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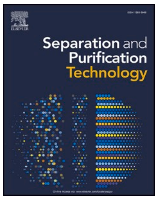

Simultaneous production of high-quality CO_2 and CH_4 via multistage process using chitosan-based membranes

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ABSTRACT

The use of biopolymers as membrane materials is a recent approach for reducing the environmental impact of CO_2 separation processes. By considering previous process engineering tasks, it was concluded that no membrane currently provides sufficient purity and recovery to meet the requirements for the simultaneous direct separation of CO_2 and CH_4 in a single stage. The aim of this study is to simulate and optimise the separation of CO_2 and CH_4 from different sources using a simple multistage process, considering up to three stages. A chitosan biopolymer-based composite membrane with organic (ionic liquid) and different inorganic fillers in the selective layer was used to tune the selectivity and robustness of commercially available membranes. The process configuration utilized membrane units operating in series to enrich CO_2 in the product stream from the permeate line, whereas the retentate line produced a CH_4-enriched stream by mixing the retentate units of each stage. The target objectives were up to 95% purity and recovery of CO_2 in the permeate outlet, corresponding to a recovery of CH_4 higher than 97% in the retentate outlet stream of the multistage process. The decision variables included the permeance of each component, and thus the pair selectivity (CO_2/CH_4) and process-related parameters, such as the stage cut of each stage. Economic evaluation of the proposed three-stage separation process was performed for different process scales, from small installations to large plants. The total costs, the contribution of each term to the total costs, and the unitary costs were estimated for each operational scale, with reference to the feed flow rate based on the plant capacity. The lowest total cost was 0.3 € $(Nm^3)^{-1}$ for a large plant with a flow rate of 1000 $Nm^3\ h^{-1}$.

1. Introduction

CO_2 separation by membrane technology is mainly used for capturing CO_2 from flue gas (e.g. power plants, cement, and iron/steel-making plants), pre-combustion H_2/CO_2 separation, natural gas sweetening, and biogas upgrading, where the objective is to separate the CO_2/CH_4 pair and to recover the CO_2 removed from biogas as a resource [1–9]. Membrane-based gas separation processes generally afford the advantages of energy-saving, space-saving, and the propensity for scale-up, in addition to a small environmental footprint during operation. The efficiency of process schemes for gas separation can be enhanced by utilizing hybrid processes based on membrane technologies and membrane-integrated systems, in line with process intensification strategies and metrics [10-13].

The development of membranes specifically designed for the separation of carbon dioxide/methane mixtures from different sources has gained attention, in line with advances in membranes and process design. In the last decade, significant progress has been made in membrane science, as new classes of polymers have been developed with improved performance for CO_2 separation and biogas upgrading. Different types of membrane materials, ranging from advanced polymers [3,14-16], such as thermally rearranged polymers and polymers of intrinsic microporosity to metal–organic frameworks [7,17], carbon [18], silica and zeolite-types [19,20], polymer ionic liquids [21,22], and more recently, biopolymers [23-25], have been investigated for achieving improved separation of CO_2 and CH_4; moreover, membrane fabrication issues such as robustness, reproducibility, toxicity, and cost have been addressed.

Mixed-matrix membranes (MMM), which are generally composed of a small amount of an inorganic or organic filler dispersed in a polymeric

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continuous matrix, are novel materials with the synergic properties of their components [5,7]. In recent years, the combination of ionic liquids (IL) with MMMs has been recognized as a promising approach [21,26,27]. The effect of ionic liquid inclusion on the performance of MMMs is related to the reduction in the interphase distance between the membrane materials, which enhances the compatibility between the polymer and inorganic filler and promotes the fabrication of defect-free membranes [28,29]. The ionic liquid may fill the potential voids between the filler particles and the polymer chains, thereby attenuating the rigidity of the polymer in the vicinity of the particles and enabling the fabrication of defect-free membranes in which the diffusion of larger gas molecules such as CH_4 across the membrane is suppressed, while attaining high CO_2 solubility or diffusivity.

The exploration of polymers derived from natural and renewable resources began approximately two decades ago. Nevertheless, the number of biopolymer membranes applied to CO_2 separation is still limited, and further efforts are required to realize the use of such bio-based materials in sustainable technology, including membrane fabrication [24,25,30].

Despite the performance improvements that novel, environmentally friendly membrane materials offer in gas separation, by evaluating previous process engineering tasks, it was concluded that single-stage permeation is insufficient for attaining high recovery efficiency of highly concentrated gases such as CO_2 and CH_4 through direct separation in a single stage [31,32]. There is a trade-off between the purity and recovery efficiency when separating gases through a membrane because the efficiency of gas separation depends on the membrane selectivity, which in turn depends on the difference in the rate of permeation of the gas components. Therefore, multistage permeation and recycling steps, as well as hybrid systems, have been the focus of research to overcome the drawbacks of single-stage membrane separation [33].

Multi-scale simulation approaches, from molecular modelling to process simulation, have also been considered to provide insight into the techno-economic feasibility of separation processes based on laboratory/bench-scale experimental data. Modelling at all length scales is required to achieve a coherent molecular understanding of membrane properties, provide insight for future material design, and clarify the fundamental mechanisms underlying the trade-off relationship between the product purity and recovery efficiency. All of the computational strategies utilized to date were designed to solve the Fickian diffusion transport or the solution-diffusion transport mechanism. Another challenge is including the computational descriptions for facilitated transport membranes, where the chemical and physical interactions need to be considered in defining the transport mechanism, together with the diffusivity and solubility of the component in the membrane matrix [34,35].

Combining material and process studies has always been a key requirement for membrane applications. For any chemical engineering target, process systems engineering (PSE) tools enable highly efficient membrane process design. PSE tools utilize different software tools and advanced concepts to optimize theories and methods [36,37].

Note that the membrane systems, formulated with PSE tools, for separating CO_2 and CH_4 are generally targeted towards the separation objectives for this pair in many industrial processes, such as natural gas treatment, biogas upgrading, and oil recovery enhancement, covering a wide range of compositions, as shown in Table 1.

The CO_2 content in natural gas obtained from gas or oil wells can vary from 4 to 50% depending on the geographic location. On the other hand, purge gas from a gas-reinjected enhanced oil recovery (EOR) well can contain as much as 90% CO_2 [38]. In biogas upgrading applications, the gas composition is highly dependent on the biogas source and the substrate used in the fermentation process [39] (Table 1).

Biogas has played an increasingly important role in the renewable energy market. The CO_2 captured from biogas can be used for other applications such as enhanced oil recovery (EOR) and algae production, which further reduces the cost of biogas production [8].

Achieving high-performance and optimizing the process designs are crucial advancements for solving the challenges of membrane systems at the industrial scale and realizing the commercial application of membranes.

A compilation of studies focusing on optimizing membrane separation processes for the separation of CO_2/CH_4 pairs in biogas upgrading is summarised in Table 2. Representative studies involving carbon dioxide removal from natural gas, as a more mature field of application, are listed in Table S1 (Supplementary Information).

In those studies, the multistage designs and superstructures were solved using various mathematical tools based on custom-built membrane unit models. The most commonly used mathematical programming software tools are GAMS (general algebraic modelling system), MATLAB, Fortran, C++, and Aspen Customs Modeler. ChemBrane was specifically developed for membrane units [34,45], whereas MemCal [46] and MEMSIC [44] can be linked or interfaced to different simulation and optimisation commercial packages (such as Aspen HYSYS or Aspen Plus).

Fixed and multistructure optimisation approaches have been utilized to simultaneously determine the process layout and minimise the gas separation costs. Qi and Henson [47] used this concept for the first time to optimise a multistage spiral-wound gas permeator system, requiring a mixed integer nonlinear programming (MINLP) solution strategy that was implemented in GAMS.

Scholz et al. [48] also used this approach in GAMS to determine the most profitable layout for a biogas upgrading process. By using a three-

Table 1
Different sources of CO_2 and CH_4 for membrane separation processes.

Sources	*CH_4 (vol%)*	*CO_2 (vol%)*	*Composition comments / Minor components*	*Ref*
Examples of biogas different sources				
– Farm biogas plant	55–58	37–38		[10,34,39]
– Sewage digester	61–65	34–38	Depending on the source, nitrogen may be present in a larger amount, as in the case of landfill / H_2O (4–7 vol%), N_2, O_2, H_2S, Aromatics hydrocarbon traces.	
– Landfill	47–57	37–41		
Raw biogas	45–75	25–55	Composition highly dependent on the biogas source and the applied substrate for fermentation / H_2O, N_2, O_2, H_2S, Organic sulfur molecules, NH_3, Aromatics (BTX), Siloxanes.	[4,40,41]
Natural gas	50–90	*balance*	CO_2 and H_2S contents varying in different geographic location /Other hydrocarbons (C2-C4) , traces of heavier hydrocarbons; Rest O_2, N_2, Ar, Xe, He.	[8,42,43]
Enhanced coal-bed methane (ECBM), enhanced oil recovery (EOR)	*balance*	30–90	CO_2 content in CBM gas or the purge gas form a gas-reinjected well varying with conditions of the coal seam and operations / Other hydrocarbons, H_2S.	[38,44]

stage layout with a single compressor, they achieved high CH_4 purity (96 mol%) and recovery (99.6%) using polyimide (PI) and cellulose acetate (CA) membranes with CO_2/CH_4 selectivity values of 60 and 20, respectively. The dynamic model was programmed in Aspen Custom Modeler and exported to Aspen Plus and Aspen Plus Dynamics to introduce control schemes for maintaining the product purity, even if significant changes in the feed gas conditions were enforced [49].

Deng and Hägg [34] evaluated an on-farm-scale biogas membrane-based upgrading system using a highly efficient CO_2-selective membrane with different predefined process layouts. They used a polyvinylamine/polyvinyl alcohol (PVAm/PVA) blended membrane, a facilitated transport membrane (FTM), with a thin selective layer on a polysulfone (PSf) membrane. Technoeconomic analysis was performed for four processes with different membrane module configurations, with and without recycling. The ‘2-stage in-cascade with recycle’ configuration was proven optimal among the four processes, where the simulation indicated up to 99% CH_4 recovery at a low cost. ChemBrane was employed as an in-house simulation membrane module interfaced with Aspen HYSYS.

More recently, Gilassi et al. [50] used a multistructure optimisation technique to determine the optimum biogas layout. In that study, a new optimisation framework was proposed for formulating the general form of a module separation model (MSM) using hollow fibre polymer membranes (i.e. Ultem 1000). By using that approach, the optimum number of modules could be determined while minimising the environmental footprint of the membrane separation plant. By optimizing the objective functions, it was demonstrated that two membrane units were sufficient for enriching CH_4 up to 98% in the retentate stream, while affording a CH_4 recovery of 99%. This approach can prospectively be applied to the design of a more compact membrane-based unit for biogas upgrading plants, as well as for offshore gas sweetening projects, where reductions in the plant structure and equipment size are challenging.

Bozorg et al. utilized superstructure representation [51] in the global optimisation of membrane upgrading processes. In that study, the synthesis process was systematically optimised to identify the most cost-effective membrane from three different materials (cellulose acetate (CA), polyimide (PI), and zeolite (CHA type)) in up to three stages. The costly, but high-performance, zeolite membrane material enabled the most cost-effective process compared to commercially available polymeric membranes. Compared with other technologies for biogas treatment at flow rates of up to $\sim$ 1000 $Nm^3\ h^{-1}$, membrane upgrading has been cited as the cheapest technology, and is a promising alternative to water scrubbing at higher biogas flow rates.

In addition to engineering toolboxes for process systems that offer relevant and efficient tools for design purposes, process synthesis methods are also expected to expand rapidly. These approaches open up new possibilities for optimizing the configurations of multistage membranes and hybrid processes, including multimembrane processes. Combined approach of materials and process design methods also offer a straightforward link between the membrane performance, optimal process structure, and cost [6,52,53]. As highlighted by Bozorg et al. [51], such studies could be extended to more complex systems, including multicomponent feeds, multimembrane systems, or multi-target applications; for example, combined biogas purification and carbon capture objectives.

Table 2

Biogas upgrading: Compilation of studies focused on optimizing membrane separation processes related to the CO_2/CH_4 pair: Multistage designs and superstructures.

Max. stages	*Membrane type andmodule unit*	*Focus of the study*	*Ref*
3	–Matrimid 5218 and Hyflon membranes (from a reference study) –Co-current flow pattern.	– Process simulation for analysing membrane-integrated systems to identify suitable operating conditions and propose possible process schemes to reach targets. Membrane performance maps. – Process intensification metrics. – Software: A house-built 1-D mathematical model for the multi-species steady-state permeation.	[10]
3	–Asymmetric PSf membrane –Counter-current flow, HF	– Process simulations: Effect of various operation conditions, and validation with pilot scale three-stage membrane process testing. – Software: COMPAQ Visual Fortran.	[40]
3	–Commercial PI, CA (permeance data), and generic optimal. –Short-cut model for gas permeation module.	– Structural optimization for both commercial and optimal membrane materials. – Impact of optimal selectivity on the process performance, where the membrane material follows the correlation for Robesońs upper bound. – Software: GAMS, MINLP problem, using BARON solver.	[48,49]
2	–PVAm/PVA blend on a PSf membrane. –Different options of configurations and flow patterns; used HF module, counter-current flow.	– Sensitivity analysis, and economic evaluation. – Software: ChemBrane tool for the simulation membrane module interfaced to Aspen HYSYS, and CAPCOST for capital cost estimation.	[34]
3	–Commercial CA, spiral wound. –Prepared PDMS, hollow fibre.	– Process modelling, simulation, and sensitivity analysis. – Software: Python programming language.	[56]
2	–Polymer Ultem 1000. –Counter-current hollow fibre.	– Optimization, F.O.: min. annual separation cost, and units (module number in each stage). – Software from AMPL, non-convex MINLP solved on the NEOS servers, solvers such as BARON and COUENNE.	[50]
3	–Generic (permeance data). –Co-current flow model.	– Process simulations, annual profitability analysis of the feasible schemes and structures. – Optimization to max. annual profit, different strategies in sequential and simultaneous model, with reference structure and superstructure (SeqRS, SeqSS, SimSS). Uncertainty in feed. – Software for process simulations: A custom user model embedded in Fortran to Aspen Plus.	[57]
3	–Commercial CA, second generation PI (patent WO2012/00727), commercial zeolite (CHA type). –Different flow patterns.	– Optimization: F.O.: min. process cost. – Evaluation of the impact of membrane performance from the process and cost perspectives. – Software: MIND in-house built program using KNITRO algorithm.	[51]
2	–Commercial modules: modified PSf AIR Products PRISM PA1020; PI UBE UMS-A5. –Co-current, or counter-current flow.	– Process modelling and simulation. – Membrane productivity calculations. – Software: A membrane module model solved in C++.	[58]
3(stages)-7 (steps)	–PEI /PI membrane module. –Co-current flow pattern.	– Process modelling, validation with experimental data for a single-stage process. – Analysis of multi-step membrane configurations considering that a separation stage can be constituted by various steps. – Software: A house-built 1-D mathematical model for the multi-species steady-state permeation.	[59]

Table 3
Experimentally determined parameters and characteristics of membranes. * Units of permeance in *m^3 STP h^{-1} m^{-2} bar^{-1}.*

Biopolymer MMMs	*Thickness (μm)*	*Permeability (CO_2) (Barrer)*	*Permeance L.CO_2 (*)*	*Selectivity (CO_2/ CH_4)*	*SF (CO_2/ CH_4)*
IL-CS [30]	12 ± 4	154.28	0.0186	4.26	4
5 wt% AM-4/ILCS	56 ± 6	98.06	0.0081	26	23
5 wt% ETS-10/ILCS	58 ± 5	389.5	0.034	20	19
5 wt% Zeolite A/ ILCS	75 ± 5	779.7	0.014	28	26

Therefore, the aim of the present study is to simulate and optimise a simple multistage process configuration, up to three stages, for the separation of CO_2 and CH_4 from different sources. The selected biopolymer-based composite membranes are ionic liquid-chitosan composite membranes prepared in our laboratory [23,30,54,55], the performance of which can be enhanced by hybridisation with compatible inorganic fillers. The three-stage separation process is simulated to optimise the target purity and recovery in both the permeate and retentate streams to control the product quality. The techno-economic feasibility of the membrane system for the simultaneous production of high-quality CO_2 and CH_4 in the permeate and retentate streams, respectively, is assessed based on cost estimation.

2. Membranes

The gas-separation performance of the chitosan-based membranes prepared in the laboratory was evaluated, as reported in an experimental study[60]. The characterisation data were introduced into the membrane unit modelling and separation process simulation tasks.

Chitosan (CS)-based mixed-matrix composite membranes were prepared by solution casting at room temperature. The membranes were prepared and characterised based on previous studies on such MMMs, focusing on CO_2/N_2 separation [29,33,61,62]. Briefly, a porous support based on commercial polyethersulfone (PES) membranes with a pore size of 0.1 μm and thickness of 132 μm (Millipore PALL), treated with 0.1 wt% trimesoyl chloride (TMC)/hexane solution, was used to avoid crystallisation of the CS layer on the pore surfaces in order to achieve a homogeneous coating layer. The coating layer comprised a CS solution blended with 5 wt% of an imidazolium ionic liquid (IL) [emim][Ac] with unreported toxicity and high CO_2 affinity, previously studied in our research group for CO_2/N_2 separation [63].

Three Na^+-containing porous inorganic fillers were included in the ILCS matrix to tune the membrane selectivity and permeability; namely, two titanosilicates (3D ETS-10 and 2D AM-4), prepared by a hydrothermal synthesis method reported elsewhere [30,62,64], and 3D zeolite 4A (Fluka, Aldrich, Spain). The filler loading was varied between 0, 5, and 10 wt% relative to the total organic matrix. Only the 5 wt% filled membranes passed the screening stage because of their favourable CO_2/CH_4 separation ability.

Table 3 summarises the experimentally determined permeation properties of the MMM composite membranes (CO_2 permeability, permeance, selectivity, and the separation factor of the mixed gas pair CO_2/CH_4) [60], where the contribution of the types and loading of fillers is highlighted. The selectivity values were calculated as the ratio of the permeabilities of the CO_2 and CH_4 components of the feed through the membrane. The separation factors were calculated by dividing the concentration ratio of both components (CO_2 /CH_4) in the permeate by the corresponding feed ratio.

The permeance of the evaluated membrane materials for CO_2/CH_4 separation was generally moderate; therefore, concentration polarisation was not considered as an issue in biogas upgrading. As reported by Scholz et al. [4,48], the effect of concentration polarisation was not accounted for in the model, but would be remarkable for membranes with selectivities and permeances as high as 1000 and 1000 GPU.

3. Process simulation

After obtaining the gas separation data, the next step is to use process simulations to evaluate the potential of such membranes in a certain process. The aim is to optimize the process design with respect to the configuration, feasibility, and costs [35].

This section briefly explains the steps used to accomplish the process simulation objectives of this study. The programming tools used for process simulation and optimisation were Aspen Customs Modeler (Aspen Technology, Inc., Bedford, MA, U.S.) and GAMS (GAMS Development Corp. Fairfax VA, U.S., and GAMS Software GmbH, Frechen, Germany), which formulated the multistage process as custom-built programming.

3.1. Membrane unit model

Each membrane unit was represented as a cross-flow membrane model based on a cell-in-series assumption, where the membrane unit was divided into *n* number of equal-sized cells, with *n* = 100, as detailed elsewhere [30,31]. A solution-diffusion model was used to describe the mechanism of transport of molecules across the membrane. To solve the steady-state material balances and transport equations, the membrane unit model was implemented in Aspen Customs Modeler as a programming tool for process modelling and simulation tasks. The equations solved for the membrane unit model are presented in Appendix A.

The separation performance was defined by the purity and recovery of each component at each outlet stream of the membrane unit. The purity and recovery were calculated from the molar flow rates of the permeate and retentate streams and the corresponding molar fractions

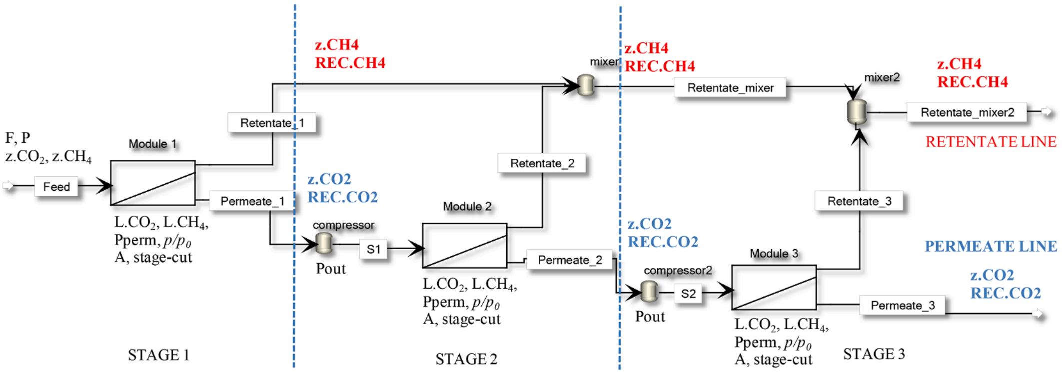

Fig. 1. Schematic of multistage process covering up to three stages, considered in this study.

Table 4
Membrane performance in the multistage process: Comparison at a fixed stage-cut of 0.5. Purity as *z component* (molar fraction); recovery from process feed as *REC component.*

Biopolymer	***PROCESS***	***PERMEATE LINE***		***RETENTATE LINE***		***Relative total area***
MMMs	***STAGE***	*z.CO$_2$*	*REC.CO$_2$*	*z.CH$_4$*	*REC.CH$_4$*	***to IL-CS***
IL-CS	1	0.510	0.720	0.810	0.620	1.0
	2	0.680	0.490	0.760	0.880	1.0
	3	0.835	0.298	0.719	0.968	1.0
5 wt% AM-4/ILCS	1	0.620	0.880	0.920	0.710	9.7
	2	0.920	0.660	0.840	0.970	7.9
	3	0.994	0.355	0.742	0.999	7.3
5 wt% ETS-10/ILCS	1	0.610	0.870	0.910	0.700	1.8
	2	0.900	0.650	0.840	0.960	1.5
	3	0.989	0.353	0.741	0.998	1.4
5 wt% Zeolite A/ILCS	1	0.620	0.880	0.920	0.710	5.8
	2	0.930	0.660	0.840	0.970	4.7
	3	0.995	0.355	0.742	0.999	4.4

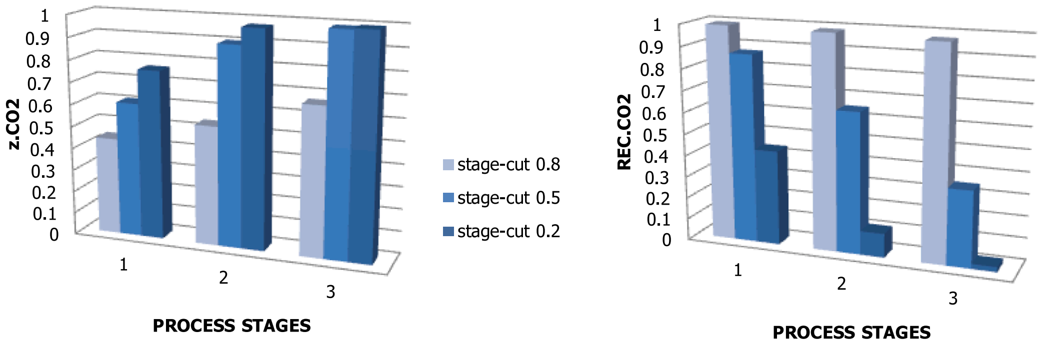

Fig. 2. Process simulation: permeate line, CO$_2$. 5 wt% ETS-10/ILCS membrane. Purity as *z component* (molar fraction); recovery from process feed as *REC component.*

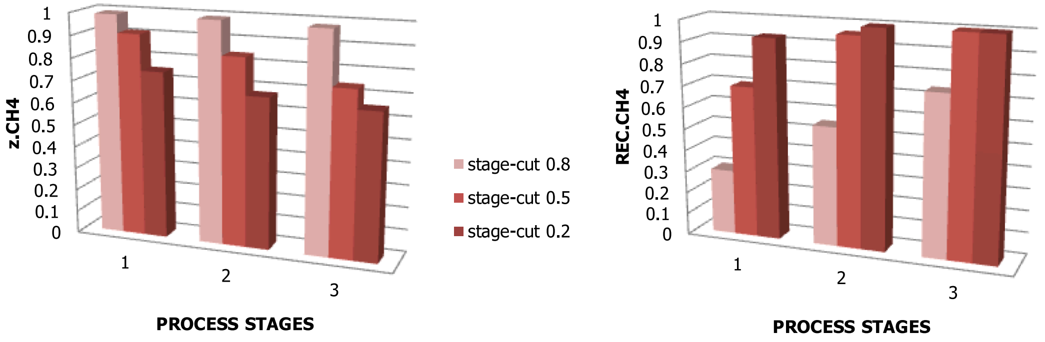

Fig. 3. Process simulation: retentate line; CH$_4$ values from mixing points. 5 wt% ETS-10/ILCS membrane. Purity as *z component* (molar fraction); recovery from process feed as *REC component.*

Table 5
Summary of Analysis Tools-Optimization data for 5 wt% ETS-10/ILCS membrane.

	Decision variables (stages 1–3)		Selectivity	PERMEATE LINE		RETENTATE LINE	
Sim-opt summary	**Stage-cut**	**L. CO$_2$ (units)** *(m^3 STP h^{-1}m^{-2}bar^{-1})*	CO$_2$/CH$_4$	z.CO$_2$	REC.CO$_2$	z.CH$_4$	REC.CH$_4$
p/p$_0$ = 4 (4:1)	0.64–0.78	0.034 (fixed)	20	0.889	0.872	0.931	0.941
	0.66–0.79	0.056–0.047	33–28	***0.900*** ***target case 1***	***0.900***	0.946	0.946
p/p$_0$ = 8 (4:0.5)	0.58–0.84	0.034 (fixed)	20	0.945	0.936	0.966	0.971
	0.66–0.80	0.042–0.048	25–28	***0.950*** ***target case 2***	***0.950***	0.973	0.973

of the components. The membrane performance was defined in terms of the permeability of the solutes and the selectivity for the CO$_2$/CH$_4$ gas pair. The process operation variables include the pressure ratio and stage-cut, which are the ratios of the permeate and feed flow rates.

3.2. *Multistage process: Configuration*

For modelling the membrane gas separation modular units, a biogas upgrading process was proposed to provide the reference feed (a binary mixture comprising 35:65% CO$_2$:CH$_4$). These modules were used to

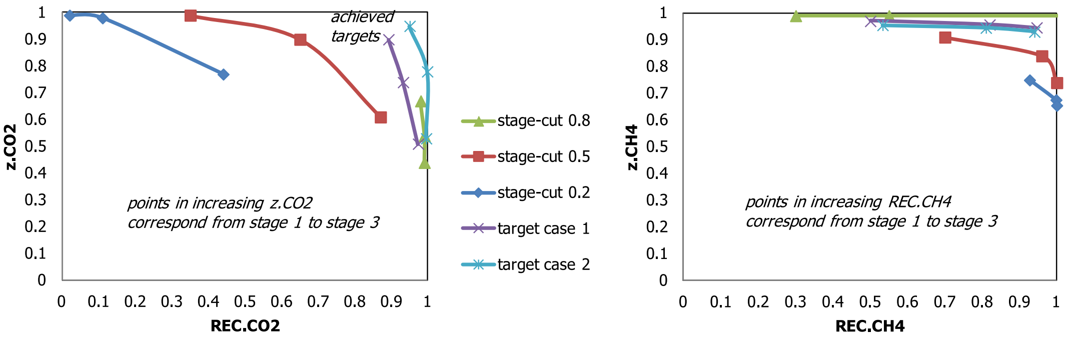

Fig. 4. CO_2 purity (as molar fraction) versus recovery ratio from stages 1 to 3. 5 wt% ETS-10/ILCS membrane. Process simulation with different stage-cut values and target cases, where top right corner indicates the achieved values (Table 5).

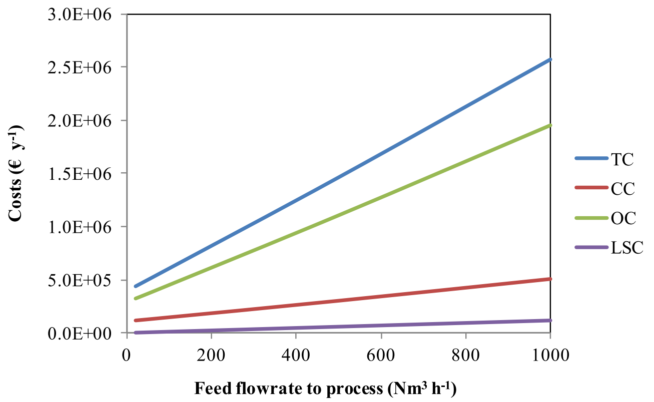

Fig. 5. Total costs (TC) and the contributions of various terms: capital costs (CC), operating costs (OC), and cost of losses for CH_4 (LSC).

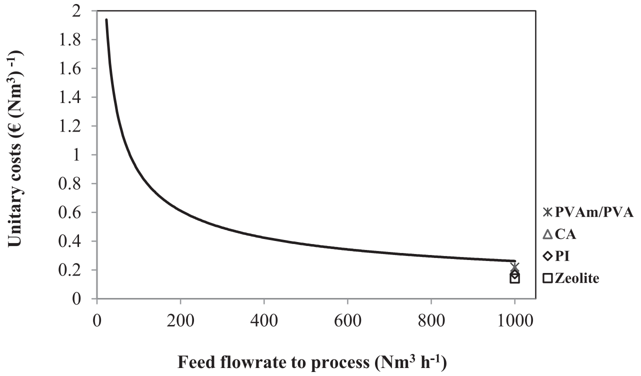

Fig. 6. Total costs per unit of feed flow rate to process: trend of unitary costs per unit plant capacity when scaling up. References of membranes at 1000 Nm^3 h^{-1}: PVAm/PVA blend [34]. CA, PI and zeolites [51].

build a multistage process with up to three stages, as shown in Fig. 1. The configuration consisted of three membrane separation units operating in series, where the permeate line produced a CO_2-enriched product stream, which was the outlet permeate stream from the third stage, while the product stream from the retentate line, a CH_4 enriched stream, was obtained by mixing the retentate from each stage.

Intermediate compressors were included in the permeate line to set the feed pressure of each membrane unit to a specific pressure ratio. The retentate line included some mixing points, which were included to obtain a CH_4-enriched product stream, and the option of using an expander for this product stream was also considered for estimating the process cost.

At each membrane separation stage, the global and component material balances were solved in conjunction with the equations for transport of each component through the membrane. The connections between the stages were described by the corresponding continuity equations, which were used to calculate the flow rates, molar compositions, and mixing points.

3.3. Multistage process: Target case studies

Considering up to three stages for the membrane separation configuration, two target scenarios were analysed with the aim to maximise the product quality variables:

- Target case 1 corresponds to a CO_2 purity of 0.90 (molar fraction) and CO_2 recovery ratio of 0.90 for the feed at the outlet stream at the permeate line (stage 3).
- Target case 2 is a more demanding scenario, corresponding to a CO_2 purity of 0.95 (molar fraction) and CO_2 recovery ratio of 0.95 for the feed from the outlet stream at the permeate line (stage 3). The membrane was also required to operate at a higher pressure ratio in the membrane unit at each stage ($p/po = 8$; Target case 1 was operated at $p/po = 4$).

The decision variables were membrane-related, such as the permeance of each component, and process-related, such as the stage cut at each stage, which also determined the membrane area for the techno-economic evaluation.

The sets of equations for modelling the multistage separation process were implemented in Aspen Custom Modeler, and the optimisation tool included in the Analysis Tools Package was used for the target scenarios. The scenarios were formulated in mathematical terms with the objective function of maximising the product quality, which was defined in terms of the purity and recovery of the components from the feed stream. Both variables correspond to the process outlet streams.

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

$$\begin{aligned} &\text{s.t. } h_m(x) = 0,\ \forall\, m \\ &g_n(x) \le 0,\ \forall\, n \\ &x \in R^n,\ X_L < x < X_U \end{aligned}$$

Here, *f(x)* is the objective function formulated as the sum of the purity and recovery of the components, with the continuous variables represented by × (i.e. stream variables and operation variables related to the equipment included in the process configuration); $h_m(x)$ refers to the equality constraints such as mass balances, separation process design equations, design specification constraints, and related cost equations and correlations; $g_n(x)$ refers to the inequality constraints, including the lower and upper bound pairs of the key variables.

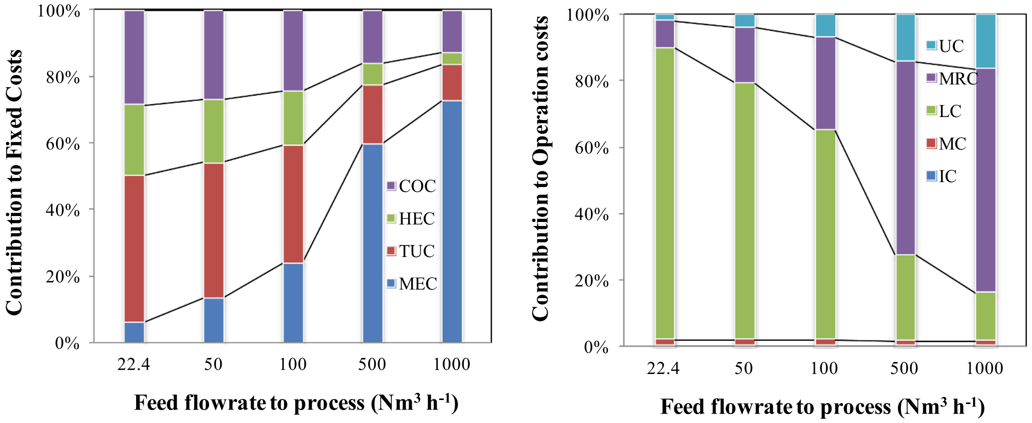

Fig. 7. Detailed contribution of terms (in percentage values) to fixed (FC) and operational (OC) costs. Fixed cost terms: membrane units (MEC), turbine (TUC), heat exchangers (HEC), compressors (COC). Operational cost terms: utilities (UC), membrane replacement (MRC), and labour (LC); maintenance (MC) and insurance costs (IC).

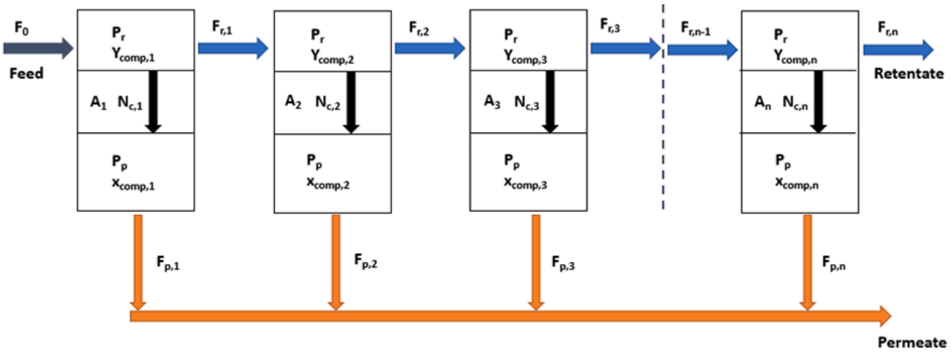

Fig. A1. Diagram of the crossflow membrane unit model.

3.4. *Multistage process: Economic evaluation*

The economic evaluation model was incorporated into the multistage process configuration with three stages to estimate the total costs (TC) of the separation process as the sum of the capital costs (CC), variable operation and maintenance costs (OC), and cost of methane losses in the permeate outlet (LSC), which were considered for upgrading low-quality natural gas or biogas. The total cost term $TC_{unitary}$, which is related to the process capacity, was defined to include the effect of the feed flow rate on the process.

$$TC_{unitary} = \frac{(CC + OC + LSC)}{Q_{Feed} t_{factor} OSF} \tag{2}$$

Here, *CC, OC, LSC* are the costs terms (y^{-1}); Q_{Feed} is the volumetric flow rate of the process feed (Nm^3 h^{-1}); t_{factor} is used to convert the reference time (h y^{-1}); and *OSF* is the on-stream factor (-), defined as the fraction of the time for which the process is in operation or working.

The capital costs (*CC*) included the fixed costs (FC) corresponding to the investment in equipment (membrane units MEC, turbine TUC, heat exchangers HEC, and compressors COC, Eq. (3)) project contingency, and start-up costs.

The operation costs (*OC*) included the consumption of resources in terms of utilities (UC), membrane replacement (MRC), and labour (LC), and related capital costs such as maintenance (MC) and insurance costs (IC) (Eq.(4).

$$FC = MEC + TUC + HEC + COC \tag{3}$$

$$OC = IC + MC + LC + MRC + UC \tag{4}$$

The contributions of the considered terms to the estimate of the fixed and operational costs were also calculated to show the significance of each term depending on the process capacity (scale), and the most relevant term. 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 are detailed elsewhere [32]. The intermediate compressors were modelled as three-stage compressors, for which the compression ratio was assumed to be the same in each stage; heat exchangers operating with refrigeration water were used after compression to cool the streams to the optimal operating temperature of the membrane.

The economic evaluation of the multistage separation process was performed using GAMS software (GAMS Development Corporation). In this study, the program was formulated for the mathematical task of cost estimation while maximising the product quality (purity and recovery variables) as a nonlinear problem. GAMS is a commercial software designed for modelling and solving linear, nonlinear, and mixed-integer optimisation problems. It is a robust tool used in process system engineering to solve multistage process configurations and related superstructures.

4. Results and discussion

The results of the simulation and optimisation for producing high-purity CO_2 and CH_4 are presented below, with the aim to contribute to advancing the design of separation processes.

4.1. *Multistage configuration and target cases*

The performance of the membranes composed of the ionic liquid–chitosan–mixed-matrix composite membranes with different fillers (5 wt% of filler loading) in the selective membrane layer (Table 3) was compared by considering the performance of the membranes in the multistage separation process (the parameters are summarized in Table 4) at a fixed stage-cut with an intermediate value of 0.5, and a feed mixture of 35–65% CO_2/CH_4. A pure IL-CS composite membrane without inorganic fillers was also included for comparison to analyse the influence of the CO_2/CH_4 selectivity.

The performance of the membranes under operation at different stage-cut values (0.2, 0.5, and 0.8) are also compiled in Tables S2–S4 (Supplementary Information). The performance was evaluated based on sensitivity analysis related to the quality of the products, namely, the purity of CO_2 from the permeate line and CH_4 from the retentate line (from the mixing points) as a molar fraction and the CO_2 recovery relative to the process feed.

Based on these results, the 5 wt% ETS-10/ILCS composite membrane was identified as the best option considering the total membrane area required to carry out the target separation from a single stage, stage 1 in this work, to a multistage process consisting of three stages.

Figs. 2 and 3 show the molar compositions and the ratios of gas recovered from the feed (CO_2 in the permeate and CH_4 in the retentate) outlet streams in the simulation of the multistage process at different stage-cut values for a feed mixture of 35–65% CO_2/CH_4.

Among the target cases, the performance of the 5 wt% ETS-10/ILCS membrane was superior, as summarized in Table 5. The trade-off between the purity and recovery of the components could be overcome with the use of this membrane under the given conditions, which influenced the decision variables.

Despite an increase in the optimal stage-cut value (i.e. from 0.66 to 0.80, Table 5), the required membrane area declined significantly from stage 1 to stage 3 (60% in stage 2 and 90% in stage 3 with respect to stage 1, as detailed in the Supplementary Information), attributed to the higher partial pressure gradient of CO_2 between both sides of the membranes when the CO_2 stream was enriched [32,65].

As shown in Table 5 and detailed in the Supplementary Information, the membrane selectivity for the CO_2/CH_4 pair should reach approximately 30. The results obtained from the simulation indicate that the targets (high product gas purity and simultaneously high recovery) are achieved by controlling the decision variables (stage cut and CO_2 permeance) (top right corner in Fig. 4); thus, the trade-off between the purity and recovery can be successfully overcome.

4.2. Economic evaluation

An economic evaluation of the proposed three-stage membrane separation process was performed to estimate various process scales, from small installations to large plants. The evaluation considered the total costs, that is, the contribution of capital (fixed and operational) costs to the total costs, and more detailed terms included in each category of costs.

This section compiles the results of the more demanding scenario, defined as target case 2. The results for target case 1 are presented in the Supplementary Information (Figs. S1–S4).

The calculations were performed for the 5 wt% ETS-10/ILCS membrane type, which exhibited the best performance in the proposed three-stage separation process.

The process scales covered feed flow rates from 22.4 to 100 $Nm^3\ h^{-1}$, representing small biogas upgrading and biomethane production units, including agricultural applications, and feed flow rates of up to 500 and 1000 $Nm^3\ h^{-1}$ for higher capacity plants, as found at the industrial scale.

The most relevant contribution to the total costs was the operation costs (Fig. 5), representing 73–76%, whereas the capital costs varied from 26 to 20% (depending on the process capacity). The difference reached up to 100% of the total costs due to the loss of CH_4 in the outlet permeate streamline.

The unitary total costs were also calculated as the ratio of total costs to the feed flow rate for the process on different scales (Fig. 6), highlighting a very important decrease when the process was operated at higher feed flow rates of up to 1000 $Nm^3\ h^{-1}$, with costs from 2.3 to 0.3 € $(Nm^3)^{-1}$.

The contributions of the different terms to the fixed and operational costs are shown in Fig. 7 (as percentage values relative to the total corresponding costs). The contributions of the different equipment-related terms to the fixed costs were highly dependent on the process scale, highlighting an increase in the membrane unit contribution from 6 to 70% of the fixed costs when the feed flow rate was increased from that for small-capacity units to that for industrial installations. In terms of the operational costs, two terms were more significantly dependent on the process scale: (i) the labour costs, from 90% contribution on the small scale to 20% on the large scale, and (ii) the membrane replacement costs, which increased to 65% of the operational costs for the largest plant, i.e. the reference of 1000 $Nm^3\ h^{-1}$.

The utility cost contribution also increased to 15% of the operational cost for a large-scale plant. This term was calculated from the energy power consumption; a range of 12–545 kW was required from the small to the large scales, corresponding to a specific energy consumption of 0.5 kWh $(Nm^3)^{-1}$ as the ratio of energy consumption per unit capacity.

In the context of biogas upgrading, the costs referenced from the literature varied considerably as a function of the biogas source, upgrading technology, plant capacity, location, etc. The reference costs of specific energy consumption were in the range of 0.15–0.8 kWh $(Nm^3)^{-1}$, covering different membrane materials, such as CA, PI and zeolites [51], carbon [18], and PVAm/PVA blend membranes [34]. For a basis of 1000 $Nm^3\ h^{-1}$ capacity plant, those reported studies were positioned in Fig. 6 that corresponds to unitary costs; pointing out the interest to provide more data on biopolymers.

The details of the energy consumption calculations for the two target scenarios are provided in the Supplementary Information (Figs. S5 and S6).

Thus, the major contributions to the total costs associated with the CO_2/CH_4 separation process are related to the operational costs. However, at higher process capacities, the unitary cost decreased significantly, reaching values comparable to those reported in the literature when conventional polymer-based membranes were employed [51]. Therefore, the biopolymer-based MMMs studied in this work can be well positioned as potential sustainable alternatives for CO_2/CH_4 separation.

5. Conclusions

Simulation of the multistage membrane separation of CO_2/CH_4 demonstrated that a three-stage separation process scheme based on membrane units, with the selected biopolymer-based MMMs, can achieve the targets imposed on product quality, yielding high-quality CO_2 and CH_4.

In the most demanding scenario, which imposed 95% purity and recovery of the CO_2 product stream from the permeate line, CH_4 recovery values higher than 97% in the retentate line could be achieved. In order to achieve these targets, the stage-cut values were indicated as decision variables from stage 1 to stage 3 (i.e. 0.66–0.80, working with 5 wt% ETS-10:IL-CS/PES as the most favourable membrane).

Despite an increase in the optimal value of the stage-cut from stages 1 to 3, the required membrane area was significantly reduced (up to 90% with respect to stage 1), attributed to the higher partial pressure gradient of CO_2 between both sides of the membrane as the CO_2 stream was enriched.

Economic evaluation of the proposed three-stage separation process was performed to estimate the total costs at different process scales ranging from small installations to large plants. The most relevant contributor to the total costs was the operational cost, representing up to 76% of the total costs. The unitary total costs decreased significantly to 0.3 € $(Nm^3)^{-1}$ for a large plant with a flow rate of 1000 $Nm^3\ h^{-1}$.

Therefore, the biopolymer-based MMMs are well positioned as sustainable prospects for CO_2/CH_4 separation pending mature development of the membrane unit.

6. Data availability

Data will be made available on request.

CRediT authorship contribution statement

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

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Appendix A. Membrane unit model

A crossflow membrane model was built using Aspen Custom modeler. For the membrane unit modeling, a cell in series model was applied where the membrane unit is divided in k number of equal sized uniform cells, being *k* variable from 1 to *n (with* $n = 100$*)* [30,31]. The permeate of each cell is recovered and mixed with the rest of the permeate streams, and the retentate of each cell being the feed for the next one, as can be seen in Fig. A1.

Steady state material balances are solved to calculate the gas composition and flowrates at both sides of the membrane, equations (A1-A3), for any *k* cell from 1 to *n*:

$$F_{r,k-1} = F_{r,k} + F_{p,k} \tag{A1}$$

$$F_{r,k-1}y_{comp,k-1} = F_{r,k}y_{comp,k} + F_{p,k}x_{comp,k} \tag{A2}$$

$$N_{comp,k} = F_{p,k}x_{comp,k} \tag{A3}$$

being $F_{r,k}$ and $F_{p,k}$ total molar flowrates (kmol h^{-1}) of retentate and permeate leaving each cell, $x_{comp,k}$ and $y_{comp,k}$ molar fractions of each component in the mixture present in the permeate and retentate streams, respectively, and $N_{comp,k}$ molar flowrate of each component permeating though the membrane cell k (kmol h^{-1}).

The transport mechanism across the membrane is described by the solution-diffusion model, with the partial pressure difference across the membrane as the driving force of permeation

$$N_{comp,k} = A_k P_{comp}\left(p_r y_{comp,k} - p_p x_{comp,k}\right) \tag{A4}$$

being P_{comp} permeance for each component across the membrane, in molar basis (kmol h^{-1} bar^{-1} m^{-2}, calculated from the experimentally obtained permeance values in m^3 (STP) h^{-1} bar^{-1} m^{-2} units), A_k membrane area of the cell *k*, and p_r and p_p are the pressure on the retentate and permeate sides of the membrane, respectively.

At the n^{th} cell, outlet of the membrane, the retentate molar flowrate and the molar fraction of each component in this stream are the calculated for $k = n$; while the permeate molar flowrate of the outlet stream is obtained as the sum from $k = 1$ to *n,* and the corresponding molar fraction of components as follows:

$$F_{p,n} = \sum_{k=1,n}\left(F_{p,k}\right) \tag{A5}$$

$$F_{p,n}\cdot x_{comp,n} = \sum_{k=1,n}\left(F_{p,k}x_{comp,k}\right) \tag{A6}$$

The stage cut is the ratio of the permeate flowrate to the feed flowrate,

$$\theta = F_p/F_f \tag{A7}$$

Two parameters are used to compare the separation performance of different membranes, the purity and recovery of each component across the membrane,

$$\text{Purity}_{\,comp}(\%) = 100\times\frac{F_{comp,out}}{F_{out}} = 100\times\frac{F_{out}y_{comp,out}}{F_{out}} = 100\times y_{comp,out} \tag{A8}$$

$$\text{Recovery}_{comp}(\%) = 100\times\frac{F_{comp,out}}{F_{comp,in}} = 100\times\frac{F_{out}y_{comp,out}}{F_{in}x_{comp,in}} \tag{A9}$$

Appendix B. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2023.124050.

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