Bio-based copolymers for membrane end products for gas separations

Membrane based Process Design and Economics

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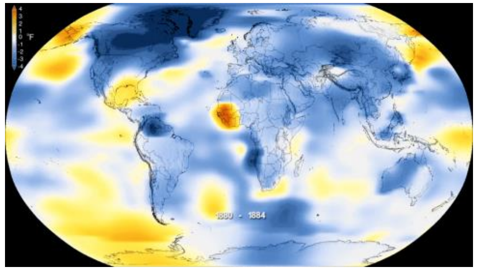
Webinar: Bio-based Membranes for CO_2 separation - 26th June 2023

CO_2 capture

- Concentration of carbon dioxide in atmosphere is rising sharply, and it is accelerating the global warming and climate change.

- CCS is a combination of technologies designed to prevent the release of CO_2 generated through conventional power generation and industrial production processes by injecting the CO_2 in suitable underground storage reservoirs.

- It is estimated that up to 90% of carbon emissions from the industrial use of fossil fuels could be captured by CCS.



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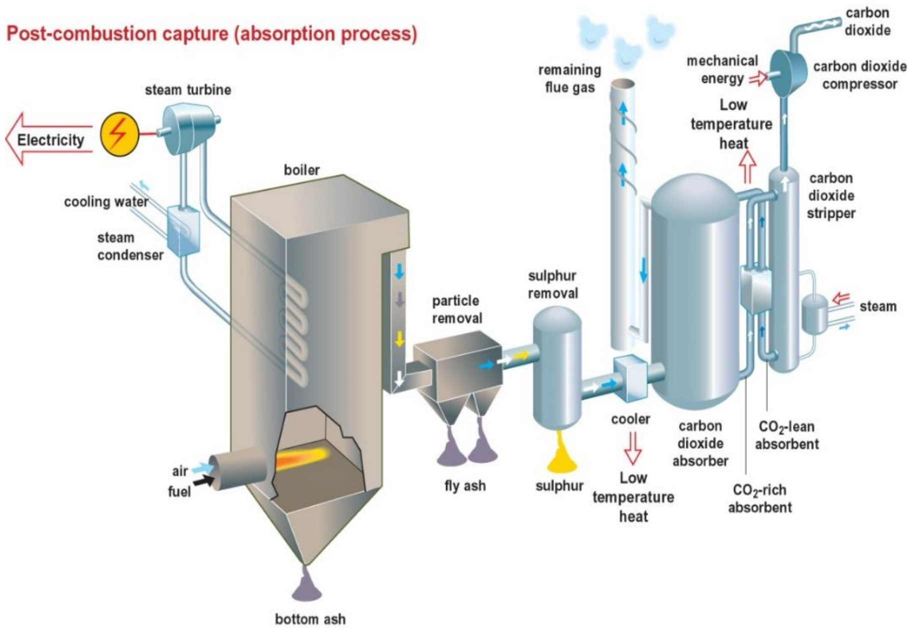
Carbon capture project explores liquid CO_2 carrier design (rivieramm.com)

CO_2 capture technologies

- Different technologies are available for removing CO_2 from different streams, e.g., cryogenic, adsorption, chemical absorption, membrane separation, and carbon fuel cells.
- The choice of technology depends on the specific application, process conditions, and economic factors.
- Absorption is a mature technology that is widely used in industrial applications, but it can be energy-intensive and requires significant space and capital investment.



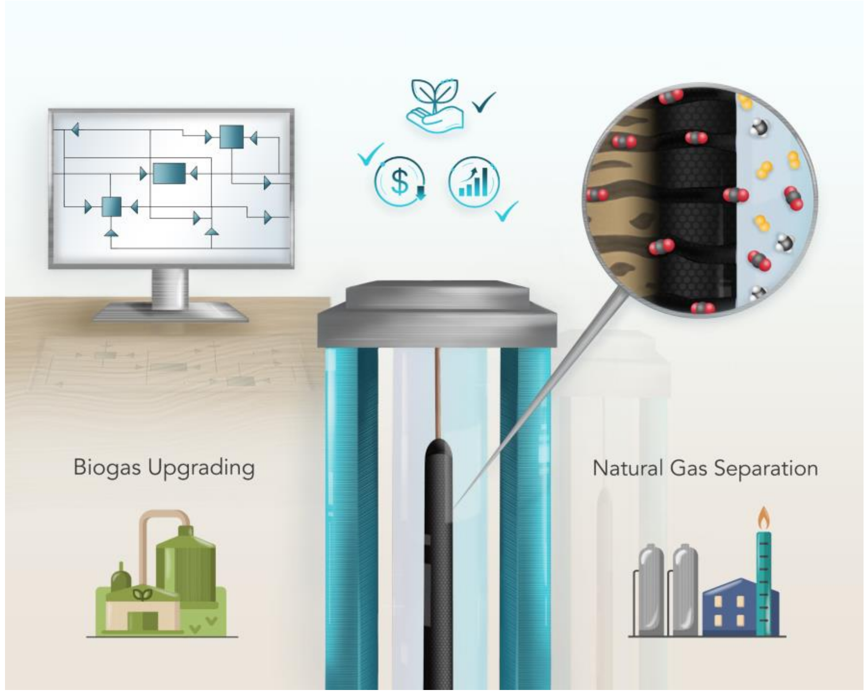
Challenge of the integration of CO_2 capture in the refining sector.

Membrane Gas Separation

- Has great potential for CO_2 capture due to its advantages such as avoiding chemical use, being simple to operate, energy-efficient, and suitable for intermittent and continuous operations.

- The potential application of the membrane process in a great measure depends on the capability of membrane materials to provide high separation performance.

- Membranes suffer from a trade-off between selectivity and permeability with an upper bound.



Steps of design of a membrane system

Process design is essential to provide an energy-efficient membrane technology for gas separation.

Feed source and feed condition

Product quality

Select flow configuration

Select number of stages

Membrane type

Optimize the membrane system

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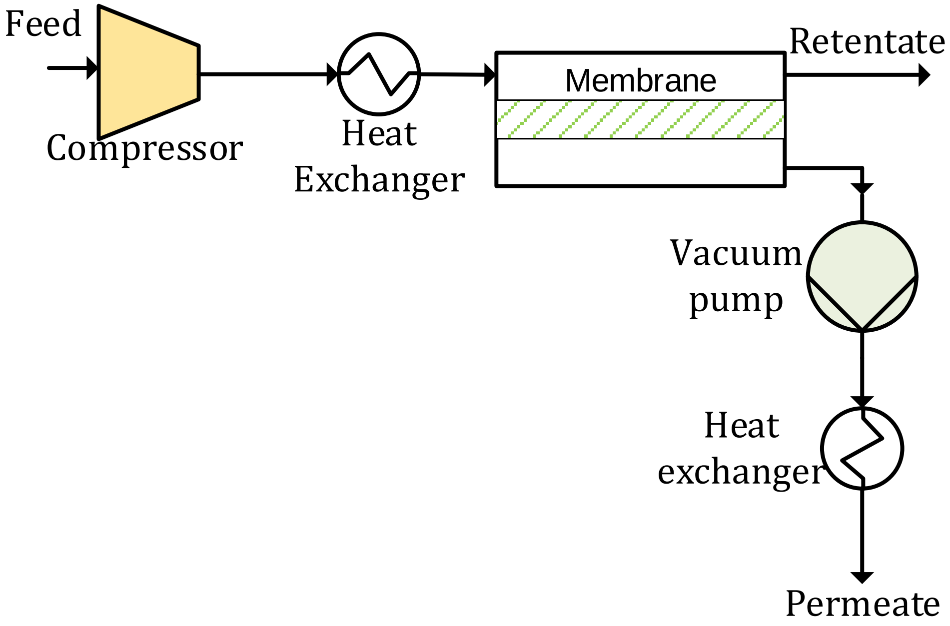
Membrane-based process design



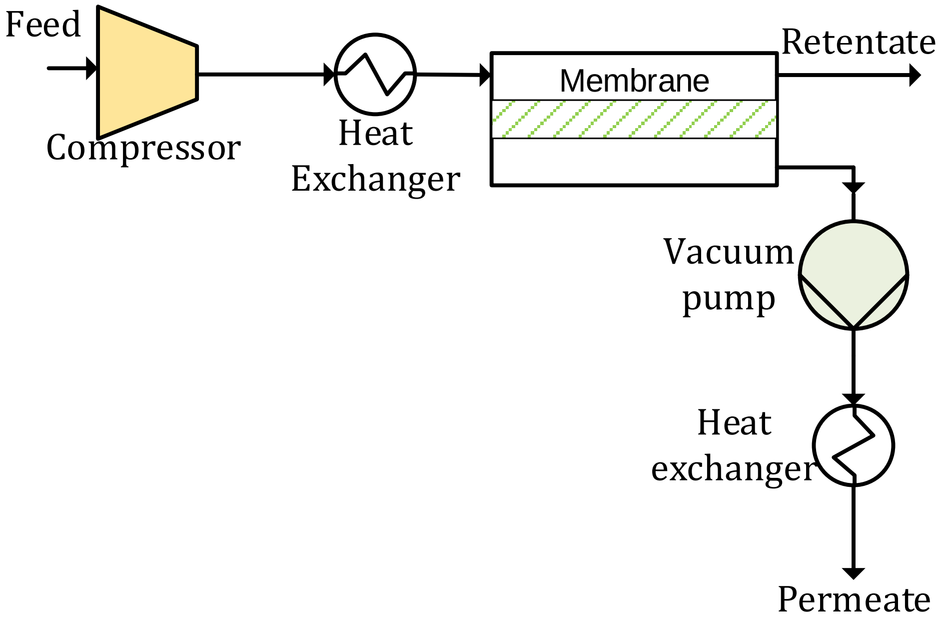
- In case of a post-combustion CO_2 capture, flue gas with atmospheric pressure is fed to a compressor to provide the required driving force for the gas separation.
- The driving force for CO_2 permeation in a membrane-based gas separation is the difference in the partial pressure of the feed and permeate side.
- The permeate stream exits the membrane at a lower pressure than the feed stream and enters either a vacuum pump or a compressor.
- The permeate stream is enriched from CO_2 while the retentate stream is enriched from N_2.

Membrane-based process design

- A single-stage membrane process cannot meet high recovery and gas purity at the same time, regardless of the membrane type used.

- CO_2/N_2 selectivity must be over 200 to achieve the target separations with CO_2 recovery and purity of >90% and >95%, respectively, in a **single-stage** membrane configuration.

- Since the single-stage membrane process cannot reach the separation goal, a multi-stage membrane system needs to be implemented.



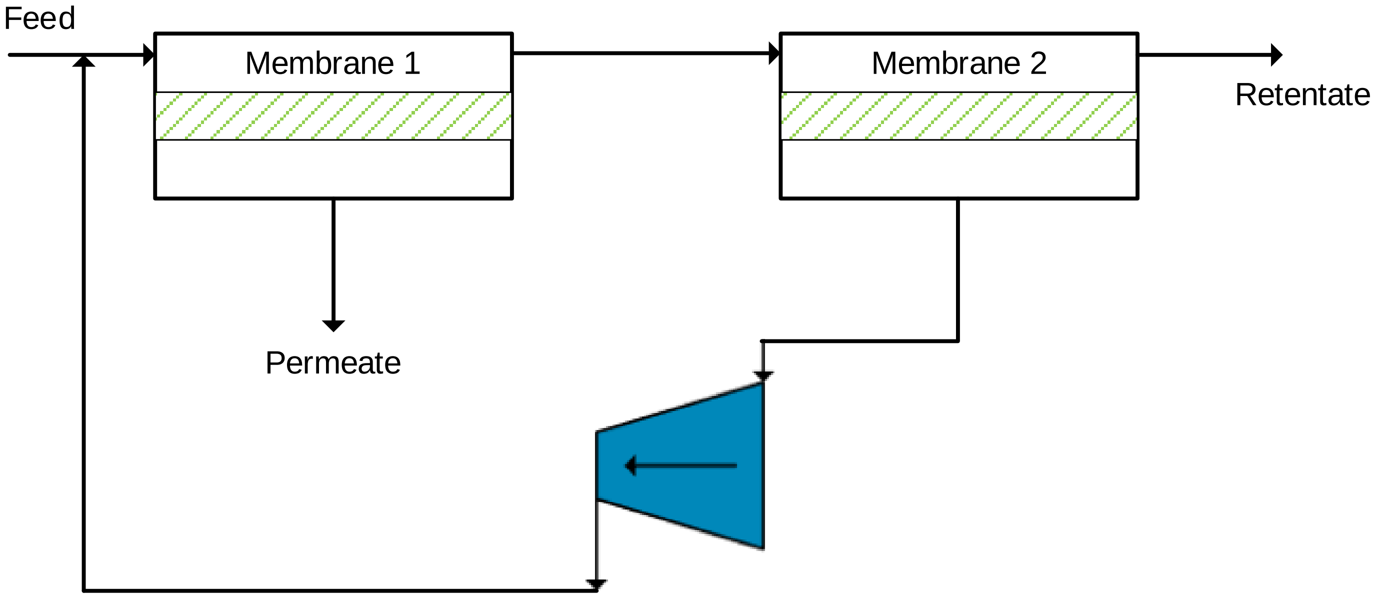
~~High purity~~

~~High recovery~~

Engineering evaluation of CO_2 separation by membrane gas separation systems, J Memb Sci. 454 (2014).

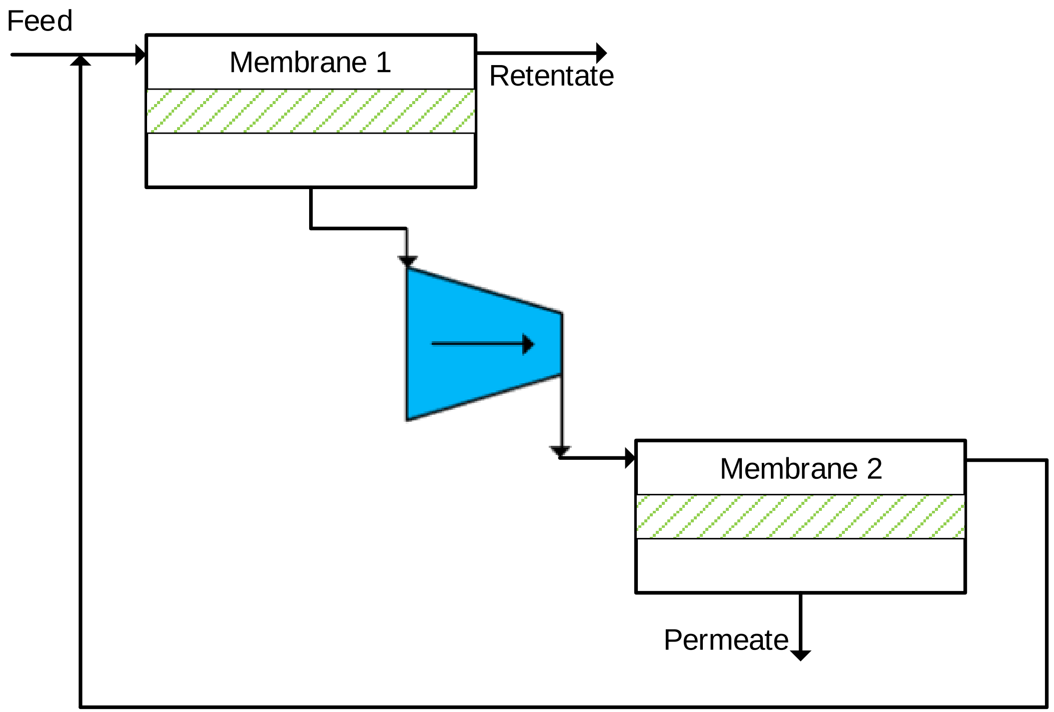
Two-stage cascade for purer retentate

- The raw gas is compressed and fed to the first membrane stage.
- The first stage performs a bulk separation of for example CO_2 and CH_4
- The retentate of the first stage is fed to a second stage in which the final product purity is obtained.
- The permeate of the second stage is recycled and mixed with the raw gas stream to enhance the CH_4 recovery.



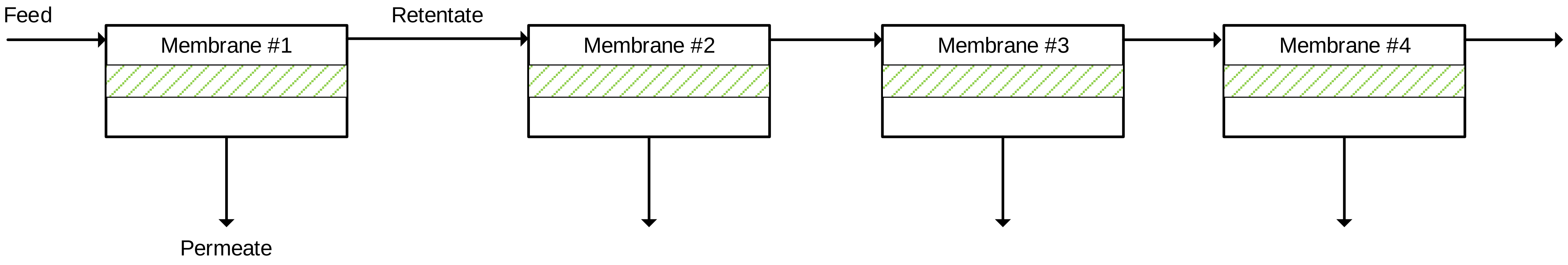
Two-stage cascade for purer permeate

- The permeate stream of the first membrane unit, after passing through a compressor and a cooler, enters the second stage
- The permeate stream of the second membrane unit is considered as the final product.
- The product purity and recovery of this configuration are higher than those of the previous configuration.
- The combination of similar membranes or/and different membranes in the two-stage process results in good separation performance as product purity reaches the desired values.



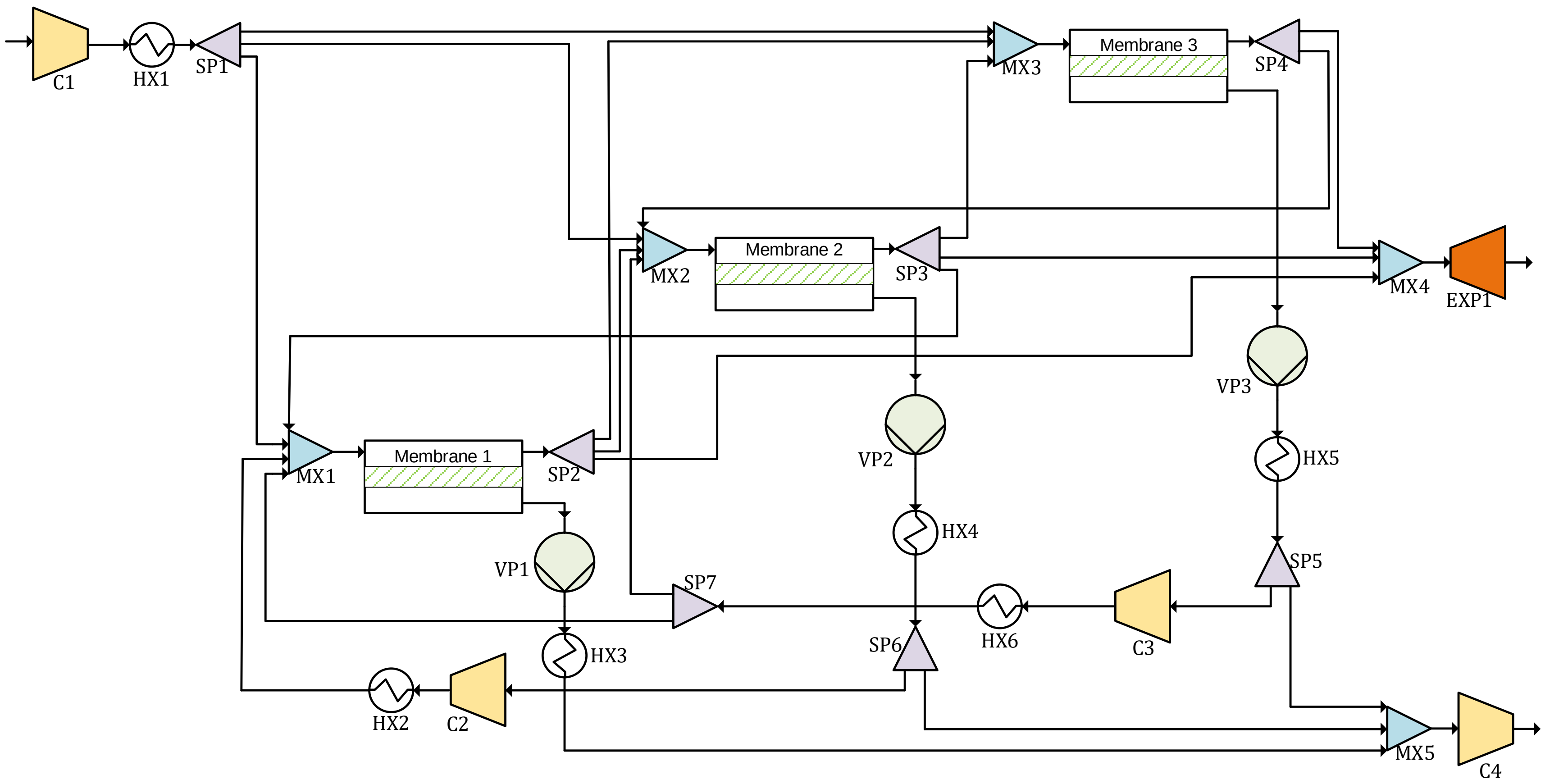
Multi-stage membrane module

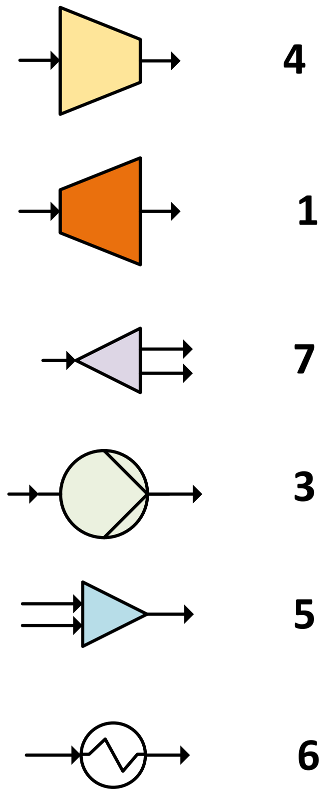
The selection of the best configuration is highly related to feed quality, separation objectives and market values.



Multi-stage membrane module

By applying a structural optimization approach, the most profitable process configuration including stage numbers can be determined.





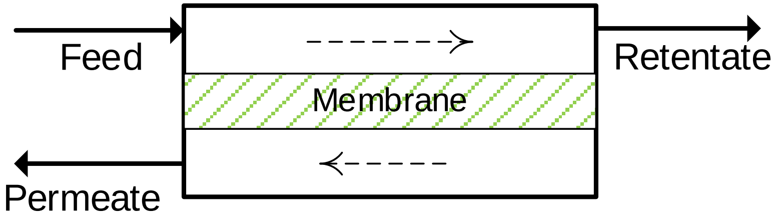
The main objective in the optimization of the multi-stage membrane design was to minimize GPC while achieving the product target purity and recovery.

Flow arrangements in membrane modules

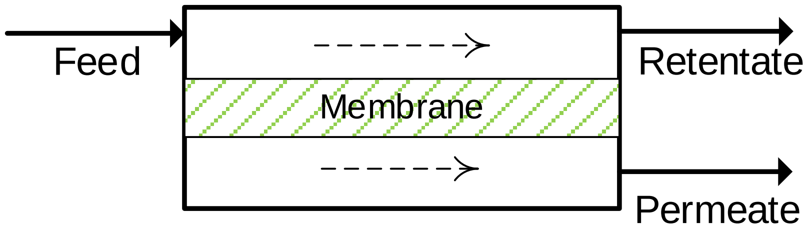
- The performance of a membrane is influenced by the way in which the permeate and retentate flow in the membrane.

- Flow arrangements of perfect mixing, co-current, counter-current, and cross flow are possible in the design of a membrane module.

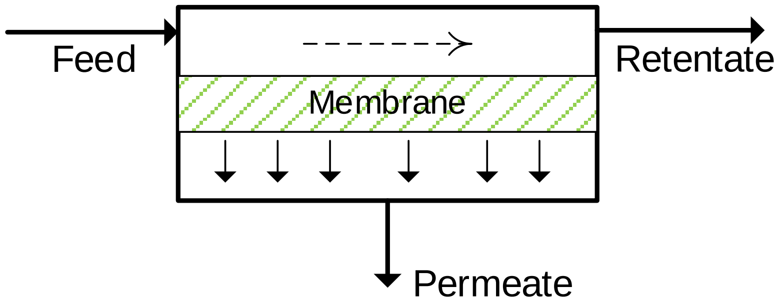
Counter-current Flow



Co-current Flow

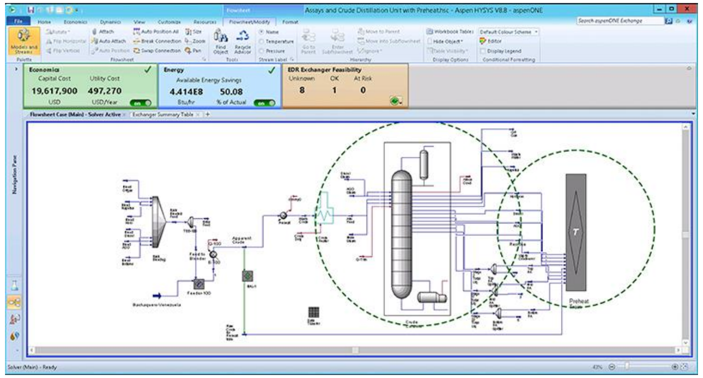


Cross Flow



Process Simulation Tools

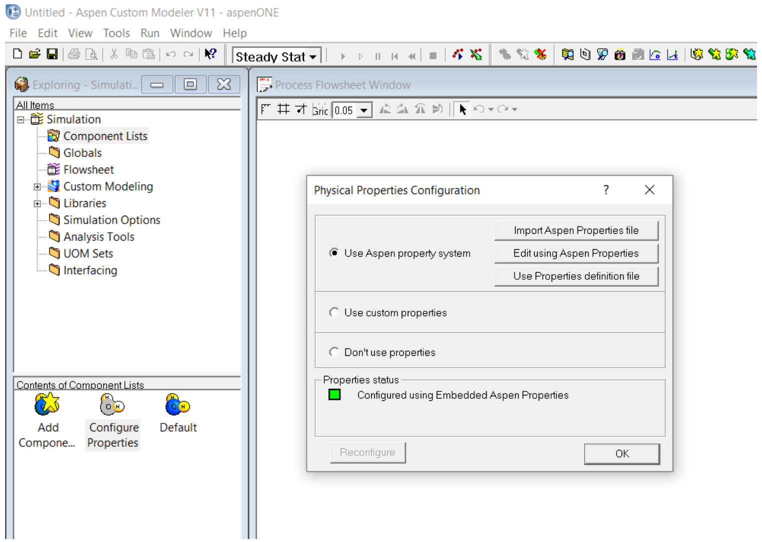
Process simulators have been proven to be successful in modeling, simulate, and optimize various industrial processes.

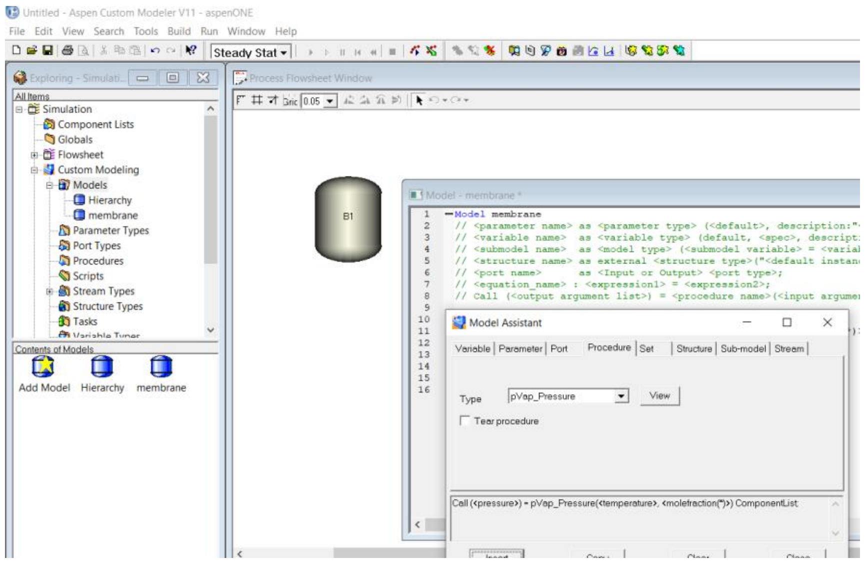


Aspen Plus **Aspen Hysys**	Can be used for batch and continuous processes for design, troubleshooting in regular operations, monitoring the plant performance through online, and real-time optimization.
gPROMS	An advanced equation oriented process modeling software, which can be used to model, analyze, and optimize in an easy-to-use process flow-sheeting environment.
PRO/II	A steady-state simulator which has an in-built membrane unit operation to simulate crossflow symmetric membranes for gas separations.
ProMax	A multifaceted process simulation software which it is designed to optimize gas processing, refining, and chemical facilities.
SuperPro Designer	A flowsheet driven simulator for batch, continuous as well as combination processes, that perform material and energy balances, equipment sizing, and costing.
Aspen Custom Modeler	Provides the capability to create unique process and equipment simulation models by describing the equations which can be exported into Aspen Plus/Hysys.

Implementation of Membrane model in Aspen Custom Modeler (ACM)

- Some process models like membrane separation are <u>not available in Aspen Plus</u>.
- The developed mass transfer model for the gas separation membrane process is coded by MATLAB.
- The model for membrane gas separation can be implemented and solved in ACM, which can be added to Aspen Plus.
- To implement the membrane model in ACM, all chemicals are defined from the component list in the Aspen Properties User Interface program.
- Fixed variables or inputs (feed temperature, pressure, composition and membrane area) are defined, and the process parameters (for example, permeance) and variables are declared.
- The model has one port for feed stream and two ports as permeate and retentate streams.





R. Kancherla et al., Computers & Chemical Engineering, 148 (2021) 107258.

Economic model

- In order to find the best configuration of the multi-stage gas membrane process, the cost analysis was conducted for:
  - Post-combustion
  - Natural gas sweetening
  - Biogas upgrading
- The aim was to minimize the cost of separation while satisfying the separation targets.
- The economic analysis of the superstructure membrane process was performed by calculating the capital cost, annual operating and maintenance, and energy cost.
- Capital cost is associated with membrane area and membrane module skids as well as the contribution of major components such as compression, expander and vacuum pumps.
- Operational cost is a sum of electricity cost, and operation and maintenance costs. Operation and maintenance of the vacuum pumps, expander and compressors is estimated at 3.6% of their capital cost and 1% for the membrane and the membrane frame.

BioCoMem

Economic model

Description		
Membrane module cost	C_m	$\$/m^2$
Compressor unit cost	C_c	$/kW
Expander unit cost	C_{ex}	$/kW
Vacuum pump unit cost	C_v	$/kW
Efficiency of pressure units	η	-
Installation factor	f_{in}	-
Electricity cost	C_e	$\$/kWh^{-1}$
Operation time per year	t_{op}	h/yr
Depreciation factor (25 years)	DF	-
Membrane depreciation factor (5 years)	DF_m	-
Membrane frame cost	$I_{m,fram} = 0.238 \times 10^6 \times \left(\frac{A_{t,mem}}{2000}\right)^{0.7} \left(\frac{P_t}{55}\right)^{0.88}$	$
Compressor cost	$CC = C_c \times W_c \times f_{in}$	$
Expander cost	$CE = C_{ex} \times W_{ex} \times f_{in}$	$
Vacuum pump cost	$CV = C_v \times W_{vp} \times f_{in}$	$
Total capital cost	$TCC = DF_m(C_m \times A_{t,m}) + DF(I_{m,fram} + CC + CE + CV)$	$/y
Operating and maintenance cost	$OMC = 0.01(C_m A_{t,m} + I_{m,fram}) + 0.036(CC + CE + CV)$	$/y
Energy cost	$EC = C_e \times t_{op} \times \sum W$	$/y
Total operational cost	$VOM = OMC + EC$	$/y
Gas processing cost	$GPC = \frac{TCC+VOM}{annual\ separated\ CO_2}$	$\$/tonne\ CO_2$

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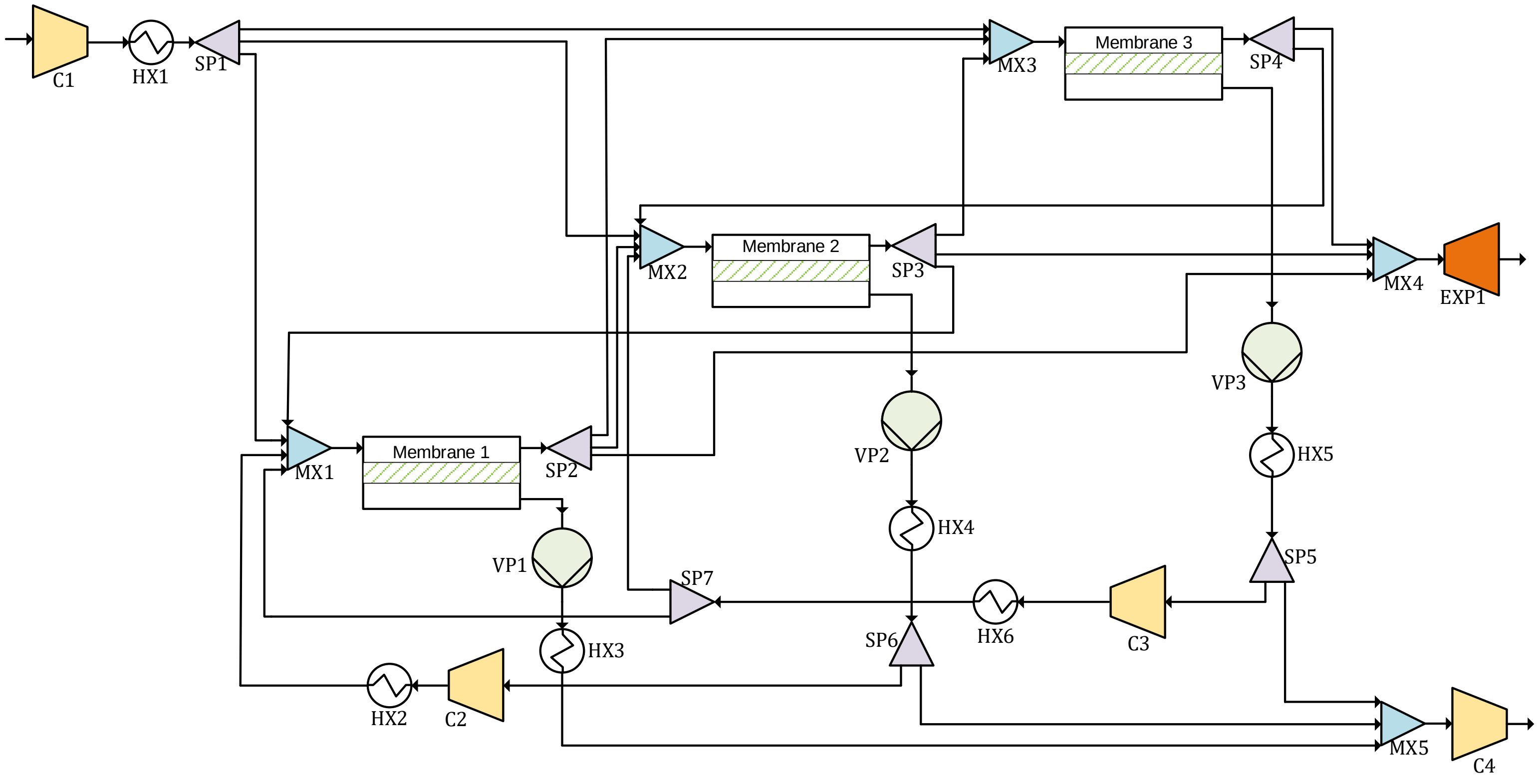
Energy Convers Manag. 246 (2021) 114633.
J Memb Sci. 598 (2020) 117796.

Optimization



- A structural optimization approach was applied to determine the most efficient membrane strategy from the point of view of gas separation cost.

- Membrane area of each stage
- Retentate pressure
- Permeate pressure of each stage
- Split fractions

Optimization

Input variables

- Feed conditions
- Membrane selectivity
- Gas permeance
- Target pressure

CO_2 or CH_4 purity
CO_2 or CH_4 recovery
Minimum GPC

Output variables

- ✓ Compressor power
- ✓ Membrane area
- ✓ CAPEX
- ✓ OPEX
- ✓ GPC
- ✓ Number of stages

Biogas Upgrading

- Biogas is a potential alternative to the world's unquenchable demand for energy and concurrently reduces waste and greenhouse gas emissions.
- CO_2 is the non-combustible portion of biogas.
- CO_2 has to be removed from CH_4 to enhance the heating value of the product gas.
- CH_4 mole fraction in the raw gas of 60% has to be increased to more than 90% in order to meet the natural gas grid requirements.
- CH_4 purity and recovery are the most important technical parameters in determining an optimal module arrangement in order to ensure a low CH_4 loss.

Feed gas characteristic	Feed flow rate	44 kmol/hr
	Feed temperature	298.15 K
	Feed pressure	1 bar
	Feed composition	40 % CO_2
		60 % CH_4
Output targets	CH_4 recovery	90 %
	CH_4 purity	95 %
	Product pressure	16 bar

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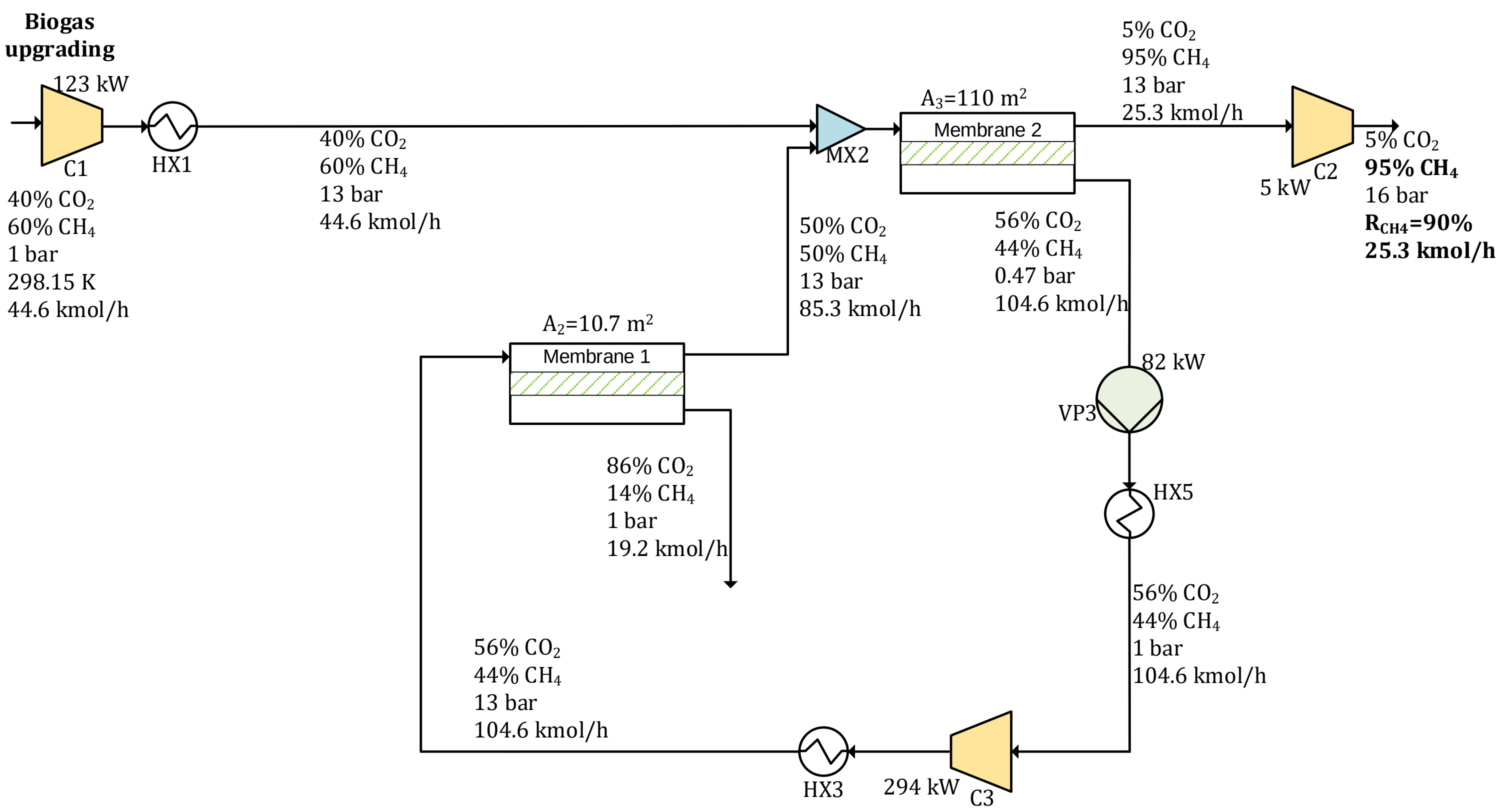
Biogas Upgrading



Variable	Biogas upgrading
CO_2/CH_4 selectivity	7.9
Methane recovery	90 %
Methane purity	95 %
Number of membrane stages	2
TCC	38899 €/yr
OMC	21225 €/yr
EC	202364 €/yr
Total power	505 kW
Power recovered in expander	-
Total net power	505 kW
Total membrane area	121 m^2
Operating pressure	13 bar
GPC	69.8 €/ton product

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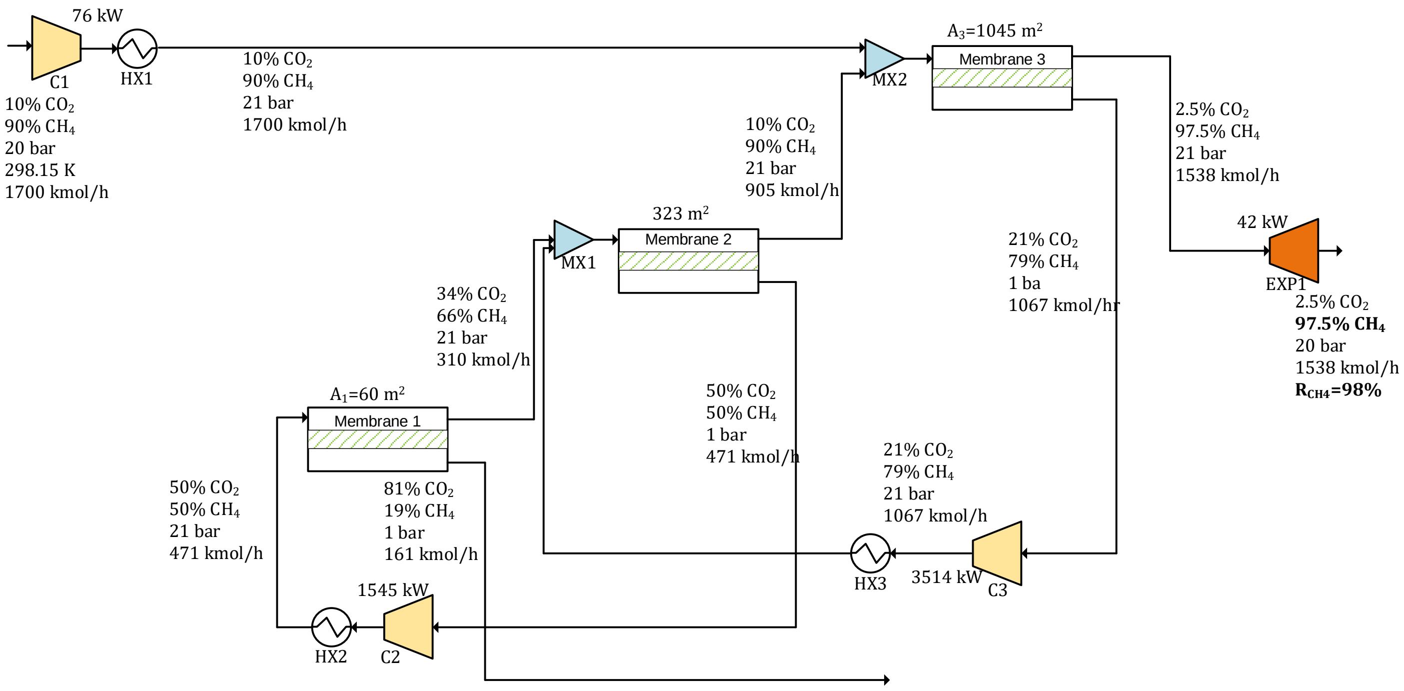
Natural gas separation

- CO_2 separation from natural gas is critical as the presence of CO_2 adversely affects the produced gas quality, and can form acids in the presence of water that corrodes the pipelines and equipment.

- To satisfy the legal requirements and gas grid specifications, CO_2 content in natural gas needs to be decreased to below 2%.

Feed gas characteristic	Feed flow rate	1700 kmol/hr
	Feed temperature	298.15 K
	Feed pressure	20 bar
	Feed composition	10 % CO_2
		90 % CH_4
Output targets	CH_4 recovery	98 %
	CH_4 purity	97.5 %
	Product pressure	20 bar

Natural gas separation



Variable	Natural gas
CO_2/CH_4 selectivity	7.9
Methane recovery	98 %
Methane purity	97.5 %
Number of membrane stages	3
TCC	345096 €/yr
OMC	186372 €/yr
EC	2.03×10^6 €/yr
Total power	5096 kW
Power recovered in expander	42 kW
Total net power	5054 Kw
Total membrane area	1428 m^2
Operating pressure	21 bar
GPC	17.4 €/ton NG

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Post-combustion CO_2 capture

The multi-stage membrane process is investigated in terms of

- capture cost
- energy consumption
- membrane area

The effects of membrane selectivity, CO_2 recovery and CO_2 purity on gas separation cost, CAPEX, OPEX and power consumption were examined.

Feed characteristic	Feed flow rate	2000 kmol/hr
	Feed temperature	308.15 K
	Feed pressure	1 bar
	Feed composition	14 % CO_2, 86 % N_2
	CO_2 emission	13 tons/hr
Output targets	CO_2 recovery	90 % and 95 %
	CO_2 purity	95 % and 98 %
	Product pressure	76 bar

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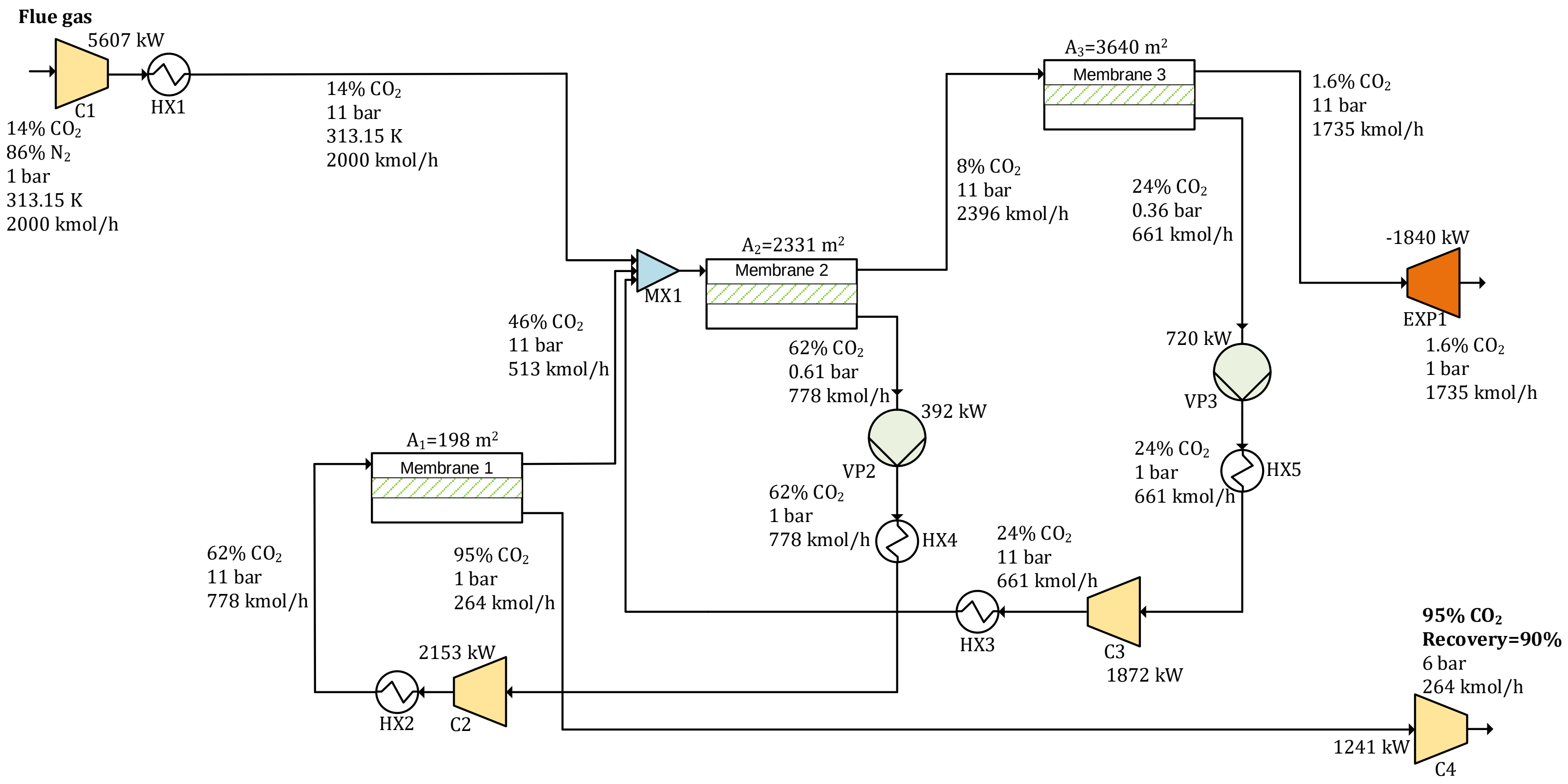
Post-combustion CO_2 capture

Optimal configuration from a capture cost point of view for CO_2 capture from flue gas with 90% CO_2 recovery and 95% purity.

Area=6170 m^2

GPC=59.6 €/ton CO_2

SEC=3.3 GJ/tonCO_2

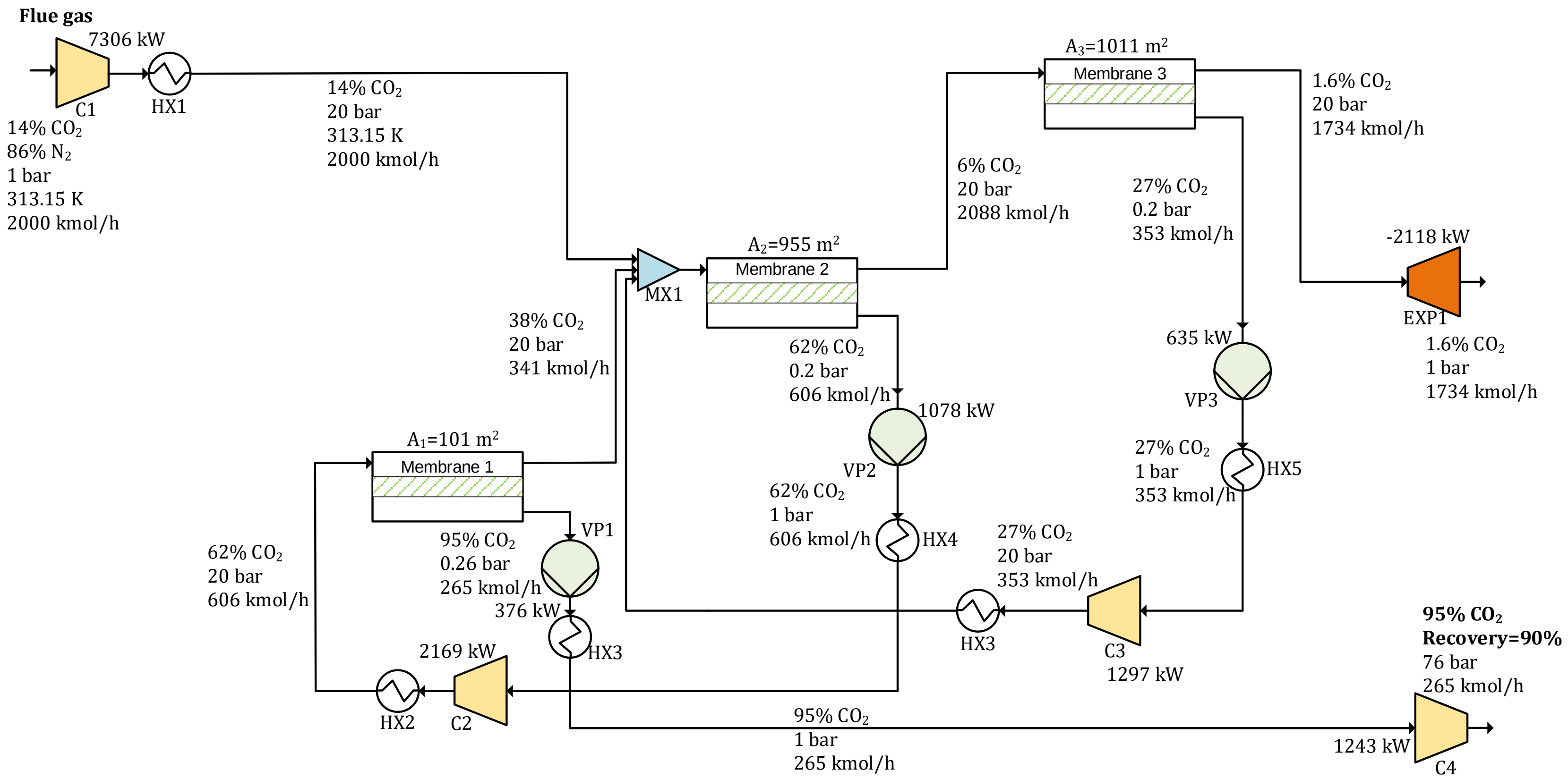


Post-combustion CO_2 capture

Optimal configuration from a membrane area point of view for CO_2 capture from flue gas with 90% CO_2 recovery and 95% purity.

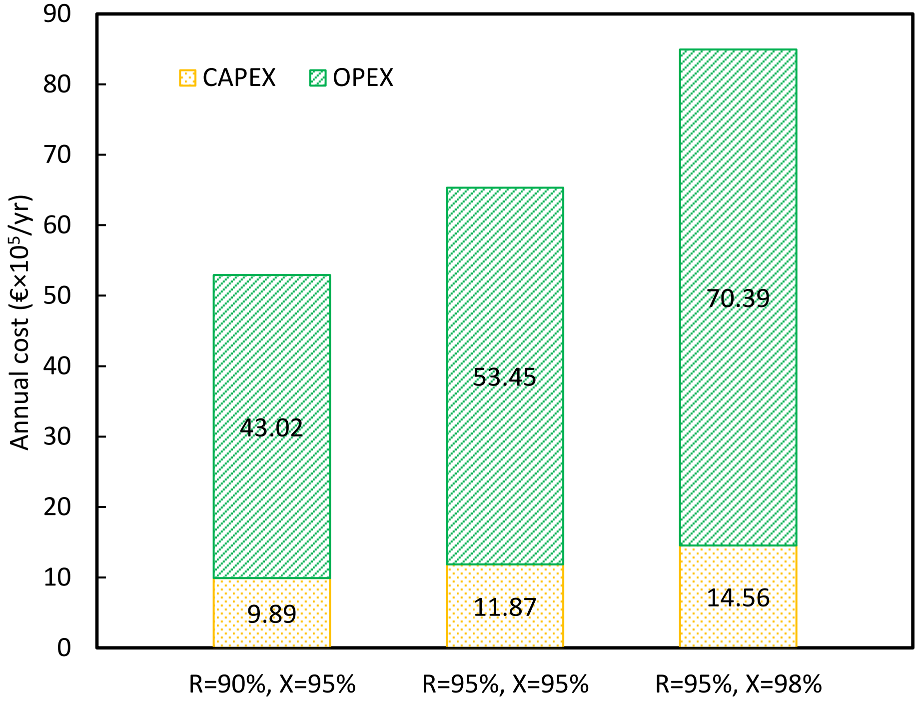
Area=2067 m^2

GPC=70 €/ton CO_2

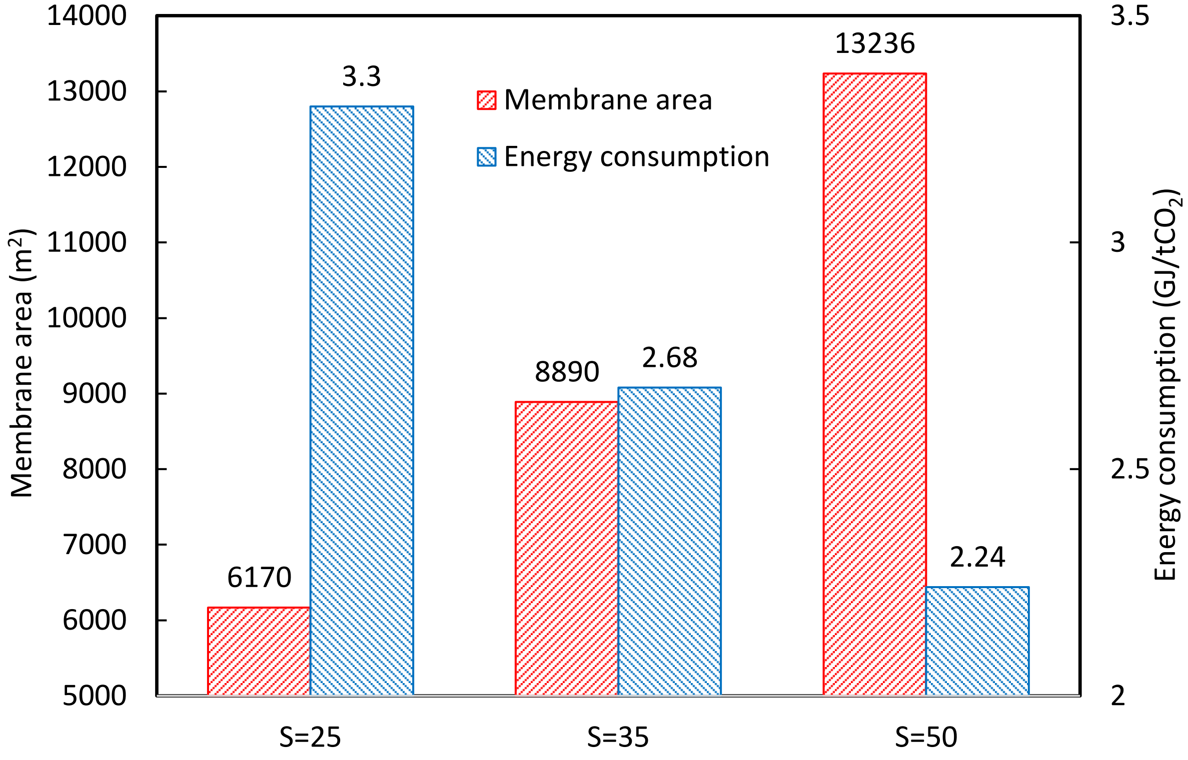


Post-combustion CO_2 capture

CO_2 recovery	90%	95%	95%
CO_2 purity	95%	95%	98%
Number of membrane stages	3	3	3
TCC	989581 €/yr	$1.18*10^6$ €/yr	$1.45*10^6$ €/yr
VOM	$4.30*10^6$ €/yr	$5.34*10^6$ €/yr	$7.04*10^6$ €/yr
Total net power	10158 kW	12661 kW	16793 kW
Power recovered in expander	1840 kW	1954 kW	2107 kW
Total membrane area	6170 m^2	5928 m^2	4910 m^2
SEC (GJ/ton CO_2)	3.30	3.9	5.16
GPC (€/ton CO_2)	59.6	69.8	90.7



Post-combustion CO_2 capture



Improving the membrane selectivity from 25 to 50 reduces the gas processing cost by 28%, from about 59 €/tonCO_2 to 42 €/tonCO_2.

Bio-based copolymers for membrane end products for gas separations

Thank you

Membrane based Process Design and Economics

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