process.

Keywords:

CO2/CH4 separation, Biogas upgrading, Chitosan biopolymer, Mixed-matrix composite membrane, Process simulation, Multistage gas separation, Techno-economic analysis

1. Introduction

Fossil fuels, such as coal, oil, and natural gas, have played a pivotal role in driving global greenhouse gas emissions and they must be considered the most significant contribution to the ongoing challenge of global warming and climate change [1]. The combustion of fossil fuels is responsible for most CO_2 emissions. The burning of coal in power plants, fuels like gasoline and diesel in cars and other means of transport, and natural gas in heating systems release vast amounts of CO_2 into the atmosphere, trapping heat and causing average global temperatures to rise.

Recognizing the role of fossil fuels in global warming is essential for addressing the urgent need to reduce emissions, transition to cleaner energy sources, and take meaningful steps towards mitigating the impacts of climate change on a global scale [2]. Besides the development of policies that promote energy efficiency; carbon capture, utilization and storage; or sustainable land use to mitigate the consequences of CO_2 emissions, the transition to cleaner and more sustainable energy sources is a critical step to replace the use of fossil fuels and avoid CO_2 emissions [3].

This search for viable alternatives to fossil fuels has been intensified, focusing on two primary categories: renewable energies and alternative fuels [4]. Renewable energies, including solar, wind, and hydroelectric power, offer significant promise in transitioning away from fossil fuels. In tandem with renewable energies, alternative fuels are crucial in diversifying the energy matrix and reducing specifically the carbon footprint of the transportation sector [5,6]. One notable option is biofuels, derived from organic matter like crops, algae, and waste lignocellulosic materials. Bioethanol and biodiesel are the most widely used biofuels, offering compatibility with existing vehicles and infrastructure. Hydrogen, though still in the early stages of development, holds immense promise as a clean fuel when produced using renewable energy sources. Additionally, synthetic fuels, such as synthetic gasoline or diesel produced from captured carbon dioxide and renewable hydrogen, have gained attention as innovative replacements for fossil fuels.

Biogas is another energy resource that can be produced through the anaerobic digestion of organic materials, such as agricultural waste, food scraps or animal manure [7]. This process involves microorganisms breaking down these organic materials in the absence of oxygen, resulting in the release of biogas, which primarily consists of methane (CH_4) and carbon dioxide (CO_2). Biogas can be captured, cleaned, and used as a substitute for natural gas, making it a sustainable and environmentally friendly energy option on the transition to complete decarbonization of the energy supply.

2. Biogas upgrading: Background

One of the main advantages of using biogas to replace fossil fuels is its environmental sustainability [8]. Unlike natural gas, biogas is a low-carbon fuel. It is considered carbon-neutral because the CO_2 released when burning biogas is offset by the CO_2 absorbed during the growth of the organic materials used to produce it. This makes biogas a valuable tool in reducing net greenhouse gas emissions and mitigating climate change. Additionally, biogas production helps manage organic waste and reduces the environmental impact of landfilling or incinerating such materials. Biogas production not only generates energy but also reduces odors, lowers the risk of groundwater contamination, and minimizes methane emissions that would otherwise occur in landfills. Biomethane can be injected into existing natural gas pipelines, making it compatible with existing infrastructure.

Both raw biogas and natural gas require treatment to reduce the CO_2 content. Natural gas fields have very different CO_2 concentrations, ranging from almost CO_2-free wells in Siberia to unexploited examples with contents above 70% in Malaysia [9]. Nevertheless, the level of

CO_2 concentration in most commercial gas fields is below 20% [10]. The typical CO_2 concentration range in biogas is 30-40% [11], although the composition of raw biogas depends strongly on the nature of the substrate and the corresponding operation conditions. Before biogas utilization, it must be purified to remove CO_2 and other impurities, like H_2S, NH_3 and other organic minor compounds. Several reviews have revised all the available technologies for upgrading biogas [12–17], and membrane technology has been proved as a viable alternative. There are even some commercially available systems based on polyimide hollow fiber membranes to purify biogas, although they do not contemplate the simultaneous recovery of CO_2 yet [18].

The separation of CO_2 and CH_4 from biogas usually employs polymeric membranes that show large permeability for CO_2 while CH_4 is retained [19] as well as resistance to the presence of impurities that shorten membrane lifetime. Besides, for membrane separation to be competitive with more mature alternatives multiple stages are required to reach the desired high CH_4 purity and overcome the trade-off between the purity and recovery efficiency. Therefore, the study of multistage permeation and recycling steps, as well as hybrid systems, has been the focus of research to overcome the drawbacks of single-stage membrane separation [20–25].

Torre-Celeizabal et al.[26] reported a compilation of studies focusing on optimizing membrane processes for the CO_2/CH_4 pair separation in biogas upgrading, as well those involving carbon dioxide removal from natural gas, as a more mature field of application. The multistage designs and superstructures were solved using various mathematical tools based on custom-built membrane unit models, most of them linked or interfaced to different simulation and optimization commercial packages, as detailed elsewhere [26]. In addition to engineering toolboxes for process systems, combined approaches of materials and process design methods also offer a straightforward link between the membrane performance, optimal process structure, and cost. Those studies could be extended to more complex systems, including multicomponent feed compositions, multimembrane systems, or multitarget problems, such as combined biogas upgrading and carbon capture objectives [24,27–31]. Significant progress has also been made in the development of membrane materials specifically designed for the separation of CO_2/CH_4 mixtures from different sources, ranging from advanced polymers, such as thermally rearranged polymers and of intrinsic microporosity to metal-organic frameworks, carbon, silica and zeolite types, and more recently, biopolymers [32,33]. Biopolymer-based membranes evaluated for biogas upgrading include micro- and nano-cellulose [34], PVA blends in nanocomposite membranes [20], poly-lactic acid (PLA)-based membranes [33,35], and chitosan (CS)-based membranes and the formulation as mixed matrix membranes (MMMs) [36–40]. These biopolymer-based MMMs seem sustainable alternatives for CO_2/CH_4 separation, pending mature development for its further implementation.

Therefore, the aim of the present work is to contribute to the evaluation of biopolymer-based membranes for the separation of CO_2/CH_4, with a techno-economic analysis employing simulation and optimization tools, to evaluate the competitiveness of a multistage configuration that provides high quality CO_2 and CH_4 as both target products. The analysis pays attention to the corresponding costs and energy consumption terms related to different plant capacities and operation conditions.

3. Description of the membrane separation system

3.1. Membrane unit

Regarding to the membrane material, a biopolymer-based composite membrane, identified as 5 wt.% ETS-10/ILCS/PES, was selected from previous studies that covered the synthesis, characterization and performance evaluation of different ionic liquid-chitosan-mixed-matrix composite membranes. The 5 wt.% ETS-10/ILCS coated membrane was selected considering the total membrane area required to carry out the target separation for CO_2/CH_4, as validated with experimental laboratory separation data [37] ETS-10/ILCS mixed matrix membranes had previously been studied for the separation of CO_2/N_2, which are important in the context of post-combustion CO_2 capture systems, obtaining experimental data on membrane composition, and solubility, diffusivity and permeability [41]. The solution-diffusion model has been used to describe the mechanism of transport of components across the membrane.

Each membrane unit was represented as a crossflow membrane model based on a cell-in-series assumption, where the membrane unit was divided into 100 equal-sized cells, to solve the steady-state material balances and transport equations, being detailed in previous studies [36,37]. The separation performance was defined by the purity and recovery of each component at the outlet stream of each membrane unit, taking CO_2 and CH_4 as key components in the permeate and retentate streams, respectively.

The simulation of the membrane unit required (i) the determined parameters of the membrane performance behaviour, and (ii) the process operation variables that included the pressure ratio and the stage-cut (as the ratio of the permeate and feed flowrates), to calculate the product streams and the required membrane area. The corresponding parameters of the selected membrane, 5 wt.% ETS-10/ILCS/PES, were given as CO_2 permeance, value of 3.4 10^{-3} m^2 STP m^{-2} h^{-1} bar^{-1}, a selectivity and a separation factor of 20 for the pair CO_2/CH_4. The pressure ratios considered in this study were set to 8 and 16 (as p/p_o 4:0.5 and 8:0.5 on bar basis respectively). In the case of setting product targets, the stage-cut was the decision variable, being considered the range 0.05-0.95.

3.2. Multistage process configuration

A multistage process was configured as three-stage membrane units operating in series on the permeate line to produce a CO_2-enriched product stream as the outlet permeate stream from the third stage. The process outlet on the retentate line was a CH_4-enriched stream, obtained from mixing the retentate streams of every stage. Intermediate compressors (and the associated heat exchangers) were included in the permeate line to set the feed pressure (and temperature) at the inlet of each membrane unit, specifying a pressure ratio for operation. The options of using a compressor to adjust the feed pressure to process, and an expander for the CH_4-enriched product stream was also considered for estimating the total processing costs. Schematic flowsheets of the three-stage separation process were provided in the following section with the results of the techno-economic analysis.

The targets considered in this study, with the stage-cut operating at each stage as decision variable, were the products quality in the process outlet streams, expressed in terms of purity and recovery of components, values $\geq$ 95% related to CO_2 in the permeate line and $\geq$97% for CH_4 in the retentate line (calculated the recovery ratios referred to the process feed stream). A feed composition of 35:65 (v/v) % CO_2:CH_4 was taken as reference of biogas. Other impurities present in raw biogas, like H_2S, NH_3 and organic compounds, were not taken into consideration. Although they may affect the performance and stability of membranes as well as the quality of the final gas streams, a preliminary study did not offer significant influences on chitosan-based composite membranes due to the high hydrophilicity resistance of these membranes. Nevertheless, further work taking into account the impurities will be carried out in a future work. Plant capacities in the range of 100-1000 Nm^3 h^{-1} were considered, to include the necessities of biogas upgrading from small plants associated to agricultural activities, to larger industrial plants.

The three-stage process was formulated as a custom-built programming of a nonlinear problem, using GAMS as the mathematical tool for the process simulation and optimisation to targets. GAMS was the first software system to combine the language of mathematical algebra with traditional programming concepts to efficiently describe and solve optimization problems and is one of the leading commercial tools for optimization [42,43].

The formulation in mathematical terms (eq.1) aimed to maximize the product quality at the process outlet with the objective function $f(x)$ defined as the sum of purity and recovery of the components from the feed stream, subject to equality constraints $h_m(x)$ such as the material balances, separation process design equations, cost equations and correlations used in the economic analysis; as well as inequality constraints $g_n(x)$ to specify the lower and upper bound of operational variables. The formulation of this optimisation problem followed the procedure detailed in a previous study [25]. T he resulted NLP problem was solved in GAMS employing the CONOPT3 solver.

$$\max f(x) \tag{1}$$

$$\text{s.t. } h_m(x) = 0, \ \forall m$$

$$g_n(x) \leq 0, \ \forall n$$

$$x \in \mathrm{R}^n, X_L < x < X_U$$

The economic evaluation of the three-stage membrane separation process units was performed to estimate the total costs, the specific costs with respect to the feed to the separation process, the contribution of cost terms to fixed and to operational costs, and a sensitivity analysis related to the effects of increased specific costs of materials and energy, such as the membrane unitary cost and the electricity cost factor.

Calculations of specific upgrading costs reported in the literature is often presented either with respect to the product or the feed flowrate [44–46]; being used the feed flowrate for its basis in this study. The specific costs were then calculated as the ratio of total costs and the feed flowrate to the separation process.

Table 1 summarized the cost terms considered in the economic analysis of the proposed separation process. The equations for the cost terms and correlations used the Chemical Engineering Plant Cost Index (CEPCI), and those corresponding to the performance of the equipment were detailed elsewhere[25,47]. This economic model was also previously applied to membrane systems for gas separation [47,48]. Regarding the particular case of the equations that define the cost of equipment (compressors, heat exchangers and turbines), they were referenced to the included in Turton et al., Smith, and Towler and Sinnott books [49–51].

Table 1. Summary of costs equations and related terms considered for the economic analysis of the three-stage membrane separation process.

Cost equations		Related to terms
Total costs of the separation process		
$TC = CC + OC + LSC$	(2)	*- CC capital costs linked to the fixed costs (FC) corresponding to the investment in equipment (eq.4) project contingency, and start-up costs.* *- OC operating costs.* *- LSC cost of CH_4 loss in permeate at process outlet.*
Total specific costs, related to plant capacity		
$TC_{specific} = \frac{(CC+OC+LSC)}{Q_{Feed}\,OSF}$	(3)	*- TC total costs (eq.2).* *- Q_{Feed} feed flowrate to process, here as $Nm^3\ y^{-1}$.* *- OSF on-stream factor of operation time.*
Fixed costs, as investment in equipment		
$FC = MEC + TUC + HEC + COC$	(4)	*- MEC membrane modules costs, as a function of total membrane area required and membrane unitary cost.* *- TUC turbine cost, correlated to work.*

	- HEC heat exchangers costs, correlated to HE area. *- COC compressors costs, correlated to work.*
Operation costs, mainly estimated from consumption of resources $OC = MRC + UC + LC + IC + MC$ (5)	*- MRC membrane replacement costs, as a function of total membrane area, unitary cost, and lifetime.* *- UC utilities costs, electricity and cooling water.* *- LC labour costs.* *- IC insurance costs, linked to CC.* *- MC maintenance costs, linked to CC.*

4. Results and discussion

The results of the simulation and optimization for producing high-purity CO_2 and CH_4 are presented below.

4.1. Process performance summary: a three-stage configuration

The process performance is summarized in Figure 1, showing the three-stage membrane unit configuration and the auxiliary equipment included for the economic evaluation. The calculations were performed for the selected 5 wt% ETS-10/ILCS based membrane, which exhibited the best performance after testing different biopolymer based MMMs. [26,37]

The component variables calculated at each stage are shown in the schemes in Figure 1 in terms of percentages values of (i) purity of CO_2 in the permeate line, and CH_4 in the retentate line (y.CO_2, y.CH_4), and (ii) recovery of each component in the permeate and retentate lines, related to its feed content to the separation process (R.CO_2, R.CH_4 values in the scheme).

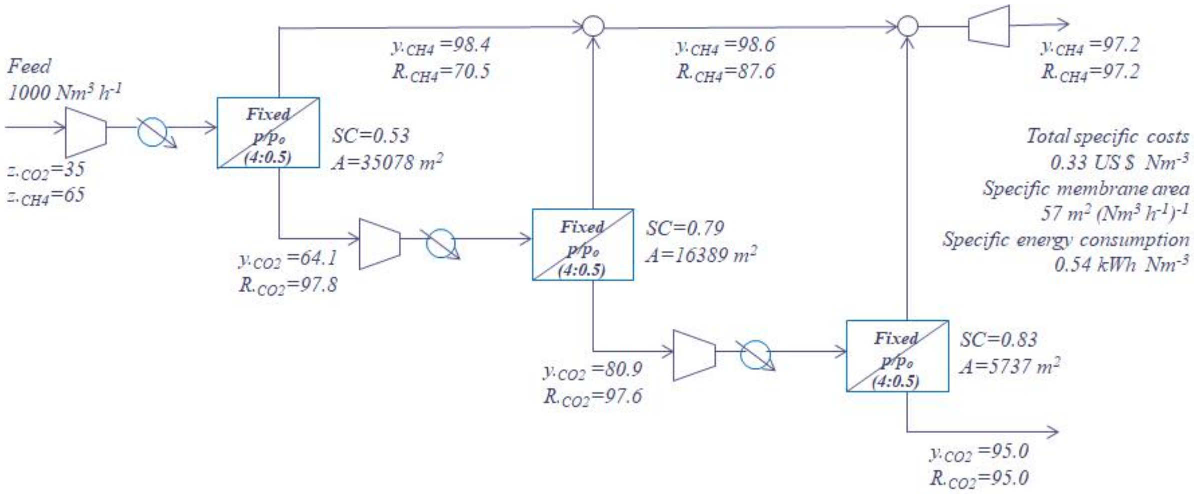
The three-stage separation scheme for producing both CH_4 and CO_2 to targets was evaluated at two operating pressure ratios: Figure 1 (a) the one validated experimentally at 4:0.5 and Figure 1(b) at 8:0.5. The comparison for two operating pressure ratios allows to quantify the effect of pressure ratio in the terms of total specific costs, specific membrane area requirement, as well as specific energy consumption, related to a plant capacity of 1000 $Nm^3\ h^{-1}$ feed volume flowrate basis and a feed composition fixed to a binary mixture comprising 35:65 % CO_2: CH_4, in the context of biogas upgrading.

The targets set at the process outlet were the values of purity and recovery $\geq$ 95% for CO_2 and $\geq$ 97% for CH_4, in the corresponding outlet lines, the three-stage separation processes shown in Figure 1 being required. The stage-cut values (SC) to operate each stage were determined to achieve these targets, observing that higher values were required as stages progressed. The results indicate that the targets of high product purity and simultaneous high recovery were achieved by adjusting the stage-cut as decision variable.

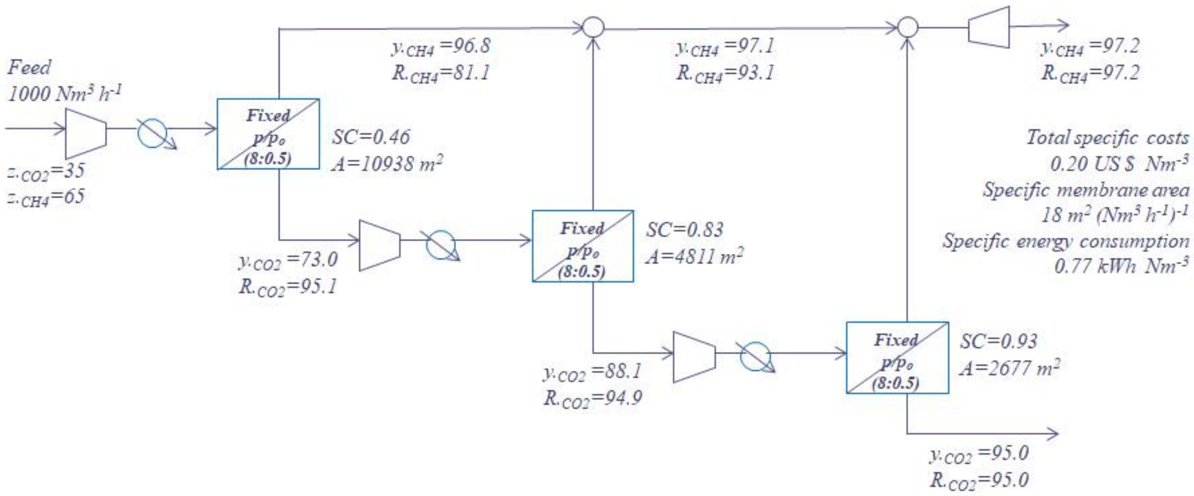
The calculated membrane area of the separation units (A, m^2) decreased as the stages progressed: there is a progressive reduction of the membrane area required in each consecutive stage. For instance, the system operating at pressure 8:0.5 represented in Figure 1b required 10938 m^2 in the first stage, 4811 m^2 in the second stage (56.0% reduction) and 2677 m^2 in the third stage (75.5% reduction). The total area requirements were also expressed in terms of the specific membrane area which is related to the feed flowrate of the process, units of $m^2\ (Nm^3\ h^{-1})^{-1}$, obtaining a significant reduction when operating to a higher pressure ratio, at the expense of greater energy consumption. The total membrane area was considered a key variable for the economic evaluation of the separation process, as it is used in the estimation of the membrane specific costs and the membrane replacement costs, affecting both fixed and operating costs. The contribution of the different terms to total process costs was detailed in the following section (4.2.) focused on the economic analysis.

The results obtained in this study positioned the 5%ETS-10/IL-CS/PES composite membrane in the same range of magnitude as commonly reported membranes in the context of biogas upgrading, such as cellulose acetate, polyimide-based membranes [22,24] and PVAm/PVA blend membranes [20], as reflected in Figure 2, considering multistage separation processes for a plant capacity of 1000 $Nm^3\ h^{-1}$. The trends of total specific costs per unit plant capacity for different scales from 100 to 1000 $Nm^3\ h^{-1}$, were also included in Figure 2, to cover the range from small biogas and biomethane production units, including agricultural applications, to higher plant capacities where the specific costs are lower.

The total specific costs were also calculated as the ratio of total costs to the feed flowrate to the separation process. The obtained values were 0.33 and 0.20 US \$ Nm^{-3}, for the installations operated with pressure ratios (a) 4:0.5, (b) 8:0.5, bar basis. The consideration of high-pressure ratios favoured the economic competitiveness of the process, since the reduction in the unitary total costs is around 40%. Therefore, the greater energy consumption derived from the operation at increased pressure ratio is compensated by the corresponding reduction of the required membrane area. Under these conditions, the specific costs were very similar to ones reported in literature [20,22,24], so the process designed to employ the biopolymer –based mixed matrix composite membrane can be considered competitive in both technical and economic terms.



(a)



(b)

Figure 1. Process performance results of a three-stage separation scheme for producing both CH_4 and CO_2 to targets, using the ETS-10/ILCS/PES composite membrane [37]. Comparison for two operating pressure ratios (a) 4:0.5 (b) 8:0.5, bar basis.

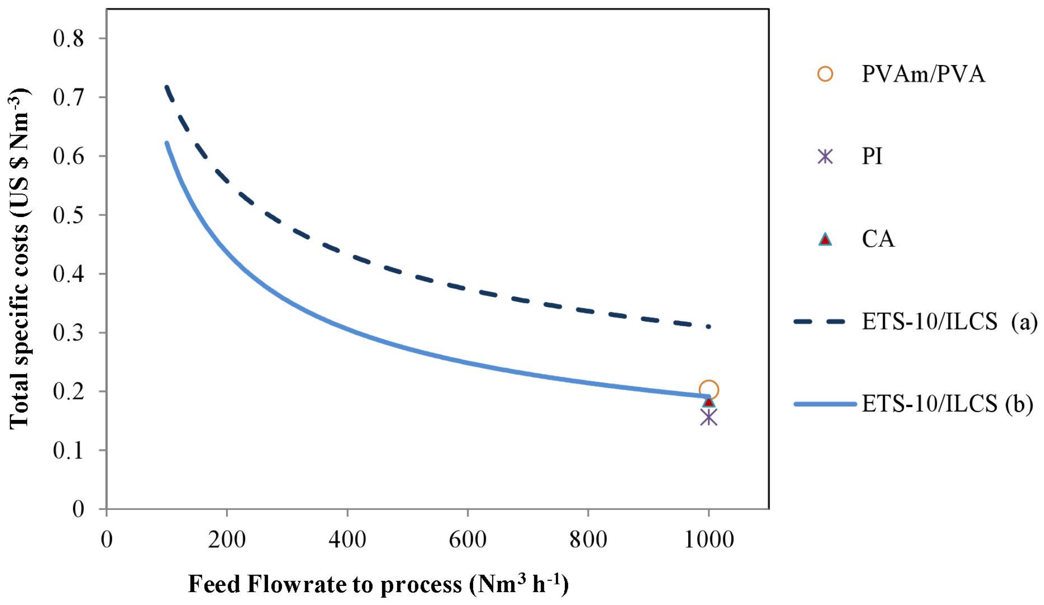


Figure 2. Trend of total specific costs per unit plant capacity, from 100 to 1000 $Nm^3\ h^{-1}$. Comparison for the two operating pressure ratios (a) 4:0.5 (b) 8:0.5, bar basis, using the ETS-10/ILCS membrane. References of other reported membranes, 1000 $Nm^3\ h^{-1}$ feed flowrate basis: PVAm/PVA blend [20], PI and CA [22,24]

4.2. Economic analysis: contribution of terms to total process costs

Two plant capacities were considered for the following analysis, 100 $Nm^3\ h^{-1}$ and 1000 $Nm^3\ h^{-1}$ feed volume flowrates, as representative of small installations related to agricultural, and a higher industrial installation scale for biogas upgrading. The comparison for the two operating pressure ratios is detailed, due to the implication of this operation variable in the energy consumption and required membrane area. These operating conditions are denoted as (a) 4:0.5, and (b) 8:0.5, bar basis. and correspond to pressure ratio values equal to 8 and 16, respectively. Similar pressure ratios have been reported in other case studies of biomethane production [52].

The contributions of the different cost terms to the total costs, the capital costs and operational costs are represented in Figures 3, 4 and 5 respectively, as percentage values relatives to the total corresponding costs. The compilation of the calculated costs was given in Table 2.

Table 2. Economic analysis: compilation of the calculated costs for the three-stage separation process using a 5 wt% ETS-10/ILCS/PES composite membrane.

Cost terms	**Plant capacities**			
	100 Nm^3 h^{-1}		**1000 Nm^3 h^{-1}**	
	(a)	***(b)***	***(a)***	***(b)***
Total costs of the separation process				
$TC = CC + OC + LSC$ *(US \$ y^{-1})*				
CC, capital costs	1.481 10^5	1.304 10^5	5.496 10^5	3.026 10^5
OC, operating costs	4.736 10^5	4.189 10^5	2.105 10^6	1.286 10^6
LSC, cost of CH_4 losses	1.234 10^4	1.234 10^4	1.234 10^5	1.234 10^5
Total specific costs, related to plant capacity				
$TC_{specific} = \frac{(CC+OC+LSC)}{Q_{Feed}\ OSF}$ *(US \$ Nm^{-3})*	0.754	0.668	0.330	0.204
Fixed costs, as investment in equipment				
$FC = MEC + TUC + HEC + COC$ *(US \$)*				
MEC, membrane units costs	6.158 10^5	2.043 10^5	5.720 10^6	1.843 10^6
TUC, turbine cost	8.027 10^5	8.045 10^5	8.454 10^5	8.633 10^5
HEC, heat exchangers costs	2.649 10^5	2.656 10^5	2.913 10^5	2.945 10^5
COC, compressor costs	5.560 10^5	5.843 10^5	9.937 10^5	1.259 10^6
Operation costs, mainly estimated from consumption of resources				
$OC = MRC + UC + LC + IC + MC$ *(US \$ y^{-1})*				
MRC, membrane replacement costs	1.539 10^5	5.108 10^4	1.430 10^6	4.607 10^5
UC, utilities costs	3.558 10^4	5.085 10^4	3.484 10^5	4.981 10^5
LC, labour costs	3.074 10^5	3.074 10^5	3.074 10^5	3.074 10^5
IC, insurance costs	2.220 10^3	1.956 10^3	8.243 10^3	4.538 10^3
MC, maintenance costs	7.402 10^3	6.519 10^3	2.748 10^4	1.513 10^4

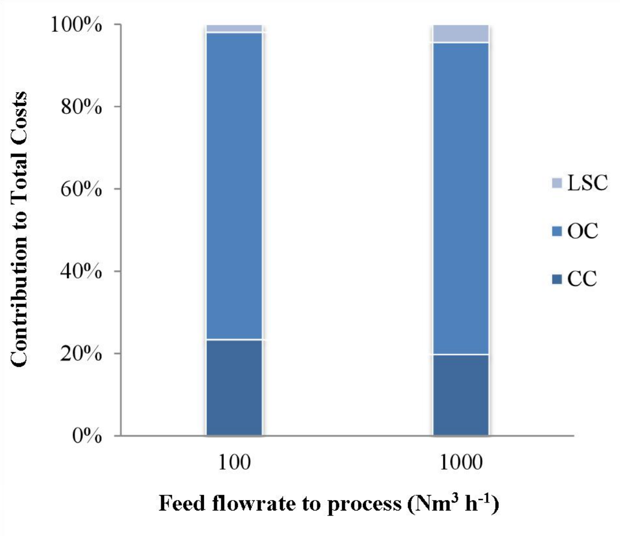
Pressure ratios, p/p_o, indicated as (a) 4:0.5, (b) 8:0.5, bar basis.

Some highlights can be summarized when the process scale is higher, from 100 to 1000 Nm^3 h^{-1} feed volume flowrate basis:

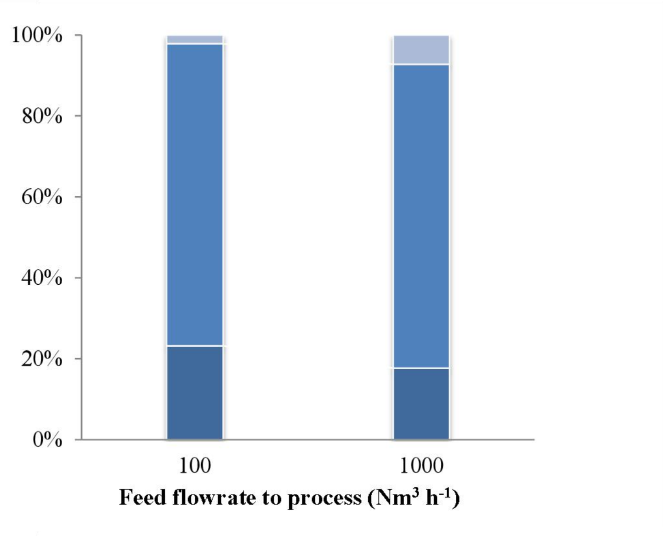
(i) Related to total costs terms, Figure 3, the capital costs (CC) contribution decreased, values 23-20 % (a), 23-18 % (b); while the costs accounting to methane losses (LSC) increased significantly, values 1.9-4.4 % (a), 2.2-7.2 % (b).

(ii) Concerning the fixed costs terms, Figure 4, the membrane units costs (MEC) increased significantly due to the higher membrane area requirements, values 27-73 % (a), 11-43 % (b); being remarked the contribution of the equipment related to compression (COC) for the case (b), up to 30 % of total fixed costs.

(iii) In regard to operational costs terms, Figure 5, the membrane replacement costs (MRC) increased significantly, also linked to the membrane area requirements, values 30-67 % (a), 12-36 % (b); pointing out the effect of the higher energy consumption in the utilities term (UC) when the pressure ratio was doubled, case (b), positioning the contribution of this term to 40% of the operational costs estimated for a 1000 Nm^3 h^{-1} plant capacity. From the cost estimation presented, it was considered relevant to analyse the implications of some costs of materials and energy, such as the membrane area that influences both fixed and operational terms, and the electricity cost factor to the utility's contribution in a more demanding case, being the focus of the following section.

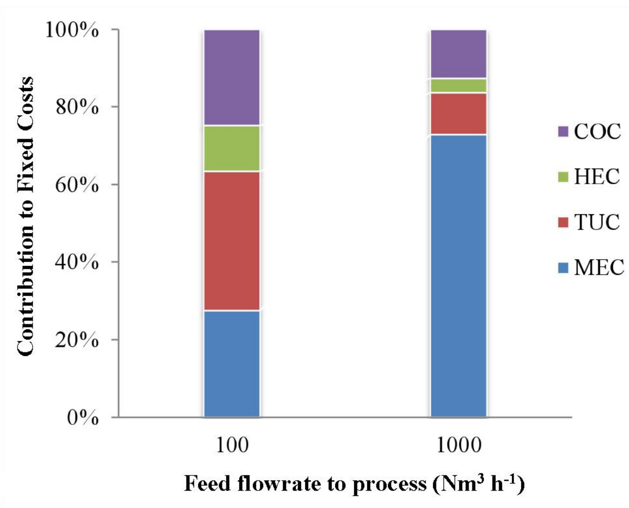


(a)

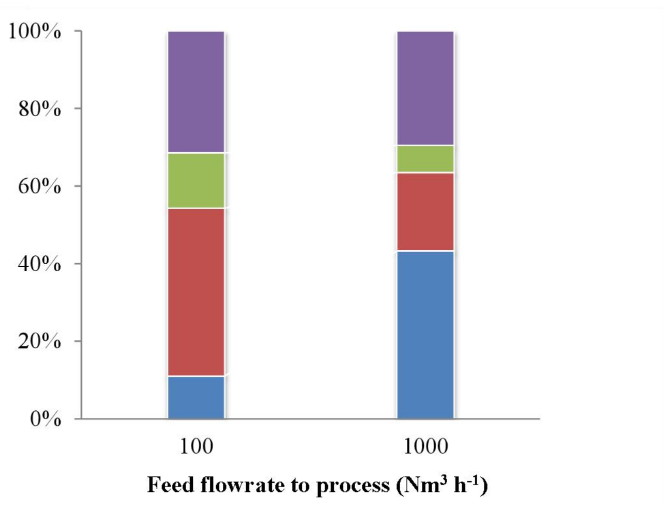


(b)

Figure 3. Contribution of terms in total costs (TC): capital costs (CC), operating costs (OC), and cost of losses for CH_4 (LSC). Plant capacities of 100 and 1000 ($Nm^3\ h^{-1}$) feed flowrate basis, operating at two pressure ratios (a) 4:0.5 (b) 8:0.5, bar basis.

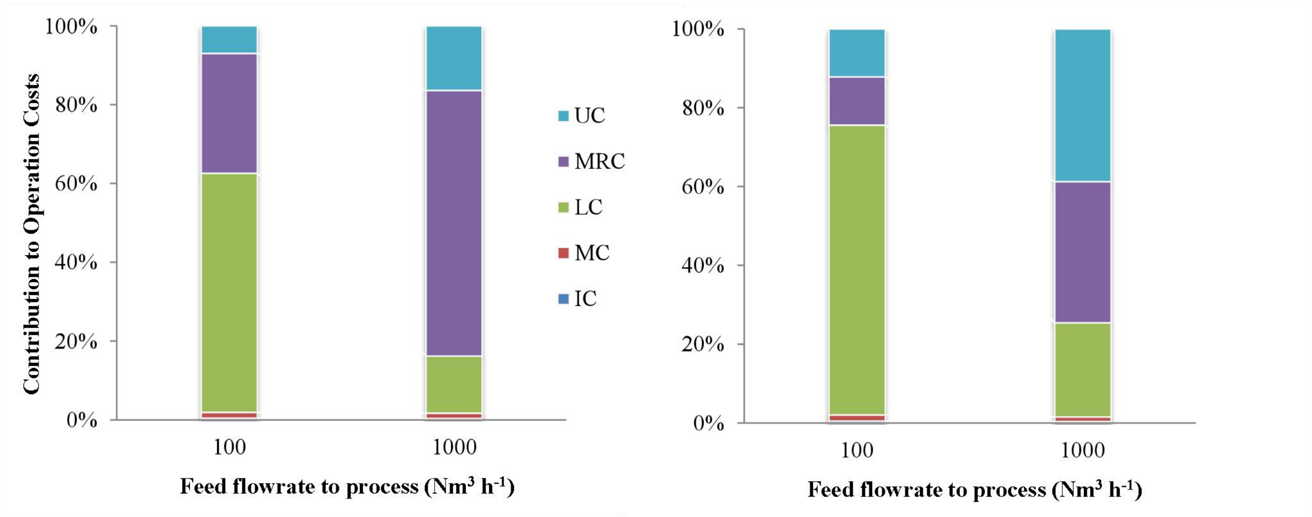


(a)



(b)

Figure 4. Contribution of terms (in percentage values) to fixed costs (FC): membrane units (MEC), turbine (TUC), heat exchangers (HEC), compressors (COC). Plant capacities of 100 and 1000 (Nm^3 h^{-1}) feed flowrate basis, operating at two pressure ratios (a) 4:0.5, (b) 8:0.5, bar basis.



(a) (b)

Figure 5. Contribution of terms (in percentage values) to operational costs (OC): utilities (UC), membrane replacement (MRC), and labour (LC); maintenance (MC) and insurance costs (IC). Plant capacities of 100 and 1000 (Nm^3 h^{-1}) feed flowrate basis, operating at two pressure ratios (a) 4:0.5, (b) 8:0.5, bar basis.

4.3. Sensitivity analysis: effects of some unit costs of materials and electricity

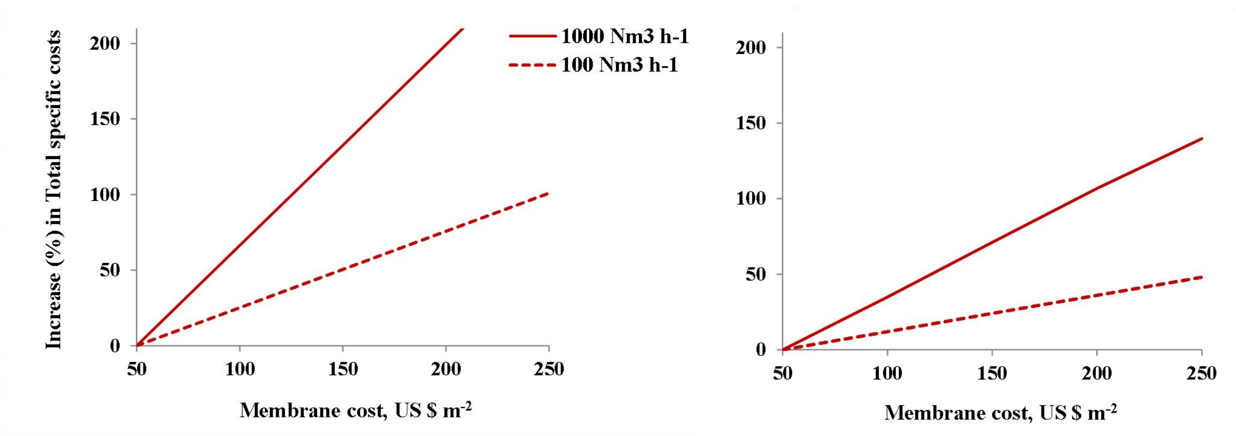
The effects of increased costs of materials and energy, such as the membrane unitary cost (*Zmem*, US\$ m^{-2}) and the electricity cost (*Zelec*, US\$ kWh^{-1}), on the total specific costs (US\$ Nm^{-3}) of the three-stage separation process were shown as trends in Figures 6 and 7, when operating plant capacities of 100 and 1000 Nm^3 h^{-1} feed flowrate, and pressure ratios denoted as (a) 4:0.5 (b) 8:0.5 bar basis.

Figure 8 compiled the specific costs values, units of US\$ Nm^{-3}, when the costs of membrane area and electricity increased up to 4-fold higher, for the installation scale of 1000 Nm^3 h^{-1} feed flowrate basis, where the effects are more pronounced. The estimation for the smaller capacity, 100 Nm^3 h^{-1} feed basis, is shown in Figure 9.

Concerning the effect of the membrane cost on the total specific costs in Figure 6, it is highly significant as it influences both capital and operation costs, which leads to increasing the contributions of MEC (membrane units costs) on the fixed costs, as well as the MRC (membrane replacement cost) in the operation costs. The scenario of double membrane cost corresponded to increases of 25% and 66% in the total specific costs of the separation process, for 100 and 1000 Nm^3 h^{-1} feed flowrate basis, respectively, operating at pressure ratio (a) 4:0.5, bar basis. At higher pressure ratio, the effect of the unitary cost of membrane area is less pronounced (12% and 35% for 100 and 1000 Nm^3 h^{-1} feed basis) at the expense of the contribution of the equipment costs for compression. The consideration of the costs of innovative membranes with still low technology readiness is subject to high uncertainty. This is the case of biopolymer-based membranes, which are not fabricated in scaled industrial processes yet. Therefore, higher costs must be contemplated at this moment, but the advances in technology readiness would reduce these costs in a near future. Moreover, the improvements in the synthesis process would result in enhanced membrane permeability and selectivity, since the relationship among membrane composition, permeability and selectivity is a key factor to produce more sustainable membranes, even considering the environmental aspects [53].

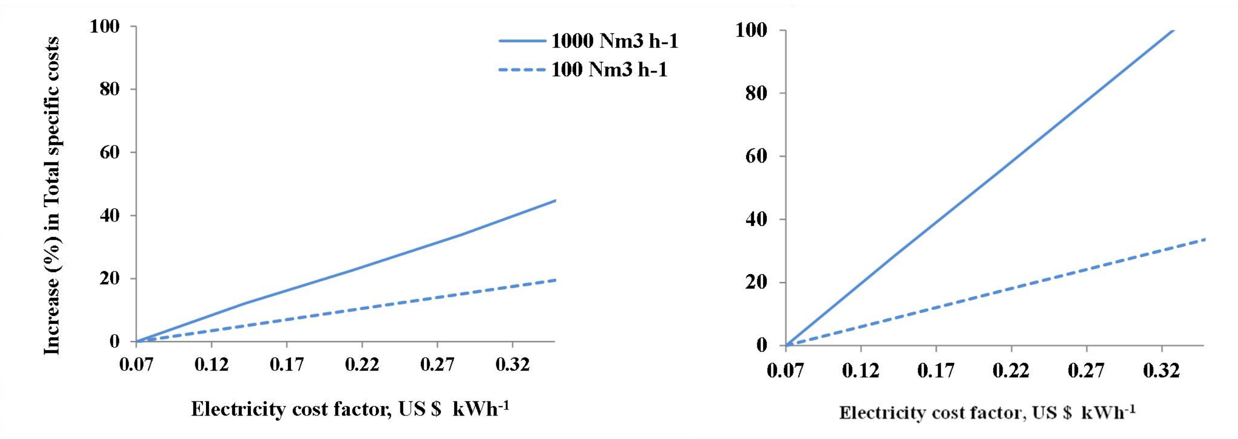
On the other hand, regarding the electricity cost factor, Figure 7 shows how it is affected by the energy consumption term in utilities costs, UC, included in the operation costs. For double electricity cost, the total specific costs were increased in 5% and 12% related to the base values for plant capacities of 100 and 1000 $Nm^3\ h^{-1}$, respectively; while the effect was more significant when the operation pressure was higher, case (b), 9 and 28% estimated increases.

A scenario of even higher electricity costs was considered, such as 4-fold higher, and the increase of total specific costs of the process were estimated at 15 % and 34% case (a), 26 % and 84 % case (b), corresponding to 100 and 1000 $Nm^3\ h^{-1}$ plant capacities, respectively.



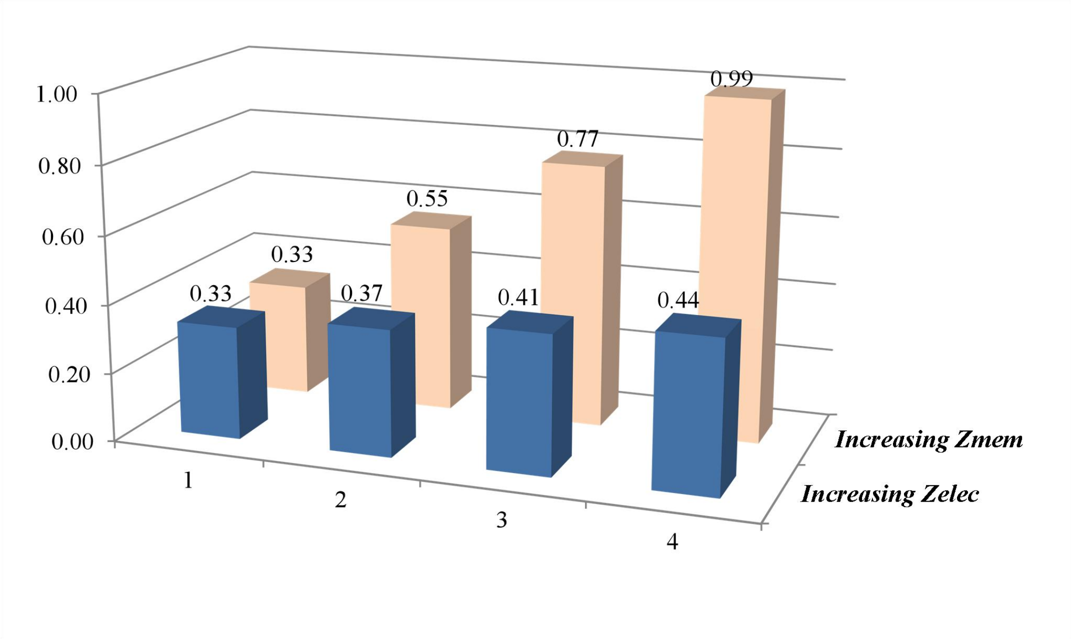
(a) (b)

Figure 6. Increase (%) in total specific costs of the separation process versus cost of membrane (*Zmem*, US$ m^{-2}). Plant capacities of 100 and 1000 ($Nm^3\ h^{-1}$) feed flowrate basis, operating at two pressure ratios (a) 4:0.5, (b) 8:0.5, bar basis.

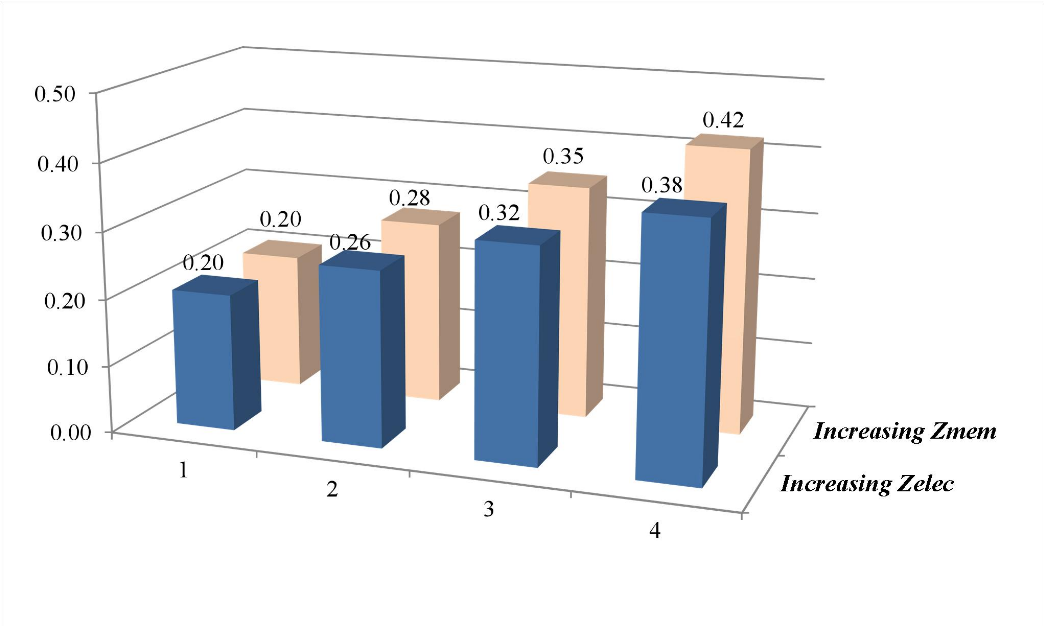


(a) (b)

Figure 7. Increase (%) in Total specific costs of the separation process versus cost of electricity (a) (*Zelec*, US\$ kWh^{-1}). Plant capacities of 100 and 1000 (Nm^3 h^{-1}) feed flowrate basis, operating at two pressure ratios (a) 4:0.5, (b) 8:0.5, bar basis.

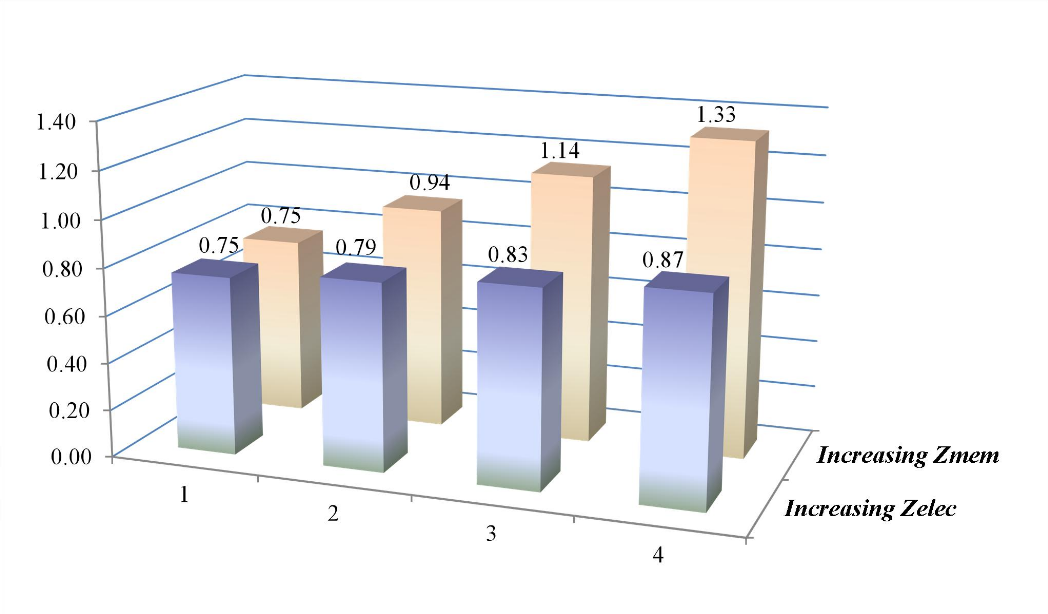


(a)

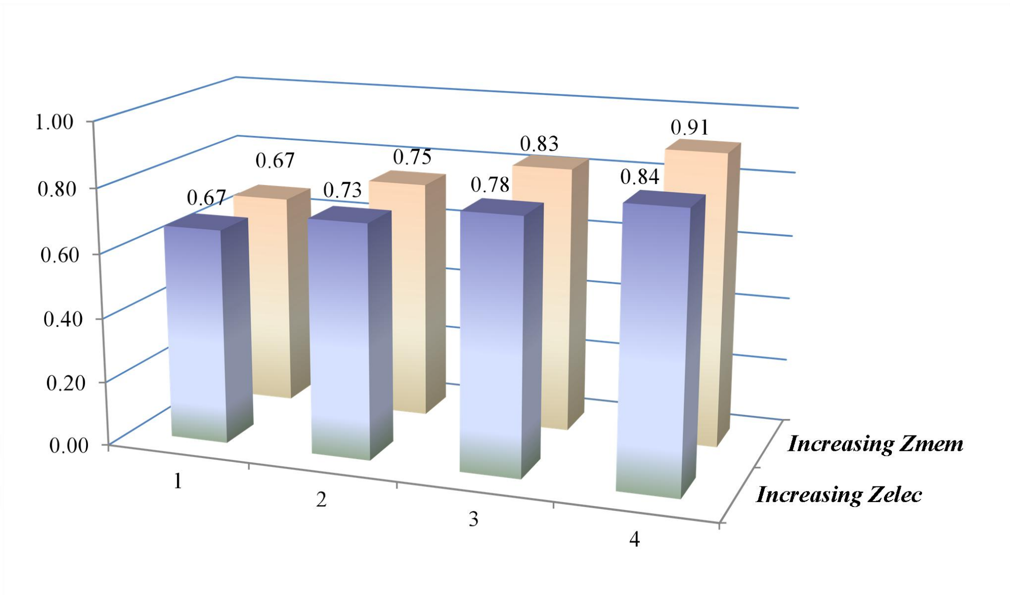


(b)

Figure 8. Values of total specific costs of the separation process (US \$ Nm^{-3}) versus cost terms of membrane (*Zmem*, US\$ m^{-2}) and electricity cost factor (*Zelec*, US\$ kWh^{-1}), to 4-fold higher each parameter. Plant capacity: 1000 Nm^3 h^{-1}, feed flowrate basis, operating at two pressure ratios (a) 4:0.5, (b) 8:0.5, bar basis.



(a)



(b)

Figure 9. Values of total specific costs of the separation process (US \$ Nm^{-3}) versus cost terms of membrane (*Zmem*, US\$ m^{-2}) and electricity cost factor (*Zelec*, US\$ kWh^{-1}), to 4-fold higher each parameter. Plant capacity: 100 Nm^3 h^{-1}, feed flowrate basis, operating at two pressure ratios (a) 4:0.5, (b) 8:0.5, bar basis.

The obtained results from the sensitivity analysis were in accordance with those reported calculations in the literature when other selective membrane materials were used. Haider et al.

[54] performed a comparison between a commercially available polymeric membrane, in a three-stage system with polyimide membranes operating up to 10 bar; and non-commercial carbon membranes (CHF, PORCHF), in a two-stage system that operated at higher pressures (50 bar as optimal value) with recycle. The effect of membrane efficiency was more prominent with carbon membranes. Considering membrane costs of 20 US \$ m^{-2} for polymeric membranes and 100 US \$ m^{-2} for carbon membranes, the reported results indicated that the membrane area would increase 30-80% total investment if the upgrading plant did not operate under the optimal pressure. Different approaches in the production process of membranes and the choice of an optimal operating pressure are proposed to reduce the processing costs. We believe that innovation in membrane materials, and the increasing the membrane life, through regeneration, if possible, would also advance in this direction.

5. Conclusions

Biogas must be purified to make it a valid replacement for natural gas and this work has demonstrated that the design of a three-stage process based on the use of a biopolymeric (chitosan) mixed matrix composite membrane whose selective layer of chitosan is hybridized by non-toxic organic (ionic liquid) and inexpensive inorganic (titanosilicate) fillers can be a competitive option for biogas purification. Both CH_4 and CO_2 were considered as target products and simultaneous high purity and recovery for both gases were imposed: 95% was the threshold defined for CO_2 purity and recovery, while 97% was the one fixed for CH_4 purity and recovery. The process configuration relies on a sequence of three membrane units operating in series to increase the concentration of CO_2 within the product stream extracted from the permeate line. Simultaneously, the retentates are gathered from each stage and blended to yield a retentate stream enriched with CH_4. Bigger plant capacities (1000 Nm^3 h^{-1} feed) resulted more economically competitive than smaller capacities (100 Nm^3 h^{-1} feed) due to the economies of scale. The minimal obtained unitary cost was 0.20 US $ Nm^{-3}, which corresponded to the bigger plant capacity operated with pressure ratio equal to 16 (8:0.5 bar basis). This cost was considered competitive when compared to the cost published in literature. The detailed analysis of the cost breakdown revealed that operation costs were clearly higher than capital costs, while the costs due to methane losses were limited below 8%. On the one hand, within capital the costs, the costs related to the acquisition of the membrane modules were the most relevant. On the other hand, within operation costs, membrane replacement was the most relevant contribution, although utility costs increased significantly when operating at higher pressure ratio. Consequently, the sensitivity analysis indicated that changes in membrane cost strongly affects to both capital and operation costs while electricity affects only to the energy consumption included in the operation costs, which are not such critical. Therefore, membranes must be considered a key factor for the design of this type of purification process for biogas. This fact points out the interest to provide more data on biopolymer-based membranes performance under different operating conditions, especially at high pressure ratios, which have been demonstrated to be the most interesting ones from an economic point of view.

CRediT authorship contribution statement

Ricardo Abejón: Conceptualization, Methodology, Software, Writing – review & editing. **Andrea Torre-Celeizabal:** Writing – review & editing, Data curation, Validation, Software. **Clara Casado-Coterillo**: Resources, Writing – review & editing, Supervision. **Aurora Garea:** Resources, Funding acquisition, Conceptualization, Software, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This research was funded by the Spanish Ministry of Science and Innovation, grant number PID2019-108136RB-C31/AEI/10.13039/501100011033, and European Union Next Generation EU/PRTR, grant number EIN2020-112319/AEI/10.13039/501100011033. A.T.C. acknowledges the Spanish Ministry of Science and Innovation for the Early-Stage researcher contract (FPI grant no. PRE2020-09765/AEI/10.13039/501100011033).

References

(1) Soeder, D. J. Greenhouse Gas Sources and Mitigation Strategies from a Geosciences Perspective. *Adv. Geo-Energy Res.* **2021**, *5* (3), 274–285. DOI:10.46690/ager.2021.03.04.

(2) Wood, N.; Roelich, K. Tensions, Capabilities, and Justice in Climate Change Mitigation of Fossil Fuels. *Energy Res. Soc. Sci.* **2019**, *52*, 114–122. DOI:10.1016/j.erss.2019.02.014.

(3) Mason, L. R.; Melton, C. C.; Gray, D.; Swallow, A. L. Climate Change, Social Work, and the Transition Away from Fossil Fuels: A Scoping Review. *Sustainability* **2022**, *14*, 7086. DOI:10.3390/su14127086.

(4) Zeppini, P.; van den Bergh, J. C. J. M. Global Competition Dynamics of Fossil Fuels and Renewable Energy under Climate Policies and Peak Oil: A Behavioural Model. *Energy Policy* **2020**, *136*, 110907. DOI:10.1016/j.enpol.2019.110907.

(5) Navas-Anguita, Z.; García-Gusano, D.; Iribarren, D. Long-Term Production Technology Mix of Alternative Fuels for Road Transport: A Focus on Spain. *Energy Convers. Manag.* **2020**, *226*, 113498. DOI:10.1016/j.enconman.2020.113498.

(6) Martinez-Villarreal, S.; Kammoun, M.; Richel, A. The Critical Role of Hydrogen in the Development of New Biofuels. *Curr. Opin. Green Sustain. Chem.* **2023,** *39*, 100716. DOI:10.1016/j.cogsc.2022.100716.

(7) das Neves, L. C. M.; Converti, A.; Penna, T. C. V. Biogas Production: New Trends for Alternative Energy Sources in Rural and Urban Zones. *Chem. Eng. Technol.* **2009**, *32* (8), 1147–1153. DOI:10.1002/ceat.200900051.

(8) Zhang, C.; Xu, Y. Economic Analysis of Large-Scale Farm Biogas Power Generation System Considering Environmental Benefits Based on LCA: A Case Study in China. *J. Clean Prod.* **2020**, *258*, 120985. DOI:10.1016/j.jclepro.2020.120985.

(9) Tan, L. S.; Lau, K. K.; Bustam, M. A.; Shariff, A. M. Removal of High Concentration CO_2 from Natural Gas at Elevated Pressure via Absorption Process in Packed Column. *J. Nat. Gas Chem.* **2012**, *21* (1), 7–10. DOI:10.1016/S1003-9953(11)60325-3.

(10) Mazzetti, M. J.; Skagestad, R.; Mathisen, A.; Eldrup, N. H. CO_2 from Natural Gas Sweetening to Kick-Start EOR in the North Sea. *Energy Procedia*, **2014**, *63*, 7280–7289. DOI:10.1016/j.egypro.2014.11.764.

(11) Baena-Moreno, F. M.; Rodríguez-Galán, M.; Vega, F.; Vilches, L. F.; Navarrete, B. Review: Recent Advances in Biogas Purifying Technologies. *Int. J. Green Energy*. **2019**, *16*(5), 401–412. DOI:10.1080/15435075.2019.1572610.

(12) Das, J.; Ravishankar, H.; Lens, P. N. L. Biological Biogas Purification: Recent Developments, Challenges and Future Prospects. *J. Environ. Manage.* **2022**, *304*, 114198. DOI:10.1016/j.jenvman.2021.114198.

(13) Angelidaki, I.; Treu, L.; Tsapekos, P.; Luo, G.; Campanaro, S.; Wenzel, H.; Kougias, P. G. Biogas Upgrading and Utilization: Current Status and Perspectives. *Biotechnol. Adv.* **2018**, *36*, 452–466. DOI:10.1016/j.biotechadv.2018.01.011.

(14) Mulu, E.; M'Arimi, M. M.; Ramkat, R. C. A Review of Recent Developments in Application of Low Cost Natural Materials in Purification and Upgrade of Biogas. *Renew. Sust. Energ. Rev.* **2021**, *145*, 11081. DOI:10.1016/j.rser.2021.111081.

(15) Prussi, M.; Padella, M.; Conton, M.; Postma, E. D.; Lonza, L. Review of Technologies for Biomethane Production and Assessment of Eu Transport Share in 2030. *J. Clean Prod*. **2019**, *222*, 565–572. DOI:10.1016/j.jclepro.2019.02.271.

(16) Gkotsis, P.; Kougias, P.; Mitrakas, M.; Zouboulis, A. Biogas Upgrading Technologies – Recent Advances in Membrane-Based Processes. *Int. J. Hydrogen Energy* **2023**, *48* (10), 3965–3993. DOI:10.1016/j.ijhydene.2022.10.228.

(17) Nguyen, L. N.; Kumar, J.; Vu, M. T.; Mohammed, J. A. H.; Pathak, N.; Commault, A. S.; Sutherland, D.; Zdarta, J.; Tyagi, V. K.; Nghiem, L. D. Biomethane Production from Anaerobic Co-Digestion at Wastewater Treatment Plants: A Critical Review on Development and Innovations in Biogas Upgrading Techniques. *Sci. Total Environ.* **2021**, *765,* 142753. DOI:10.1016/j.scitotenv.2020.142753.

(18) Bright Renewables. Biogas upgrading to biomethane (2023). https://www.bright-renewables.com/biogas-upgrading-purepac/ (accessed 2023/10/03).

(19) Chen, X. Y.; Vinh-Thang, H.; Ramirez, A. A.; Rodrigue, D.; Kaliaguine, S. Membrane Gas Separation Technologies for Biogas Upgrading. *RSC Adv.* **2015**, *5* (31), 24399–24448. DOI:10.1039/C5RA00666J.

(20) Deng, L.; Hägg, M.-B. Techno-Economic Evaluation of Biogas Upgrading Process Using CO_2 Facilitated Transport Membrane. *Int. J. Greenh. Gas Control.* **2010**, *4* (4), 638–646. DOI:10.1016/j.ijggc.2009.12.013.

(21) Scholz, M.; Melin, T.; Wessling, M. Transforming Biogas into Biomethane Using Membrane Technology. *Renew. Sust. Energ. Rev.* **2013**, *17*, 199–212. DOI:10.1016/j.rser.2012.08.009.

(22) Scholz, M.; Alders, M.; Lohaus, T.; Wessling, M. Structural Optimization of Membrane-Based Biogas Upgrading Processes. *J. Memb. Sci.* **2015**, *474*, 1–10. DOI:10.1016/j.memsci.2014.08.032.

(23) Gilassi, S.; Taghavi, S. M.; Rodrigue, D.; Kaliaguine, S. Optimizing Membrane Module for Biogas Separation. *Int. J. Greenh. Gas Control* **2019**, *83*, 195–207. DOI:10.1016/j.ijggc.2019.02.010.

(24) Bozorg, M.; Ramírez-Santos, Á. A.; Addis, B.; Piccialli, V.; Castel, C.; Favre, E. Optimal Process Design of Biogas Upgrading Membrane Systems: Polymeric vs High Performance Inorganic Membrane Materials. *Chem. Eng. Sci.* **2020**, *225*. DOI:10.1016/j.ces.2020.115769.

(25) Abejón, R.; Casado-Coterillo, C.; Garea, A. Techno-Economic Optimization of Multistage Membrane Processes with Innovative Hollow Fiber Modules for the Production of High-Purity CO_2 and CH_4 from Different Sources. *Ind. Eng. Chem. Res.* **2022**, *61* (23), 8149–8165. DOI:10.1021/acs.iecr.2c01138.

(26) Torre-Celeizabal, A.; Casado-Coterillo, C.; Abejón, R.; Garea, A. Simultaneous Production of High-Quality CO_2 and CH_4 via Multistage Process Using Chitosan-Based Membranes. *Sep. Purif. Technol.* **2023**, *320*, 124050. DOI:10.1016/j.seppur.2023.124050.

(27) Khalilpour, R.; Mumford, K.; Zhai, H.; Abbas, A.; Stevens, G.; Rubin, E. S. Membrane-Based Carbon Capture from Flue Gas: A Review. *J. Clean Prod.* **2015**, *103*, 286–300. DOI:10.1016/j.jclepro.2014.10.050.

(28) Castel, C.; Bounaceur, R.; Favre, E. Engineering of Membrane Gas Separation Processes: State of the Art and Prospects. *J. Membr. Sci. Res.* **2020**, *6* (3), 295–303. DOI:10.22079/JMSR.2020.123897.1363.

(29) Favre, E. The Future of Membrane Separation Processes: A Prospective Analysis. *Front. Chem. Eng.* **2022**, *4*. DOI:10.3389/fceng.2022.916054.

(30) Brunetti, A.; Lei, L.; Avruscio, E.; Karousos, D. S.; Lindbråthen, A.; Kouvelos, E. P.; He, X.; Favvas, E. P.; Barbieri, G. Long-Term Performance of Highly Selective Carbon Hollow Fiber Membranes for Biogas Upgrading in the Presence of H_2S and Water Vapor. *Chem. Eng. J.* **2022**, *448*, 137615. DOI:10.1016/j.cej.2022.137615.

(31) Seong, M. S.; Kong, C. I.; Park, B. R.; Lee, Y.; Na, B. K.; Kim, J. H. Optimization of Pilot-Scale 3-Stage Membrane Process Using Asymmetric Polysulfone Hollow Fiber Membranes for Production of High-Purity CH_4 and CO_2 from Crude Biogas. *Chem. Eng. J.* **2020**, *384*, 123342. DOI:10.1016/j.cej.2019.123342.

(32) Galiano, F.; Briceño, K.; Marino, T.; Molino, A.; Christensen, K. V.; Figoli, A. Advances in Biopolymer-Based Membrane Preparation and Applications. *J. Memb. Sci*. **2018**, *564*, 562–586. DOI:10.1016/j.memsci.2018.07.059.

(33) Russo, F.; Galiano, F.; Iulianelli, A.; Basile, A.; Figoli, A. Biopolymers for Sustainable Membranes in CO_2 Separation: A Review. *Fuel Process. Technol.* **2021**, *213*, 106643. DOI:10.1016/j.fuproc.2020.106643.

(34) Dai, Z.; Deng, J.; Yu, Q.; Helberg, R. M. L.; Janakiram, S.; Ansaloni, L.; Deng, L. Fabrication and Evaluation of Bio-Based Nanocomposite TFC Hollow Fiber Membranes for Enhanced CO_2 Capture. *ACS Appl. Mater. Interfaces* **2019**, *11* (11), 10874–10882. DOI:10.1021/acsami.8b19651.

(35) Iulianelli, A.; Russo, F.; Galiano, F.; Manisco, M.; Figoli, A. Novel Bio-Polymer Based Membranes for CO_2/CH_4 Separation. *Int. J. Greenh. Gas Control* **2022**, *117*, 103657. DOI:10.1016/j.ijggc.2022.103657.

(36) Torre-Celeizabal, A.; Casado-Coterillo, C.; Garea, A. Biopolymer-Based Mixed Matrix Membranes (MMMs) for CO_2/CH_4 Separation: Experimental and Modeling Evaluation. *Membranes* **2022**, *12* (6), 561. DOI:10.3390/membranes12060561.

(37) Torre-Celeizabal, A.; Casado-Coterillo, C.; Gomis-Berenguer, A.; Iniesta, J.; Garea, A. Chitosan-Based Mixed Matrix Composite Membranes for CO_2/CH_4 Mixed Gas Separation. Experimental Characterization and Performance Validation. *Sep. Purif. Technol.* **2023**, *325*. 124535. DOI:10.1016/j.seppur.2023.124535.

(38) Abejón, R.; Casado-Coterillo, C.; Garea, A. Multiobjective Optimization Based on “Distance-to-Target” Approach of Membrane Units for Separation of CO_2 /CH_4. *Processes* **2021**, *9* (11), 1871. DOI:10.3390/pr9111871.

(39) Casado-Coterillo, C.; Garea, A.; Irabien, A. Effect of Water and Organic Pollutant in CO_2/CH_4 Separation Using Hydrophilic and Hydrophobic Composite Membranes. *Membranes* **2020**, *10* (12), 405. DOI:10.3390/membranes10120405.

(40) Borgohain, R.; Pattnaik, U.; Prasad, B.; Mandal, B. A Review on Chitosan-Based Membranes for Sustainable CO_2 Separation Applications: Mechanism, Issues, and the Way Forward. *Carbohydr. Polym.* **2021**, *267*, 118178. DOI:10.1016/j.carbpol.2021.118178.

(41) Casado-Coterillo, C.; Del Mar López-Guerrero, M.; Irabien, A. Synthesis and Characterisation of ETS-10/Acetate-Based Ionic Liquid/Chitosan Mixed Matrix Membranes for CO_2/N_2 Permeation. *Membranes* **2014**, *4*(2), 287–301. DOI:10.3390/membranes4020287.

(42) Bussieck, M. R.; Meeraus, A. General Algebraic Modeling System (GAMS). In *Modeling Languages in Mathematical Optimization*; Kallrath, J., Ed.; Springer US, **2004**; pp 137–157. DOI:10.1007/978-1-4613-0215-5_8.

(43) Grossmann, I. E. *Advanced Optimization for Process Systems Engineering*; Cambridge University Press, **2021**. DOI: 10.1017/9781108917834.

(44) Scholz, M.; Frank, B.; Stockmeier, F.; Falß, S.; Wessling, M. Techno-Economic Analysis of Hybrid Processes for Biogas Upgrading. *Ind. Eng. Chem. Res.* **2013**, *52* (47), 16929–16938. DOI:10.1021/ie402660s.

(45) Miltner, M.; Makaruk, A.; Harasek, M. Review on Available Biogas Upgrading Technologies and Innovations towards Advanced Solutions. *J. Clean Prod.* **2017**, *161*, 1329–1337. DOI:10.1016/j.jclepro.2017.06.045.

(46) Rafiee, A.; Khalilpour, K. R.; Prest, J.; Skryabin, I. Biogas as an Energy Vector. *Biomass Bioenergy*. **2021**, *144*, 105935. DOI:10.1016/j.biombioe.2020.105935.

(47) Aliaga-Vicente, A.; Caballero, J. A.; Fernández-Torres, M. J. Synthesis and Optimization of Membrane Cascade for Gas Separation via Mixed-Integer Nonlinear Programming. *AIChE J.* **2017**, *63* (6), 1989–2006. DOI:10.1002/aic.15631.

(48) Hao, J.; Rice, P. A.; Stern, S. A. Upgrading Low-Quality Natural Gas with H_2S- and CO_2-Selective Polymer Membranes. Part II. Process Design, Economics, and Sensitivity Study of Membrane Stages with Recycle Streams. *J. Memb. Sci.* **2008**, *320* (1–2), 108–122. DOI:10.1016/j.memsci.2008.03.040.

(49) Turton, R., Bailie, R.C.; Whiting, W.B.; Shaeiwitz, J.A.; Bhattacharyya, D., Analysis, Synthesis, and Design of Chemical Processes. Prentice Hall, **2012**.

(50) Smith, R., Chemical Process Design and Integration. Wiley, **2016**.

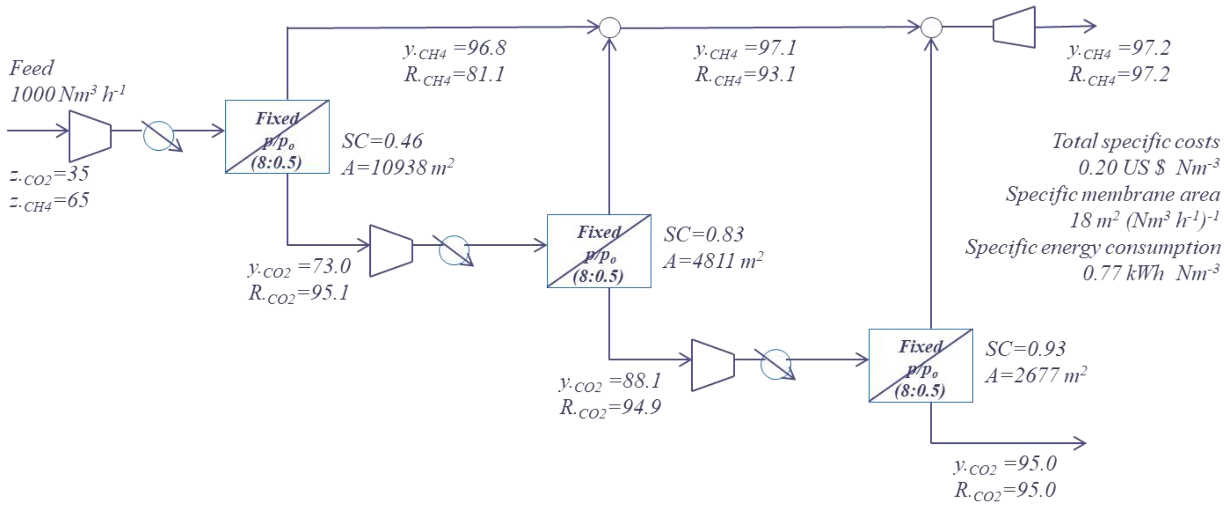
(51) Towler, G.; Sinnott, R., Chemical Engineering Design, Principles, Practice and Economics of Plant and Process Design, Elsevier, **2022**.

(52) Molino, A.; Nanna, F.; Migliori, M.; Iovane, P.; Ding, Y.; Bikson, B. Experimental and Simulation Results for Biomethane Production Using Peek Hollow Fiber Membrane. *Fuel* **2013**, *112*, 489–493. DOI:10.1016/j.fuel.2013.04.046.

(53) Echarri, I.; Casado-Coterillo, C.; Rumayor, M.; Navajas, A.; Gandía, L. M. Environmental Impact Improvement of Chitosan-Based Mixed-Matrix Membranes Manufacture for CO_2 Gas Separation by Life Cycle Assessment. *Chem. Eng. Technol.* **2023**, *46* (10), 2184–2191. DOI:10.1002/ceat.202200397.

(54) Haider, S.; Lindbråthen, A.; Hägg, M.-B. Techno-Economical Evaluation of Membrane Based Biogas Upgrading System: A Comparison between Polymeric Membrane and Carbon Membrane Technology. *Green Energy Environ.* **2016**, *1* (3), 222–234. DOI:10.1016/j.gee.2016.10.003.

For Table of Contents Use Only



A three-stage separation process for biogas upgrading by means of a more sustainable biopolymer based mixed matrix membrane is techno-economically competitive