Bio-based copolymers for membrane end products for gas separations

Membrane-based Process Design and Economics

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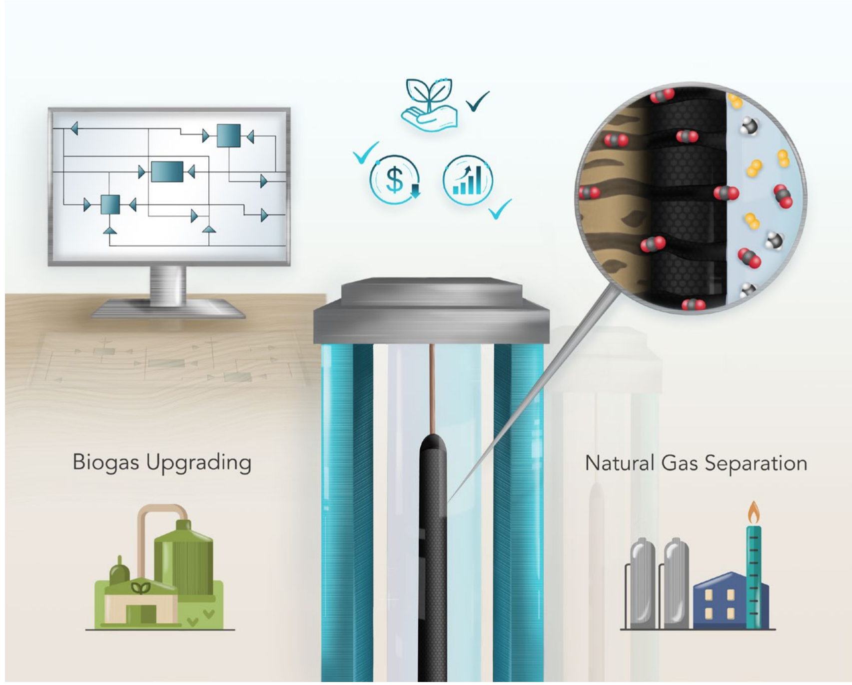
Membrane-based Gas Separation

- 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.
- An optimal flowsheet of membrane-based gas separation can remarkably decrease capture cost and energy consumption.
- The development of efficient and cost-effective multi-stage membrane processes as well as improvements in membrane selectivity and permeance is of major importance.



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

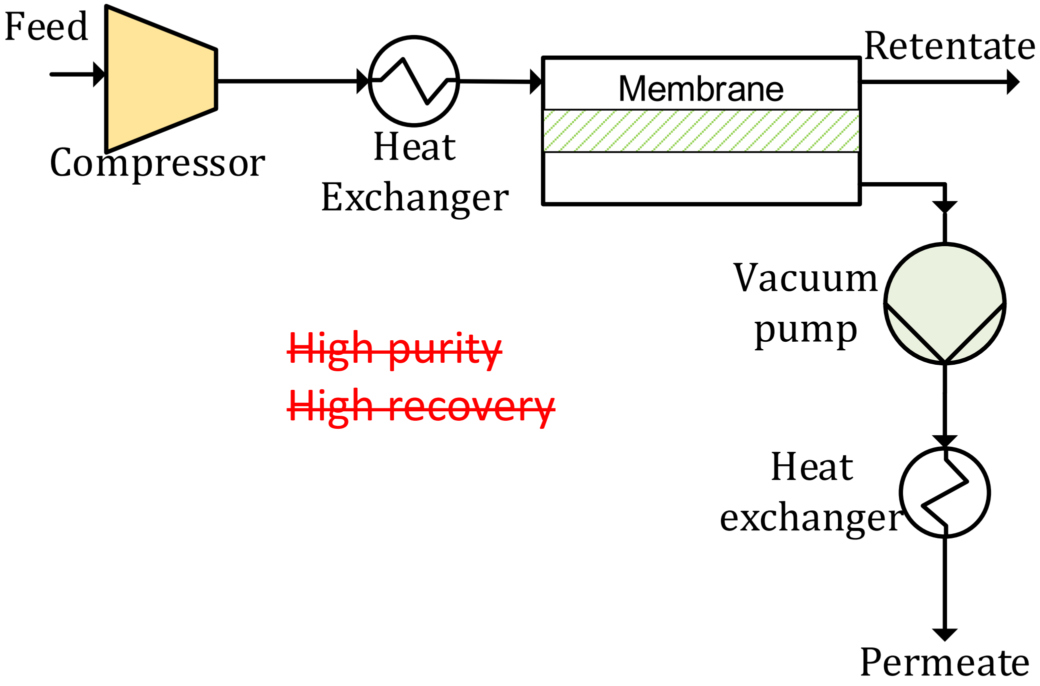
Select flow configuration

Select number of stages

Membrane type

Optimize the membrane system

Membrane-based process design (single stage)



~~High purity~~

~~High recovery~~

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

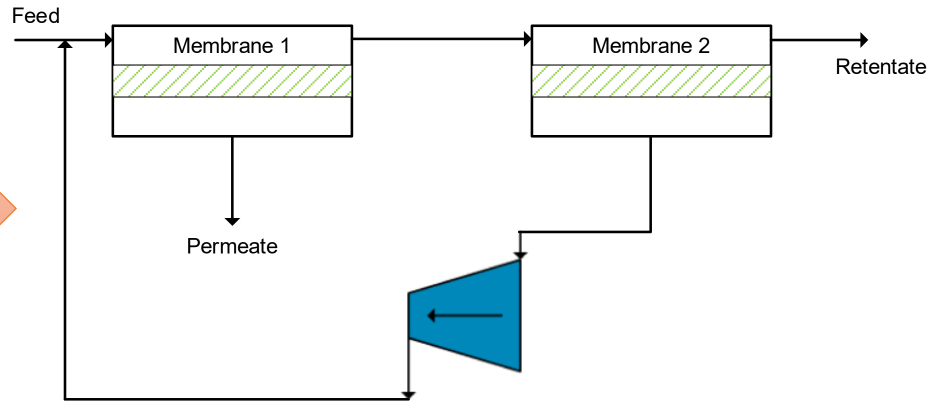
Two-stage cascade for purer retentate or permeate

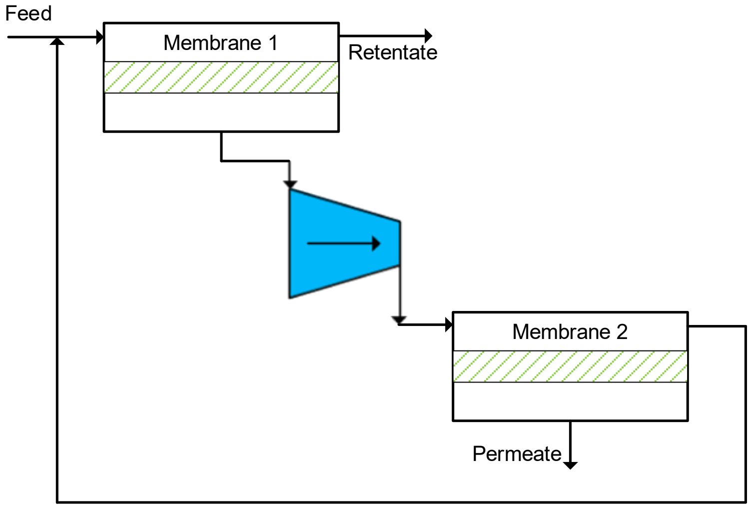
The raw gas is compressed and fed to the first membrane stage

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.

Permeate of the second stage is recycled and mixed with the raw gas stream



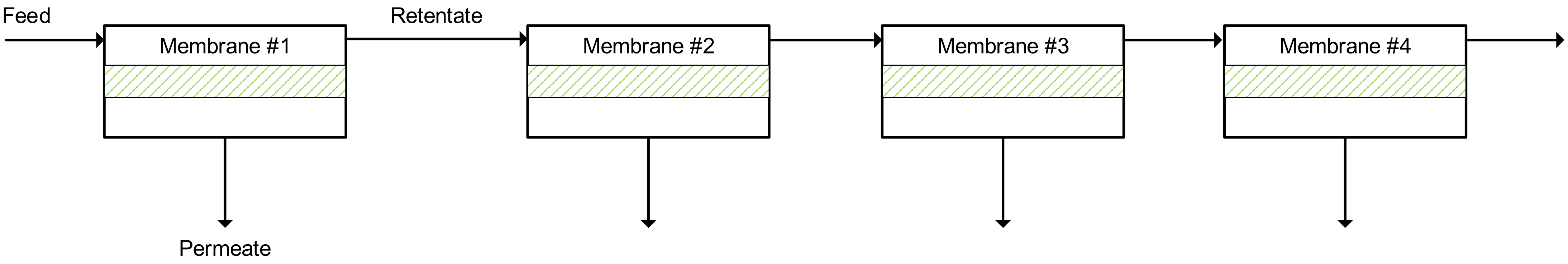


The permeate stream of the first membrane, after passing through a compressor, enters the second stage

The permeate stream of the second membrane is considered as the final product

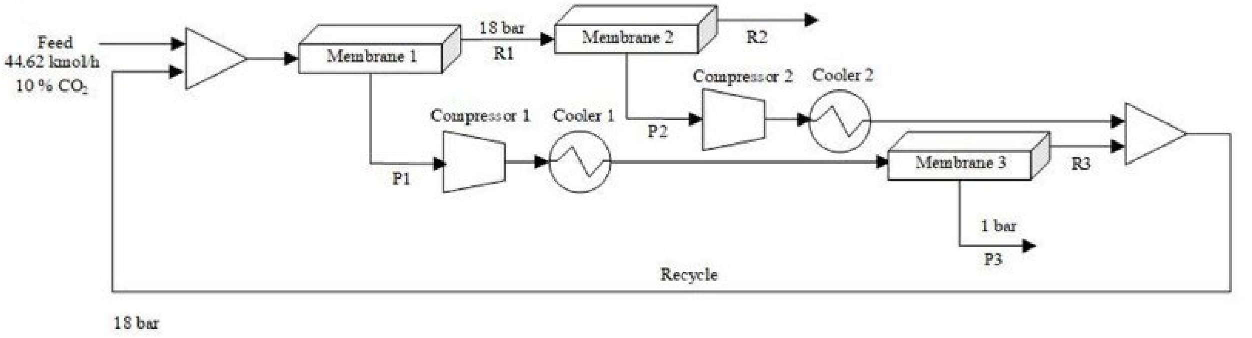
Multi-stage membrane module

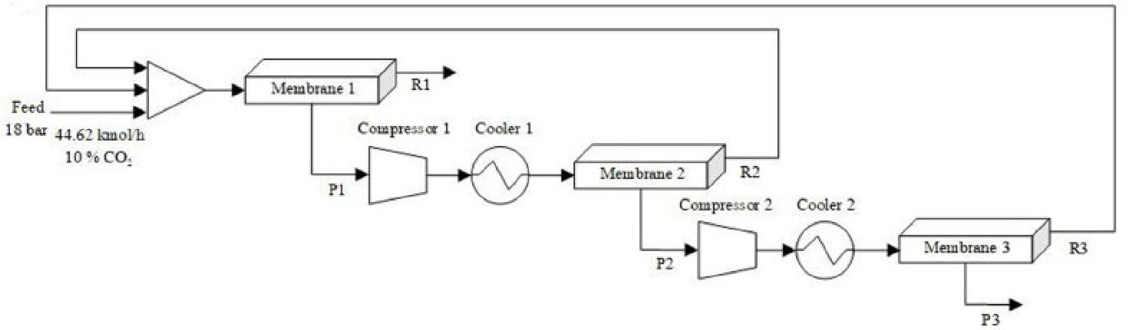
The selection of the best configuration is highly related to feed quality, separation objectives and market values.

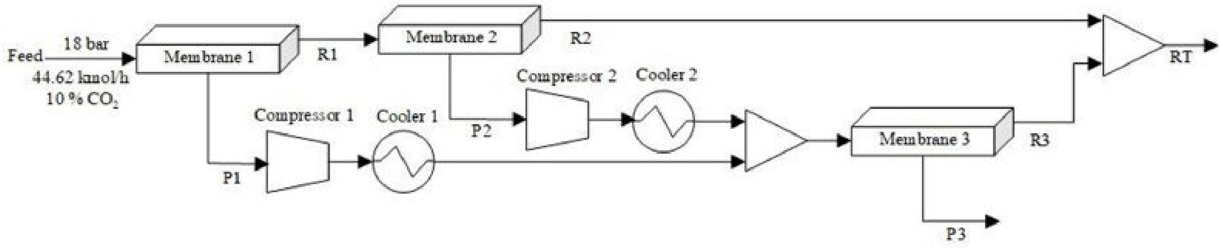


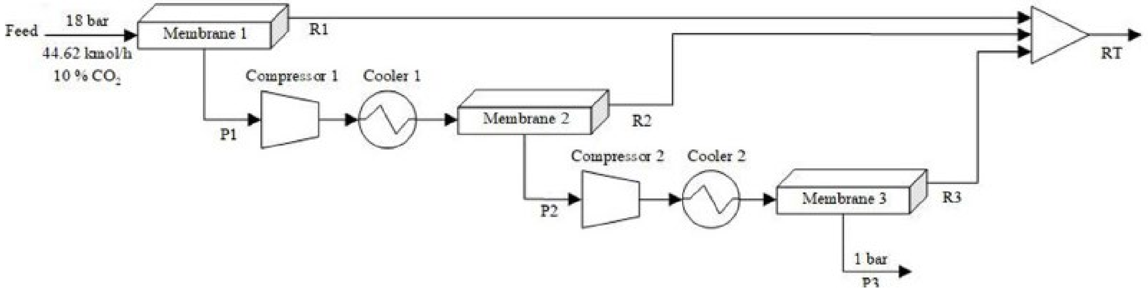
Three-stage membrane module

- In most of the literature's examined works, the optimization results were typically derived from heuristic design experience.
- Although using this approach does yield an optimum separation system but is in no way viable to assure whether the capture cost is a global optimum.





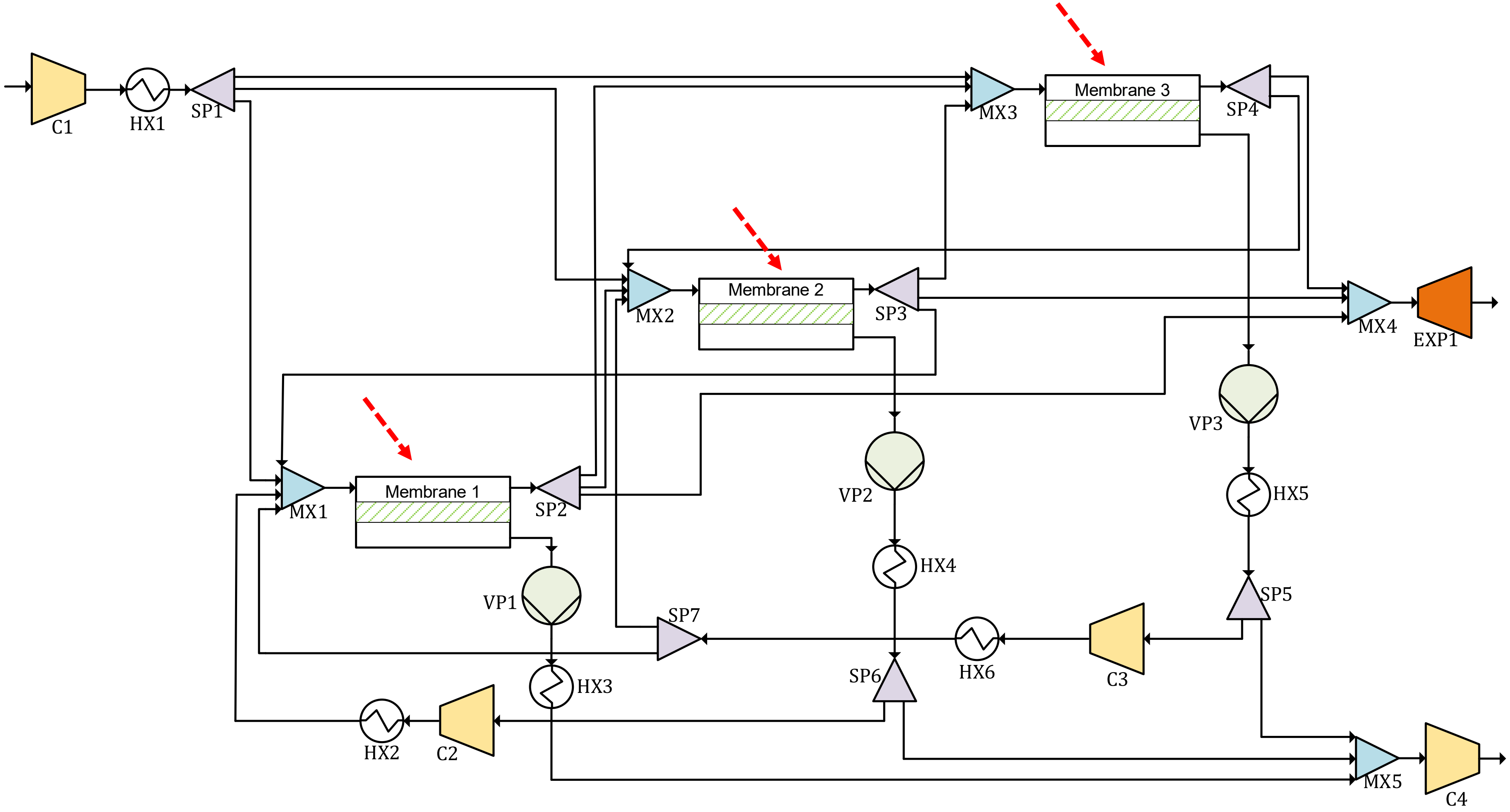


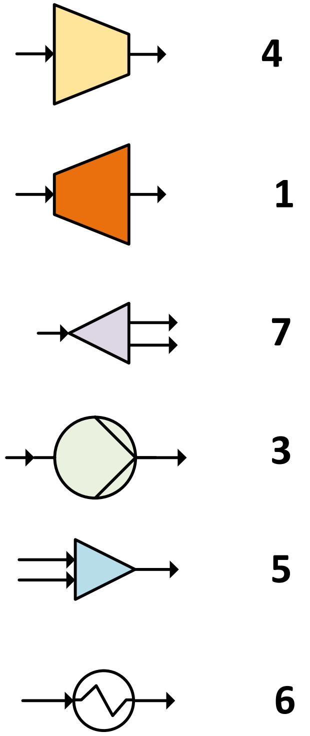


**M. Samei, A. Raisi, Chemical Engineering and Processing - Process Intensification, 170, 2022, 108676.*

Superstructure membrane module

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





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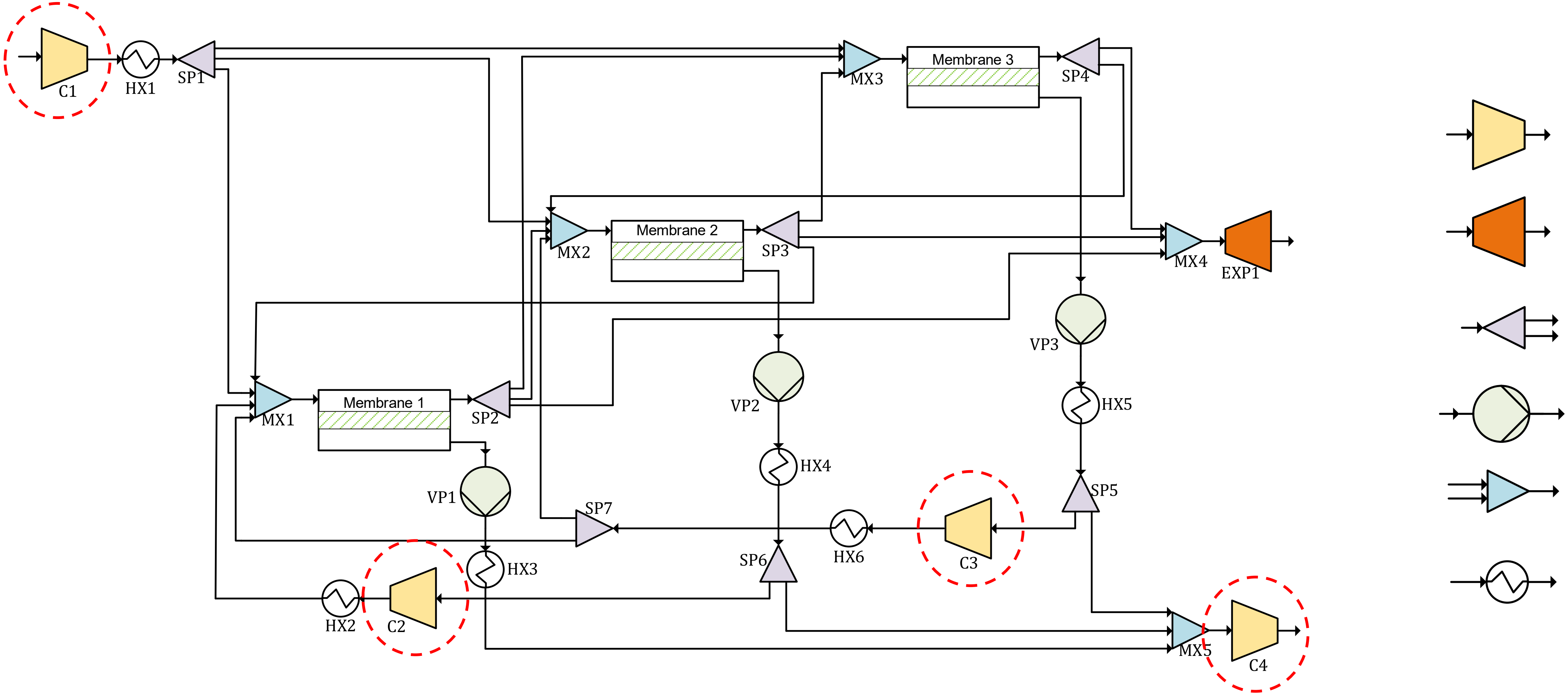

Superstructure membrane module

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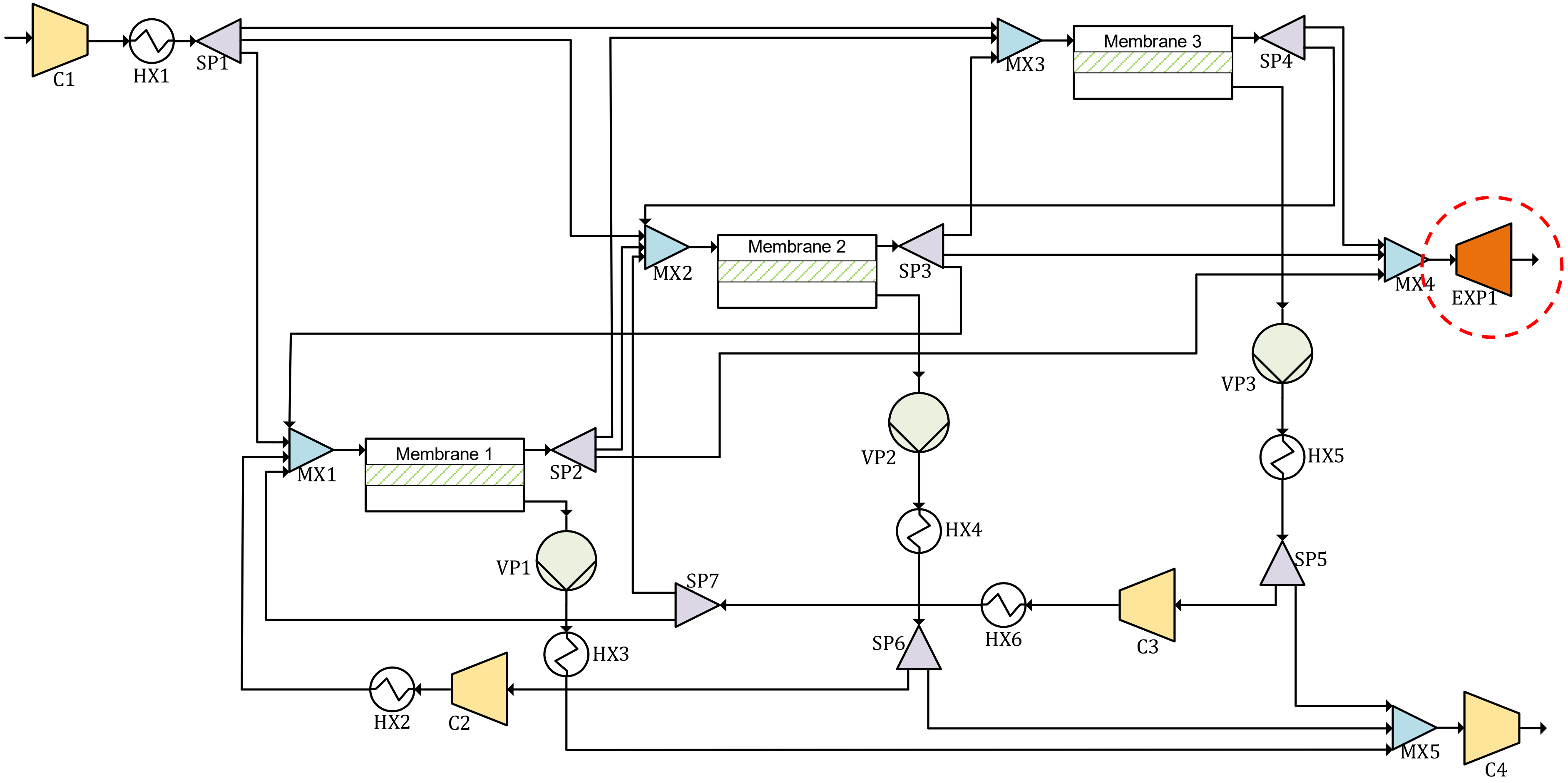

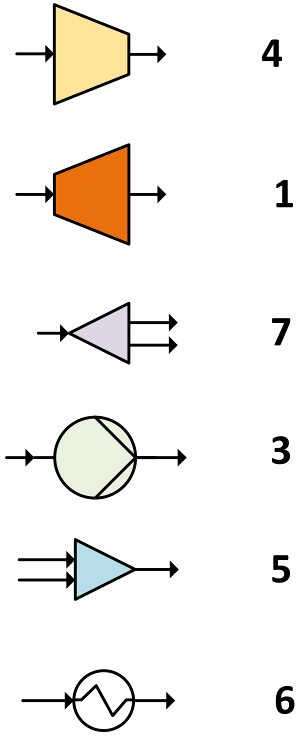

Superstructure membrane module

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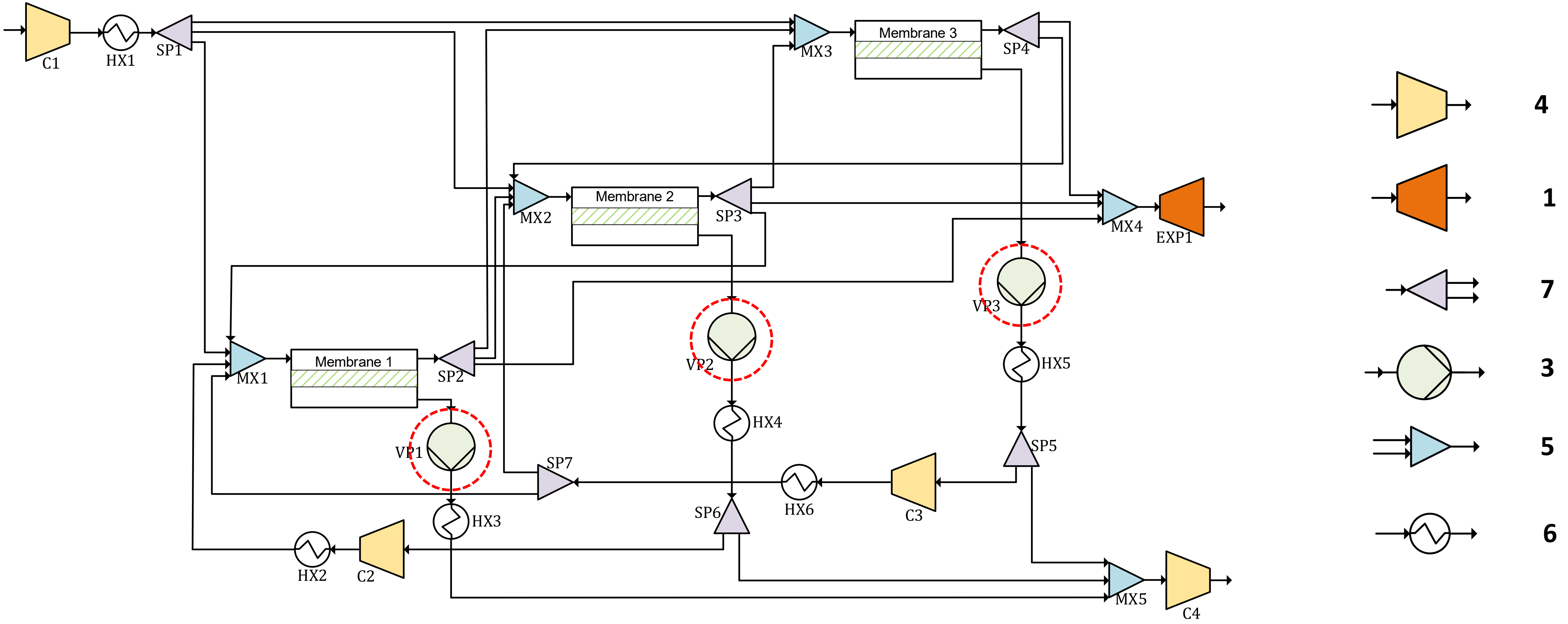

Superstructure membrane module

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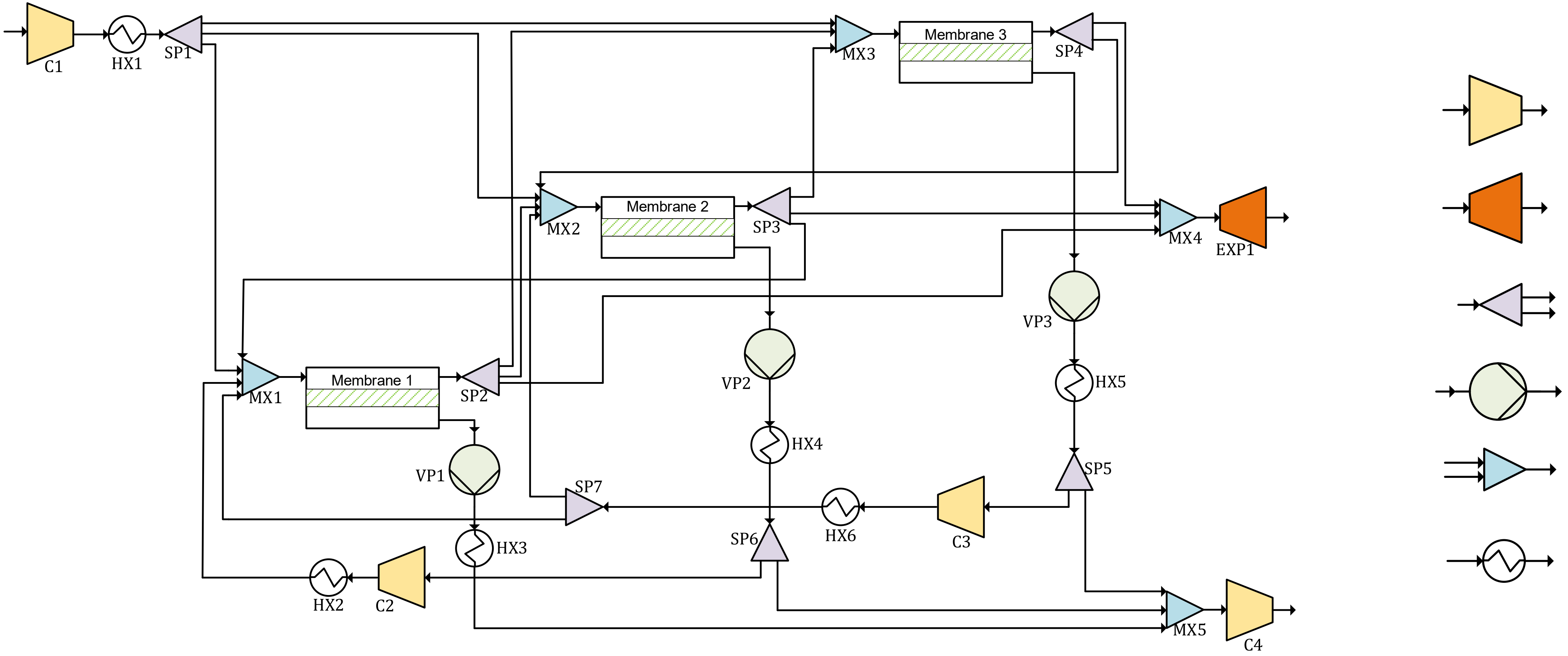
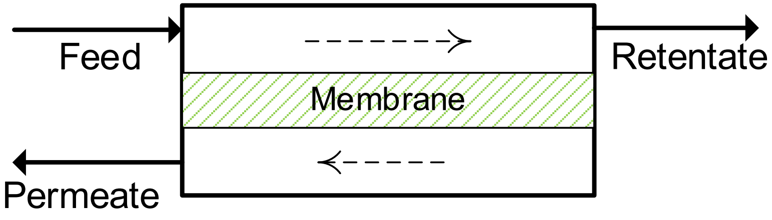


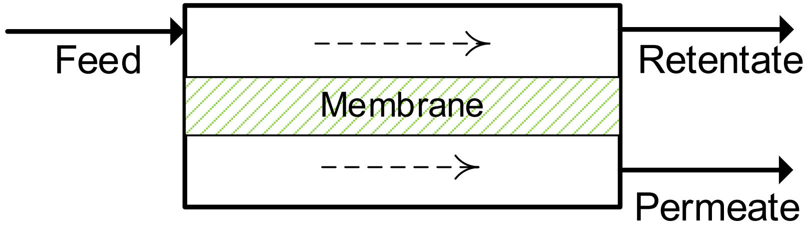
Flow arrangements in membrane modules

- ☐ 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.

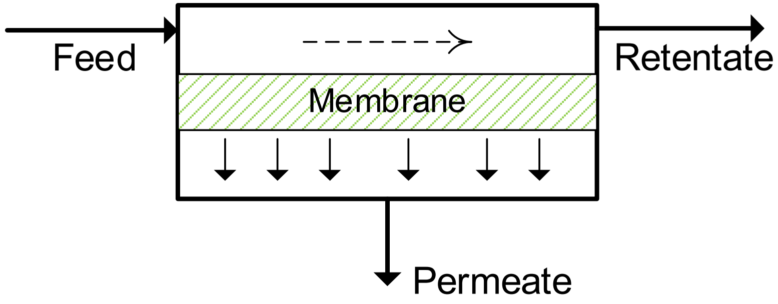
Counter-current Flow



Co-current Flow

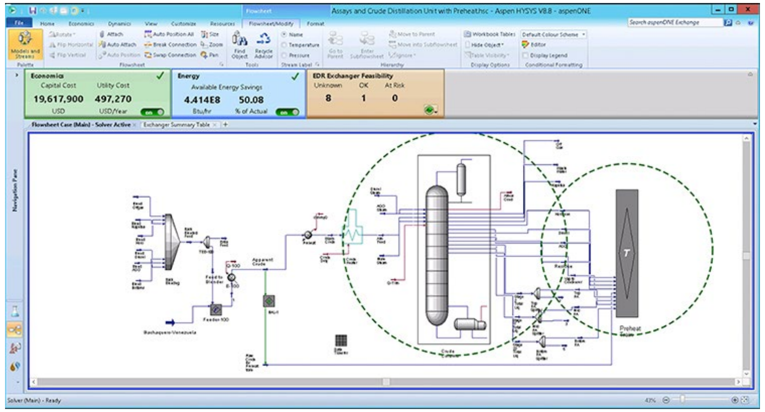


Cross Flow



Process Simulation Tools

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



Assays and Crude Distillation Unit with Preheat.hsc - Aspen HYSYS V8.8 - aspenONE

Economics: Capital Cost 19,617,900 USD; Utility Cost 497,270 USD/Year

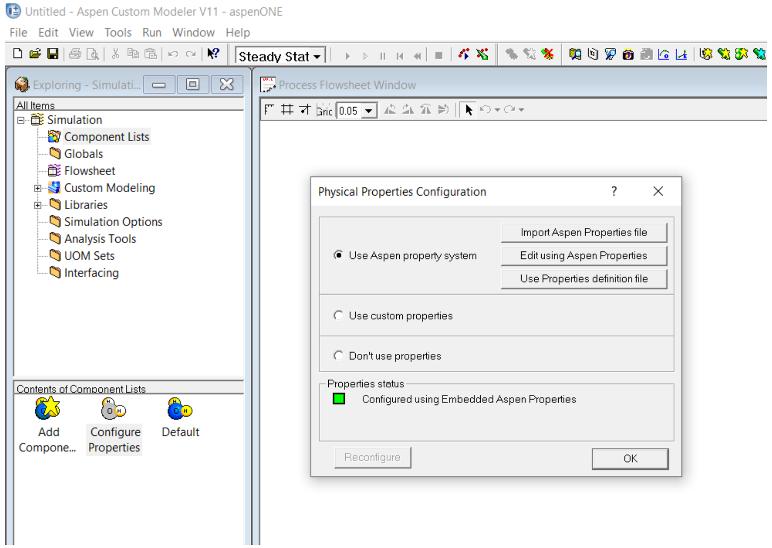
Energy: Available Energy Savings 4.414E8 Btu/hr; 50.08 % of Actual

EDR Exchanger Feasibility: Unknown 8; OK 1; At Risk 0

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

- The developed mass transfer model for the gas separation membrane process is coded.
- 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.



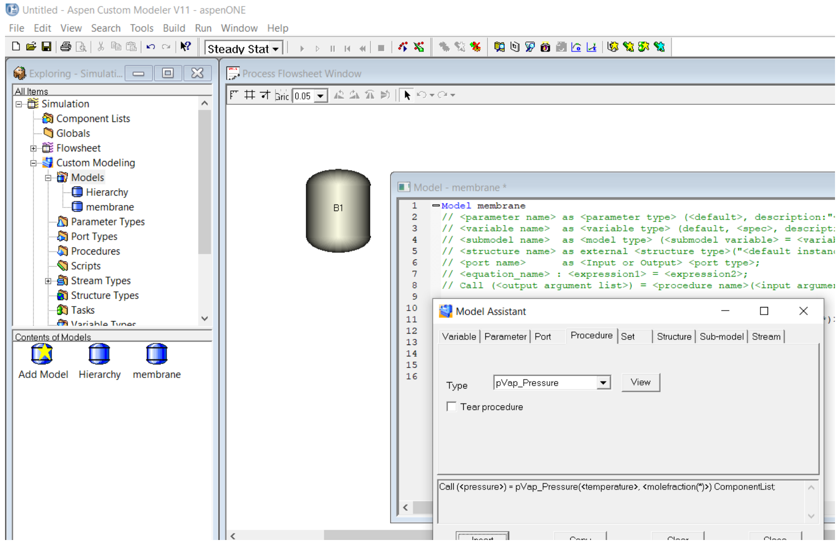
● Use Aspen property system

○ Use custom properties

○ Don't use properties

Properties status

🟩 Configured using Embedded Aspen Properties



```
Model membrane
// <parameter name> as <parameter type> (<default>, description:"
// <variable name>  as <variable type> (default, <spec>, descript
// <submodel name>  as <model type> (<submodel variable> = <varia
// <structure name> as external <structure type>("<default instan
// <port name>      as <Input or Output> <port type>;
// <equation_name> : <expression1> = <expression2>;
// Call (<output argument list>) = <procedure name>(<input argume
```

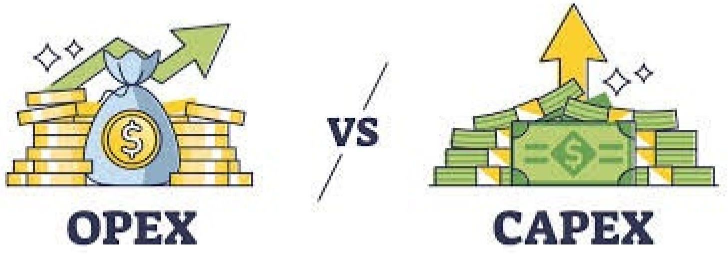
Type: pVap_Pressure

☐ Tear procedure

Call (<pressure>) = pVap_Pressure(<temperature>, <molefraction(*)>) ComponentList;

Economic model

☐ 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 is 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.

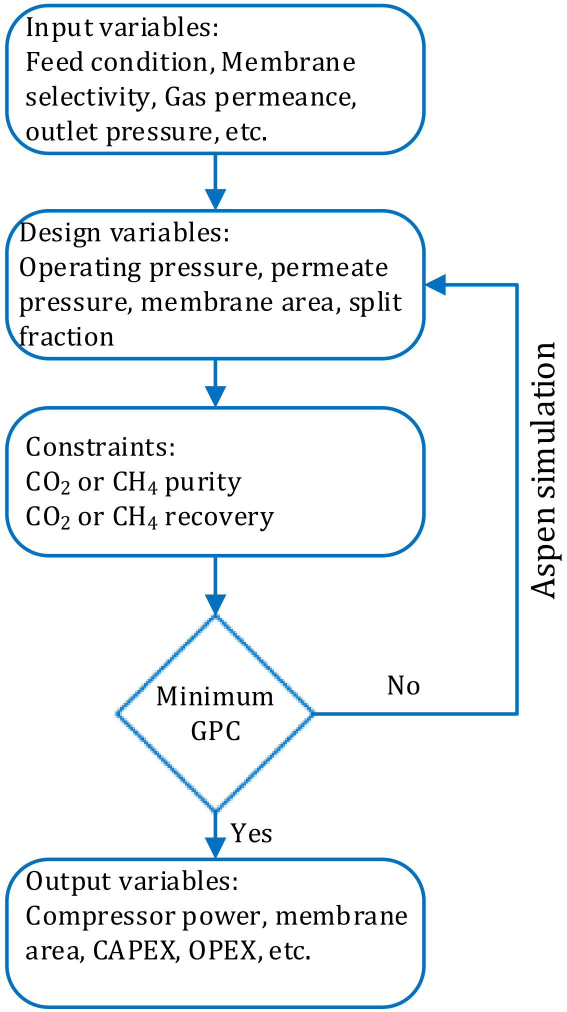
☐ **Operational cost** is a sum of electricity cost, and operation and maintenance costs. Operation and maintenance of the vacuum pumps, expander and compressors is estimated at 3.6% of their capital cost and 1% for the membrane and the membrane frame.

Economic model

Description		
Membrane module cost	C_m	$\$/\mathrm{m}^2$
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	$\$/\mathrm{kWh}^{-1}$
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	$TCC = DF_m\left(C_m \times A_{t,m}\right) + DF\left(I_{m,fram} + CC + CE + CV\right)$	$/y
Operating and maintenance cost	$OMC = 0.01\left(C_m A_{t,m} + I_{m,fram}\right) + 0.036(CC + CE + CV)$	$/y
Energy cost	$EC = C_e \times t_{op} \times \sum W$	$/y
Total operational cost	$VOM = OMC + EC$	$/y
Gas processing cost	$\boxed{GPC = \frac{TCC+VOM}{annual\ separated\ CO_2}}$	$\$/\text{tonne CO}_2$

Optimization strategy

- ➢ Input variables: Feed conditions, Membrane selectivity and gas permeance, target pressure, product specification
- ➢ Targets: CO_2 or CH_4 recovery and purity, minimum GPC
- ➢ Decision variables: Membrane area of each stage, retentate pressure, permeate pressure of each stage, split fractions
- ✓ Output variables: Compressor power, membrane area, CAPEX, OPEX, GPC, number of stages


Input variables:
Feed condition, Membrane selectivity, Gas permeance, outlet pressure, etc.

Design variables:
Operating pressure, permeate pressure, membrane area, split fraction

Constraints:
CO_2 or CH_4 purity
CO_2 or CH_4 recovery

Minimum GPC

Output variables:
Compressor power, membrane area, CAPEX, OPEX, etc.

1. Post-combustion CO_2 capture

Post-combustion CO_2 capture should meet conditions of low energy consumption, small footprint, high CO_2 purity (≥ 90%) and recovery (≥ 90%), no adverse environmental impact, and minimal gas processing costs.

The flue gas produced from coal combustion has low CO_2 composition and a high-volume flow rate. For example, a 500 MW coal-fired power plant emits approximately 426 tons of CO_2 per hour

TFCM	Permeance (GPU)		Selectivity
	N_2	CO_2	CO_2/N_2
Prototype A	65	2027	31.0
Prototype A1	46	1598	34.4

Feed characteristic	
Feed flow rate	80,000 kmol/hr
Feed temperature	308.15 K
Feed pressure	1 bar
Feed composition	14 % CO_2 86 % N_2
CO_2 emission	505 tons/hr
Output targets	
CO_2 recovery	90 % and 95 %
CO_2 purity	95 % and 98 %
Product pressure	76 bar

1. Post-combustion CO_2 capture

Prototype A1

CO_2/N_2 selectivity=34.4

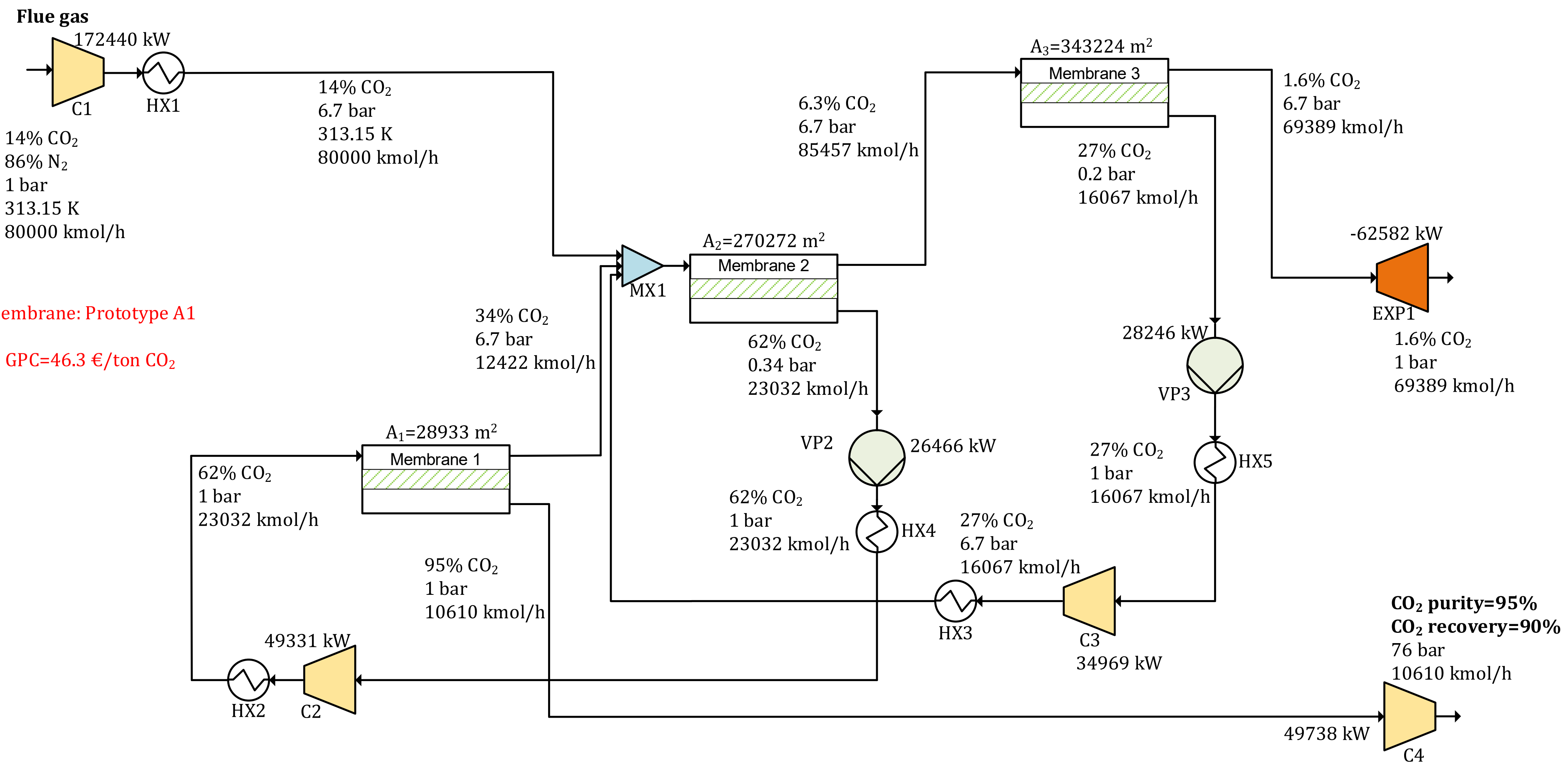
CO_2 purity= 95 %

CO_2 recovery=90 %

Area= 642430 m^2

GPC= 46.3 €/tonCO_2

SEC= 2.4 GJ/tonCO_2

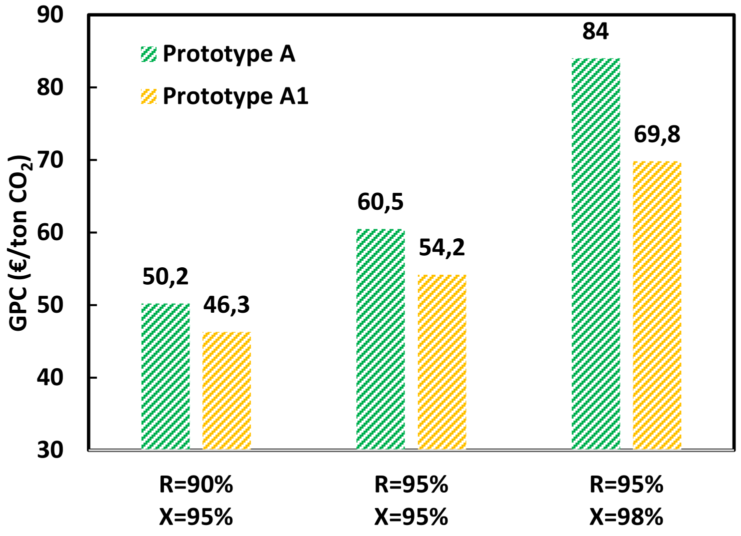


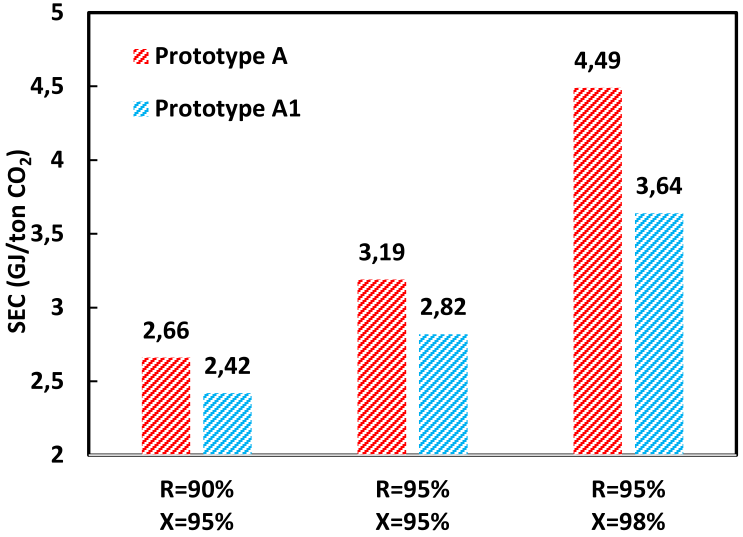
Membrane: Prototype A1

GPC=46.3 €/ton CO_2

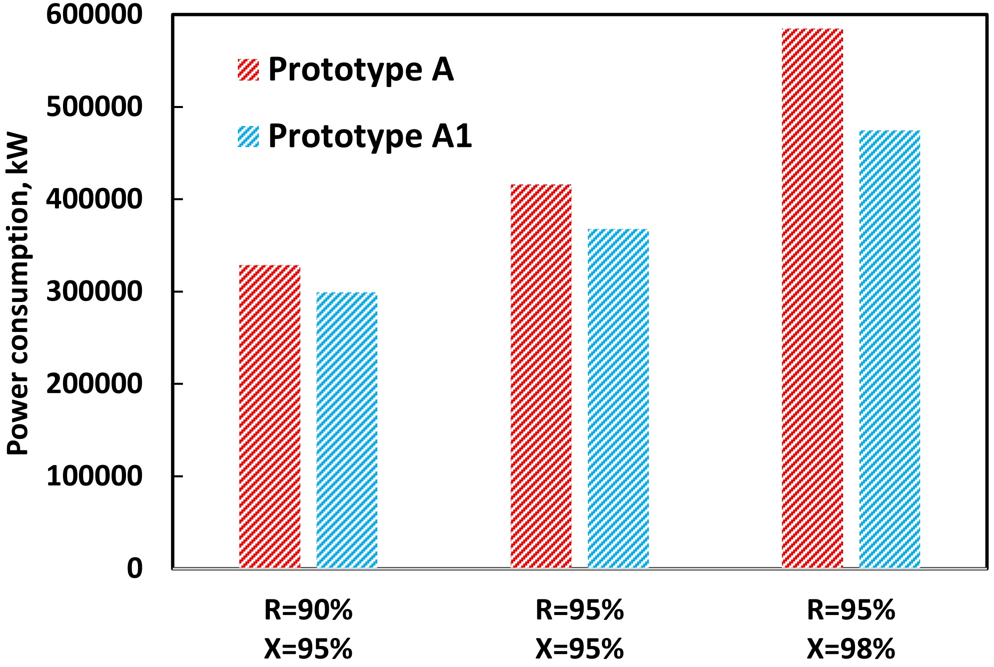
1. Post-combustion CO_2 capture

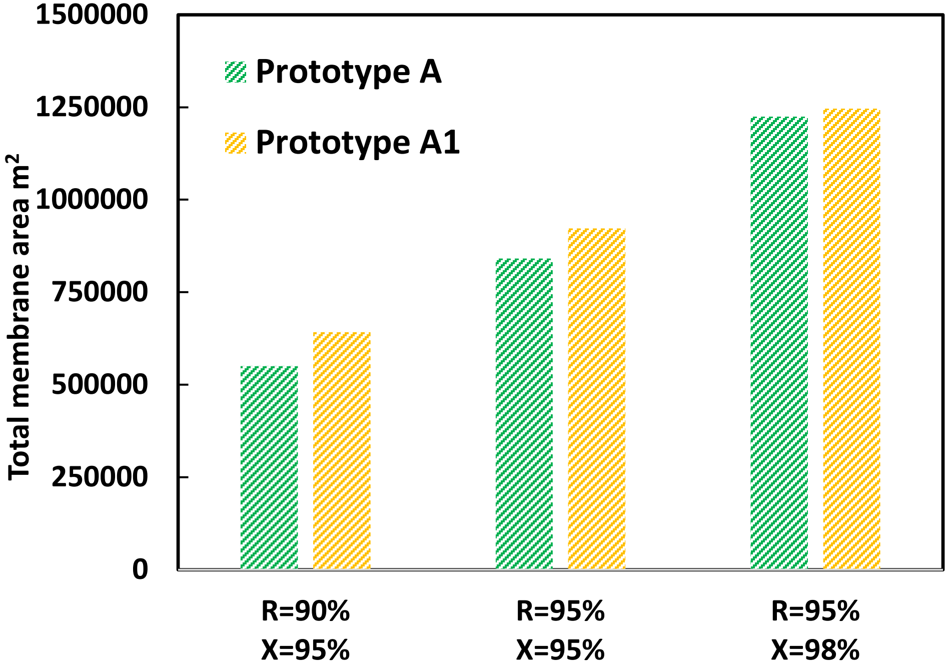
	Prototype A			Prototype A1		
CO_2 permeance	2027	2027	2027	1598	1598	1598
N_2 permeance	65	65	65	46	46	46
CO_2/N_2 selectivity	31	31	31	34.4	34.4	34.4
CO_2 recovery	90%	95%	95%	90%	95%	95%
CO_2 purity	95%	95%	98%	95%	95%	98%
Stages	3	3	3	3	3	3
CAPEX, *€/yr*	37×10^6	49×10^6	68×10^6	36×10^6	45×10^6	59×10^6
OPEX, *€/yr*	140×10^6	177×10^6	249×10^6	128×10^6	157×10^6	202×10^6
Power, *kW*	328,841	415,899	584,585	299,364	367,919	474,508
Membrane area, *m^2*	550,268	841,188	1,224,300	642,430	922,526	1,245,790
SEC, *$GJ/tonCO_2$*	2.66	3.19	4.49	2.42	2.82	3.64
GPC, *€/$tonCO_2$*	50.2	60.5	84	46.3	54.2	69.8





1. Post-combustion CO_2 capture





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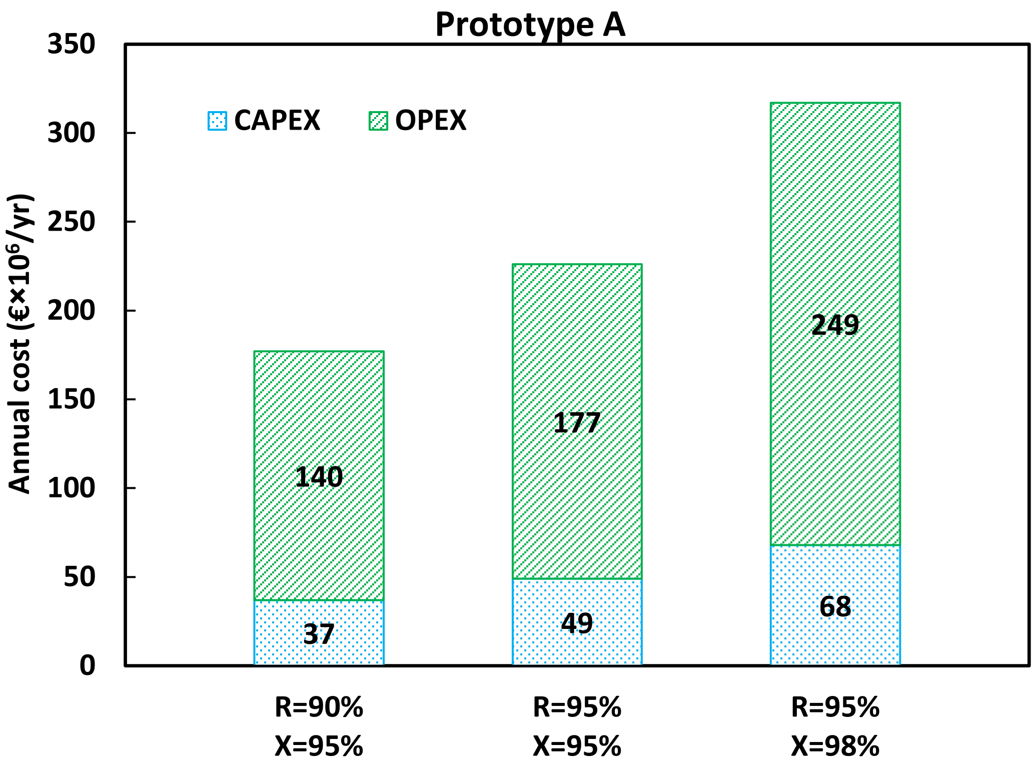
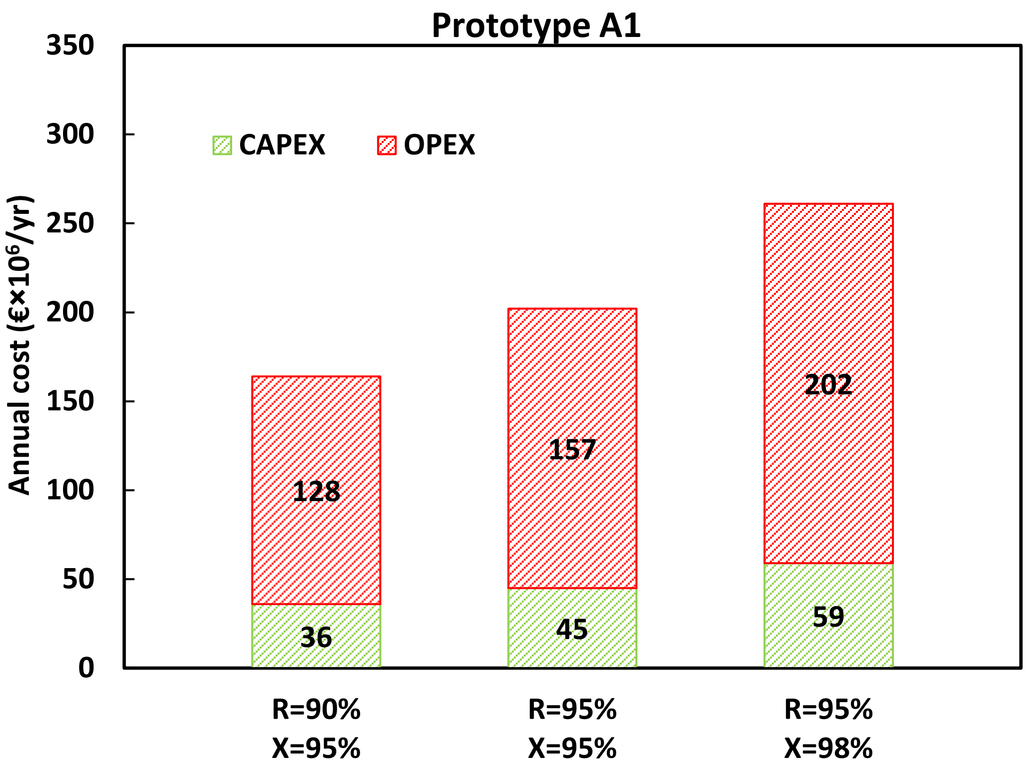




R=CO_2 recovery
X=CO_2 purity

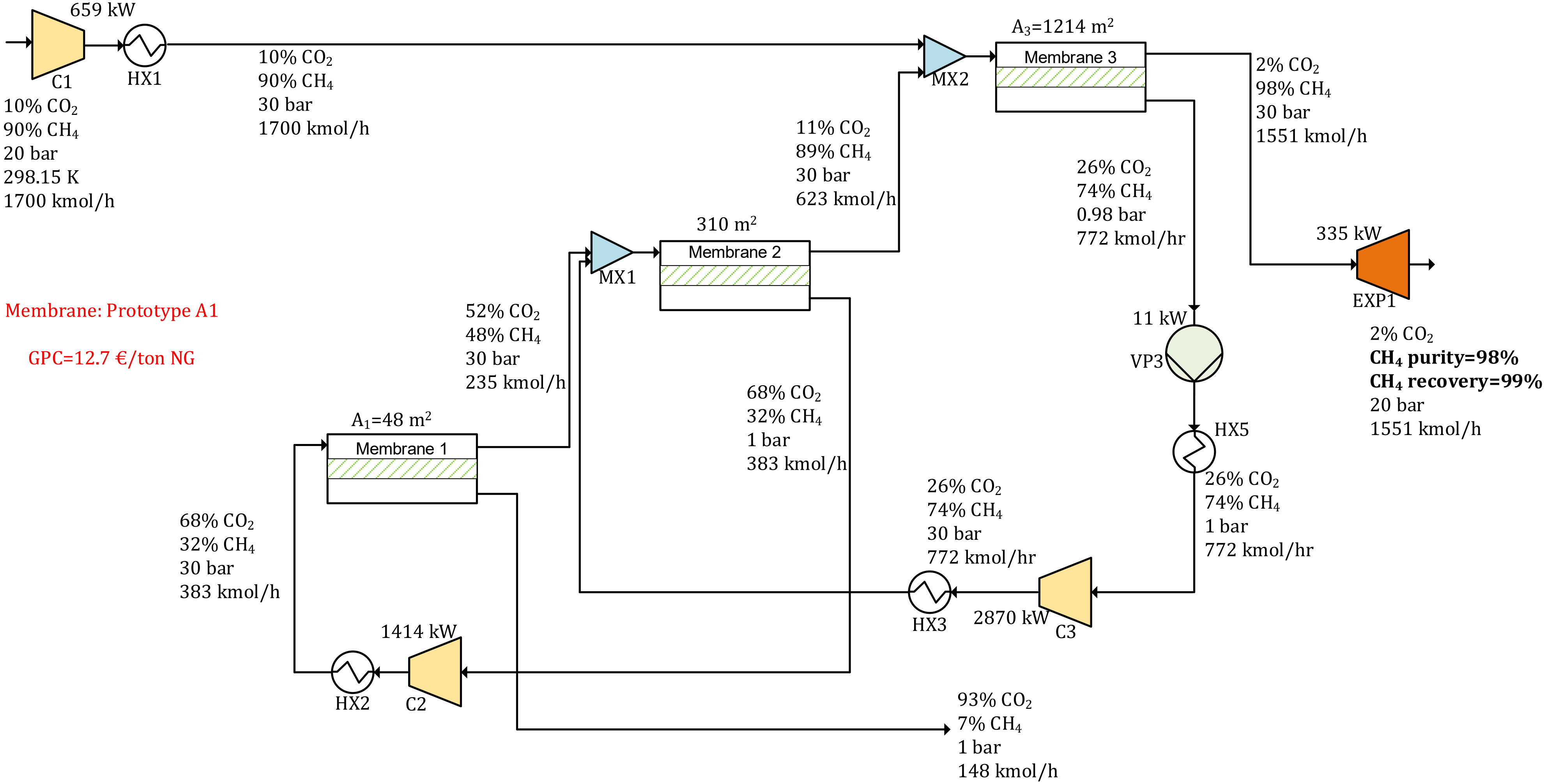
2. Natural gas separation

- ☐ Every year, the world uses close to 3.9 trillion cubic meters of natural gas.
- ☐ 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.
- ☐ CO_2 content in natural gas needs to be decreased to below 3%.

TFCM	Permeance (GPU)		Selectivity
	CH_4	CO_2	CO_2/CH_4
Prototype A	204	2027	9.9
Prototype A1	142	1598	11.2

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	99 %
	CH_4 purity	98 %
	Product pressure	20 bar

2. Natural gas separation



Natural gas

659 kW

10% CO_2
90% CH_4
20 bar
298.15 K
1700 kmol/h

10% CO_2
90% CH_4
30 bar
1700 kmol/h

A_3=1214 m^2

2% CO_2
98% CH_4
30 bar
1551 kmol/h

11% CO_2
89% CH_4
30 bar
623 kmol/h

26% CO_2
74% CH_4
0.98 bar
772 kmol/hr

310 m^2

335 kW

Membrane: Prototype A1

GPC=12.7 €/ton NG

52% CO_2
48% CH_4
30 bar
235 kmol/h

11 kW

2% CO_2
CH_4 purity=98%
CH_4 recovery=99%
20 bar
1551 kmol/h

68% CO_2
32% CH_4
1 bar
383 kmol/h

A_1=48 m^2

26% CO_2
74% CH_4
1 bar
772 kmol/hr

26% CO_2
74% CH_4
30 bar
772 kmol/hr

68% CO_2
32% CH_4
30 bar
383 kmol/h

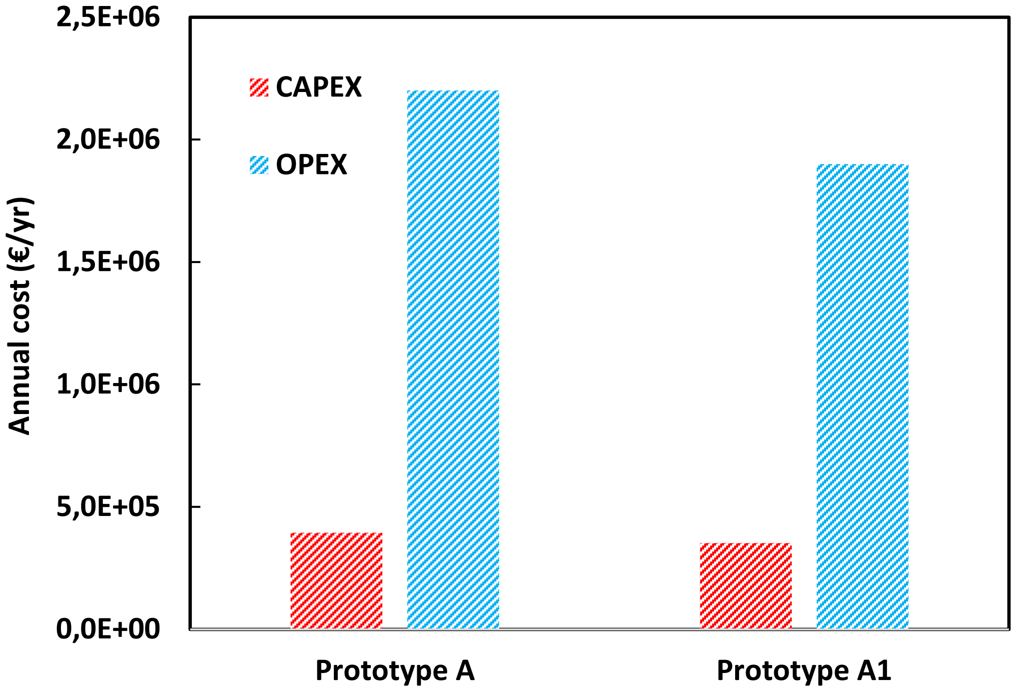
2870 kW

1414 kW

93% CO_2
7% CH_4
1 bar
148 kmol/h

2. Natural gas separation

	Prototype A	Prototype A1
CO_2 permeance	2027	1598
CH_4 permeance	204	142
CO_2/CH_4 selectivity	9.9	11.2
CH_4 recovery	99 %	99 %
CH_4 purity	98 %	98 %
Stages	3	3
CAPEX, *€/yr*	394000	352031
OPEX, *€/yr*	2.2×10^6	1.9×10^6
Power	5338 kW	4622 kW
Membrane area	1348 m^2	1574 m^2
GPC	15.0 €/ton NG	12.7 €/ton NG



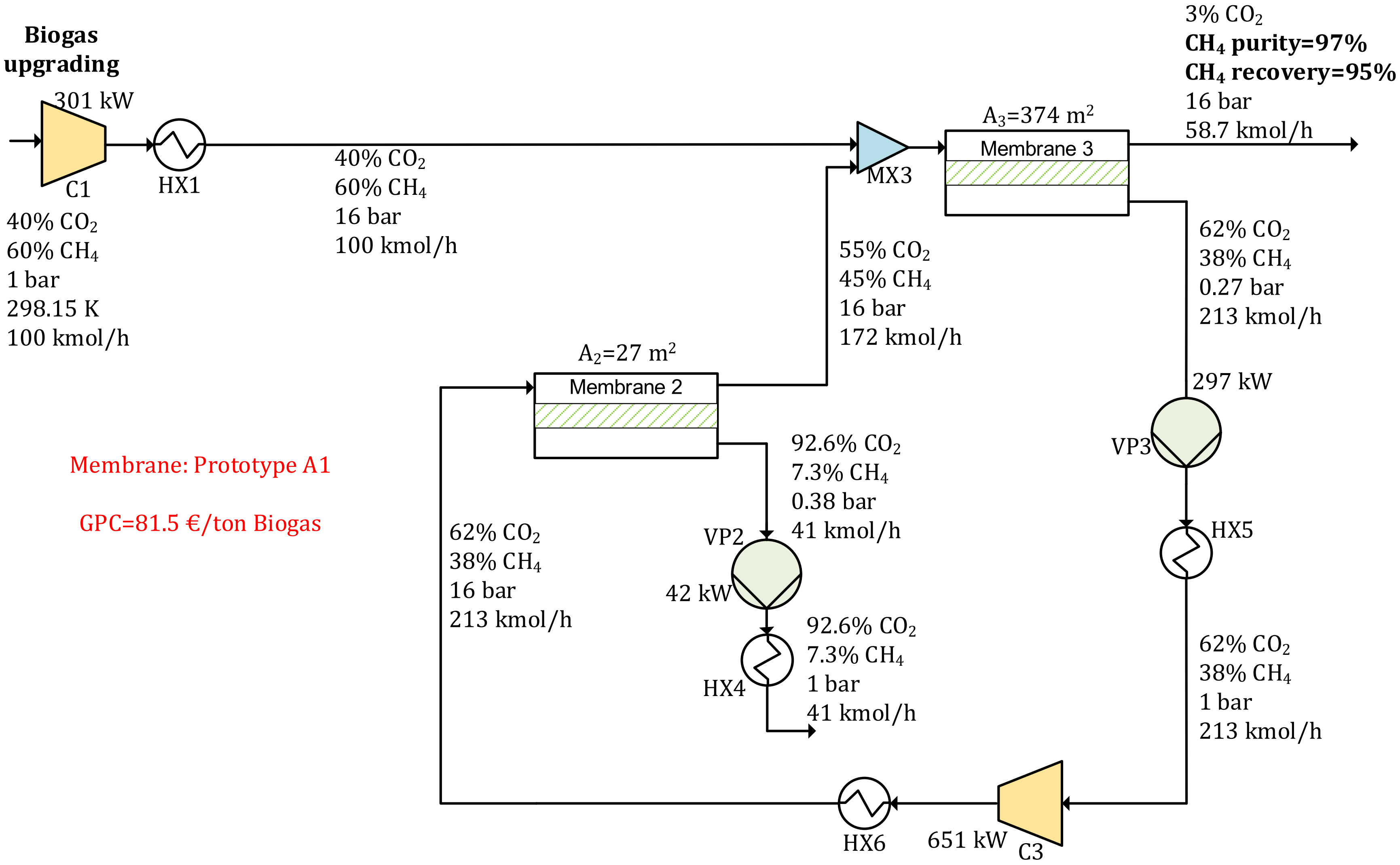
3. Biogas Upgrading

- 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 to ensure a low CH_4 loss.

Feed gas characteristic	Feed flow rate	100 kmol/hr
	Feed temperature	298.15 K
	Feed pressure	1 bar
	Feed composition	40 % CO_2 60 % CH_4
Output targets	CH_4 recovery	95 %
	CH_4 purity	97 %
	Product pressure	16 bar

TFCM	Permeance (GPU)		Selectivity
	CH_4	CO_2	CO_2/CH_4
Prototype A	204	2027	9.9
Prototype A1	142	1598	11.2

3. Biogas Upgrading

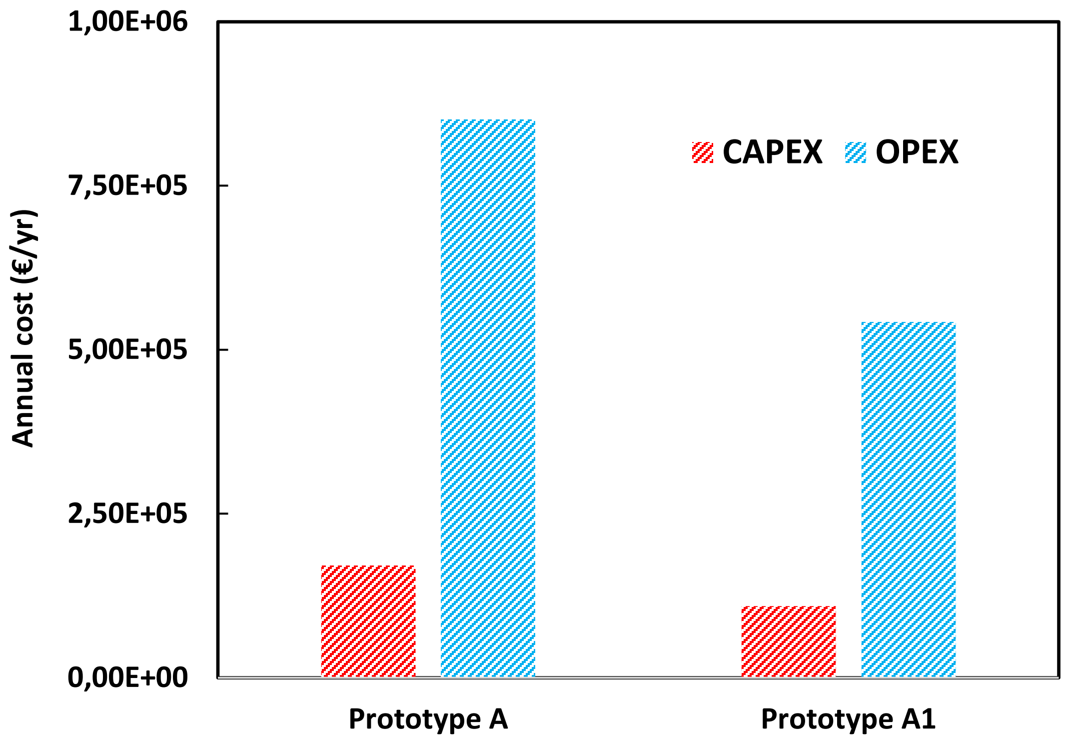


Membrane: Prototype A1

GPC=81.5 €/ton Biogas

3. Biogas Upgrading

	Prototype A	**Prototype A1**
CO_2 permeance	2027	1598
CH_4 permeance	204	142
CO_2/CH_4 selectivity	9.9	11.2
CH_4 recovery	95%	95%
CH_4 purity	97 %	97 %
Stages	2	2
CAPEX, €/yr	171019	109147
OPEX, €/yr	850959	542137
Power	2036 kW	1298 kW
Membrane area	490 m^2	402 m^2
GPC, €/ton Biogas	128.8	81.5



Conclusion

- The proposed superstructure is beneficial for further reduction of the cost associated with membrane CO_2 capture process and can be successfully applied for various applications.
- The membrane selectivity plays a key role on final gas separation cost.
- Three-stage structure with two recycle streams and two vacuum pumps is the most profitable layout for post-combustion CO_2 capture.
- The gas separation costs increased from about 46 to 70 €/ton CO_2 and specific energy consumption increased from 2.4 to 3.6 GJ/ton CO_2, when product targets increased from 90% recovery and 95% purity to 95% recovery and 98% purity.
- A two-stage process with one recycle stream is able of upgrading biogas to meet the separation targets of 95% recovery and 97% CH_4 purity.
- The optimal configuration for a 99% CH_4 recovery and 98% CH_4 purity in natural gas included three membrane stages with two permeate recycles and one vacuum pump at 12.7 €/ton NG.

Bio-based copolymers for membrane end products for gas separations

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