3rd Trondheim Gas Technology Conference 4-5 June 2014

CO_2 Removal from High Pressure Natural Gas Using a Novel Fixed-site-carrier Membrane

Xuezhong He and May-Britt Hägg

Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU)

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Outline of presentation

- ❖ Background
- ❖ Membrane preparation and testing
  - Large membrane preparation
  - Module design and high pressure gas permeation testing
- ❖ Challenges for up-scaling
- ❖ Techno-economic feasibility analysis
  - Process simulation
  - Economic feasibility analysis
- ❖ Summary

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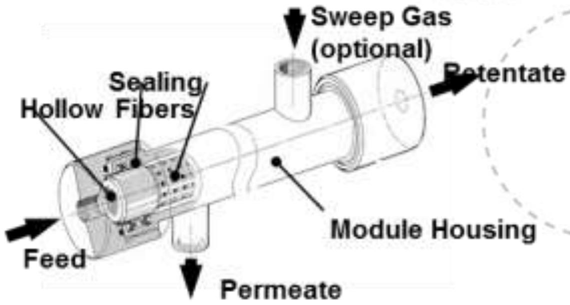
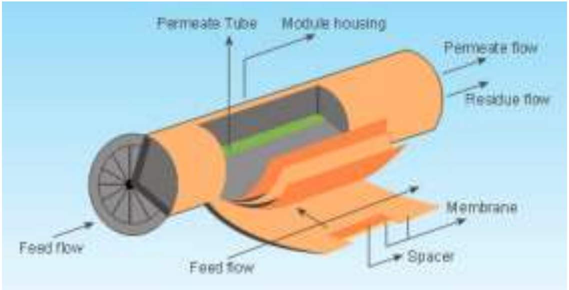
Natural gas sweetening

Natural gas (NG) is becoming one of the most attractive growing fuels for world primary energy consumption. However, the raw natural gas usually contains considerable amount of CO_2 which should be removed to meet the natural gas network grid specifications

- Amine absorption is the state-of-the-art technology
- Membrane can reduce the environmental impacts and operational costs, has been commercially used for this application about 25 years
- Commercial membranes are made from cellulose acetate (CA, spiral-wound), or polyimides (PI, hollow fibers)





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Commercial membranes for natural gas sweetening

Membrane	Material	Company	Module
Separex™	Cellulose acetate	Honeywell's UOP	Spiral wound
Cynara®	Cellulose acetate	NATCO	Hollow fiber
Prism®	Polysulfone	Air Products	Hollow fiber
Cytop	Perfluoropolymers	MTR	-
Medal	Polyimide	Air Liquide	Hollow fiber

He X, Yu Q, Hägg M-B. CO_2 Capture. In: Hoek EMV, Tarabara VV, eds. Encyclopedia of Membrane Science and Technology: John Wiley & Sons, Inc. 2013

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Challenges for polymer membranes

- Low CH_4 loss (<2%): Good CO_2 / CH_4 selectivity
- Smaller membrane area: High CO_2 flux
- Tolerant to high operating pressure (up to 80bar)
- Durable to H_2S, HHC, TEG, MEG and water
- Easy to fabricate, operate, maintain
- High operation stability and long lifetime

Potential strategies

❖ Cross-linking of the polymer materials

❖ Adding inorganic nanoparticles

❖ Optimization of membrane preparation conditions

❖ Optimization of process operating conditions

Natural Gas Processing by the use of New Membrane Materials (NaGaMa), 2011-2014

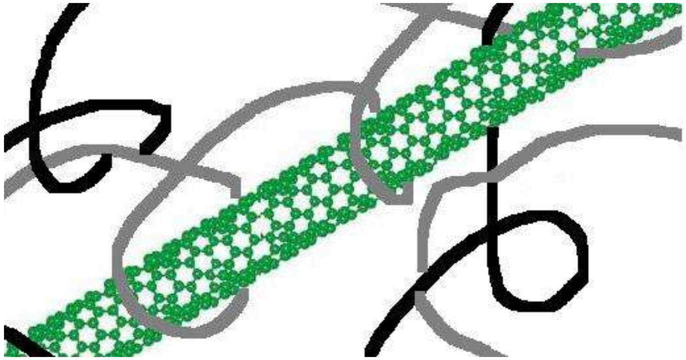
- ❖ Potential improvement of the membrane performance compared to the commercial membranes, including the selectivity and permeance
- ❖ The novel fixed-site-carrier (FSC) membranes might have a potential to reduce the pre-treatment cost
- ❖ Tolerant to H_2S, and most likely will be removed together with CO_2

The main tasks

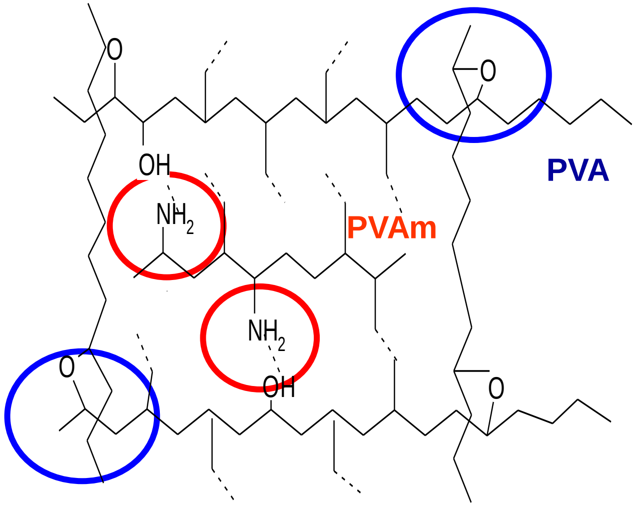
- o Development of flat sheet FSC membranes (lab- and small pilot-scale)
- o High pressure (up to 80bar) gas permeation testing
- o Durability testing, exposure to H_2S, TEG,MEG, and HHC
- o Fabrication of hollow fiber FSC membranes
- o Techno-economic feasibility analysis

Nanoparticles reinforced PVAm /PVA blend fixed-site-carrier (FSC) membranes

- Cross-linked PVAm/PVA blend (heat treatment)
- Compatible polymers and nanoparticles (carbon nanotubes)
- Composite membranes (coating selective layer on a support)
- Giving desired properties (high permeance and selectivity)

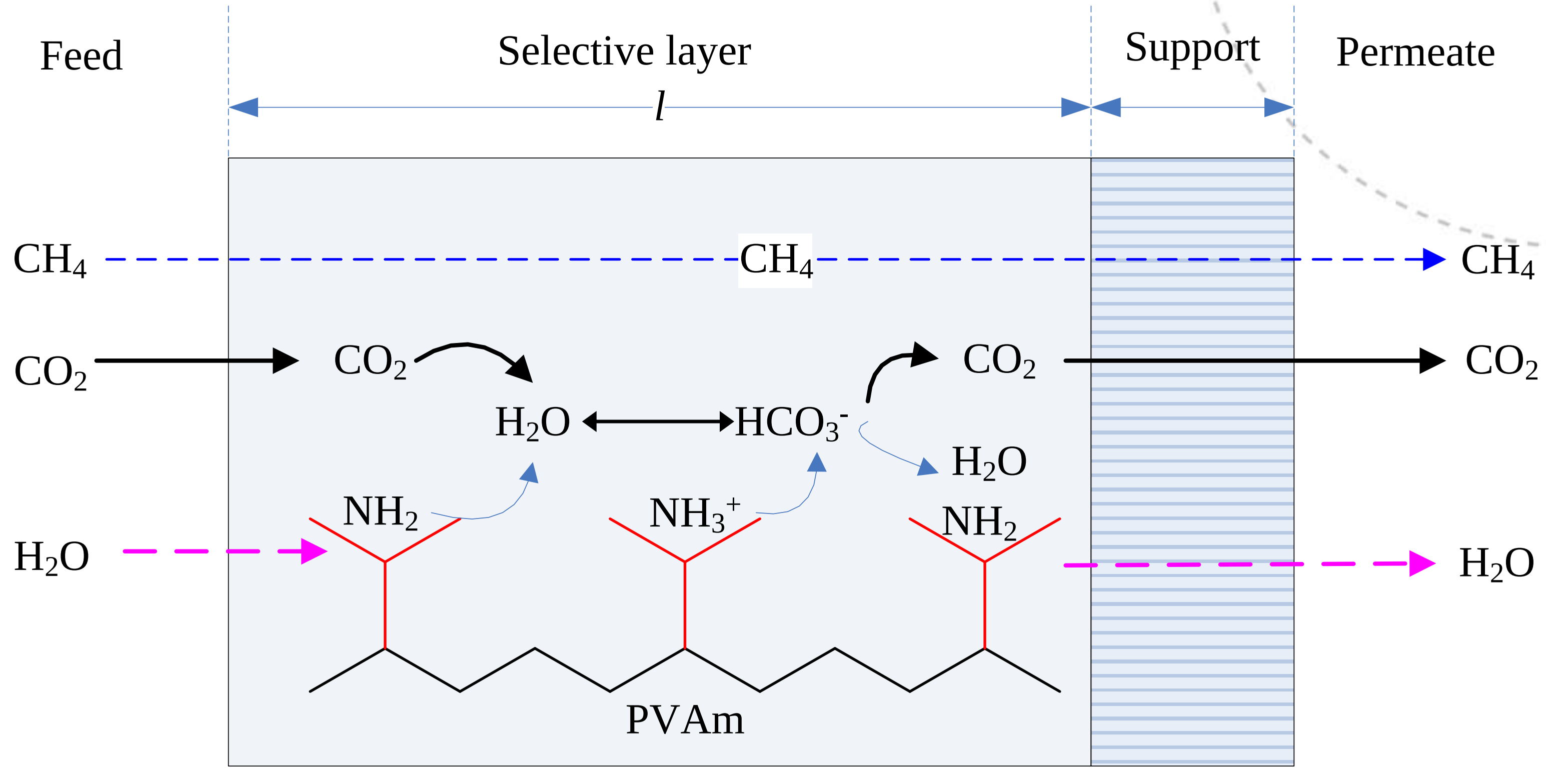


CNTs/Polymer



PVAm/PVA blend polymer framework

Transport mechanism of FSC membranes



- Water is crucial for CO_2 transport through the amino-based FSC membranes
- Challenging to achieve a high water content in a high pressure feed gas

Membrane material design

- Materials

  Polysulfone (PSf) UF membranes, MWCO, 20K

  Polyvinylamine (PVAm, MW 340,000)

  Polyvinylalcohol (PVA, MW 72,000)

  Carbon nanotubes, CNTs (D/L, 15 nm / 3 μm)

- Synthetic mixed gas

  10% CO_2 / 90% CH_4

  50% CO_2 / 50% CH_4

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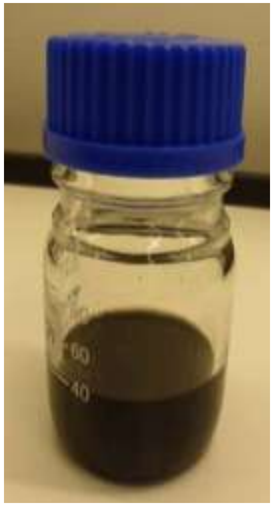
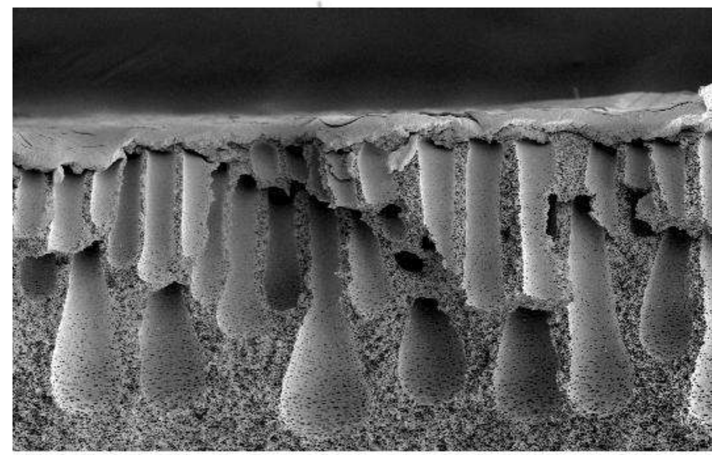
Membrane preparation



Coating



CNTs/PVAm/PVA solution

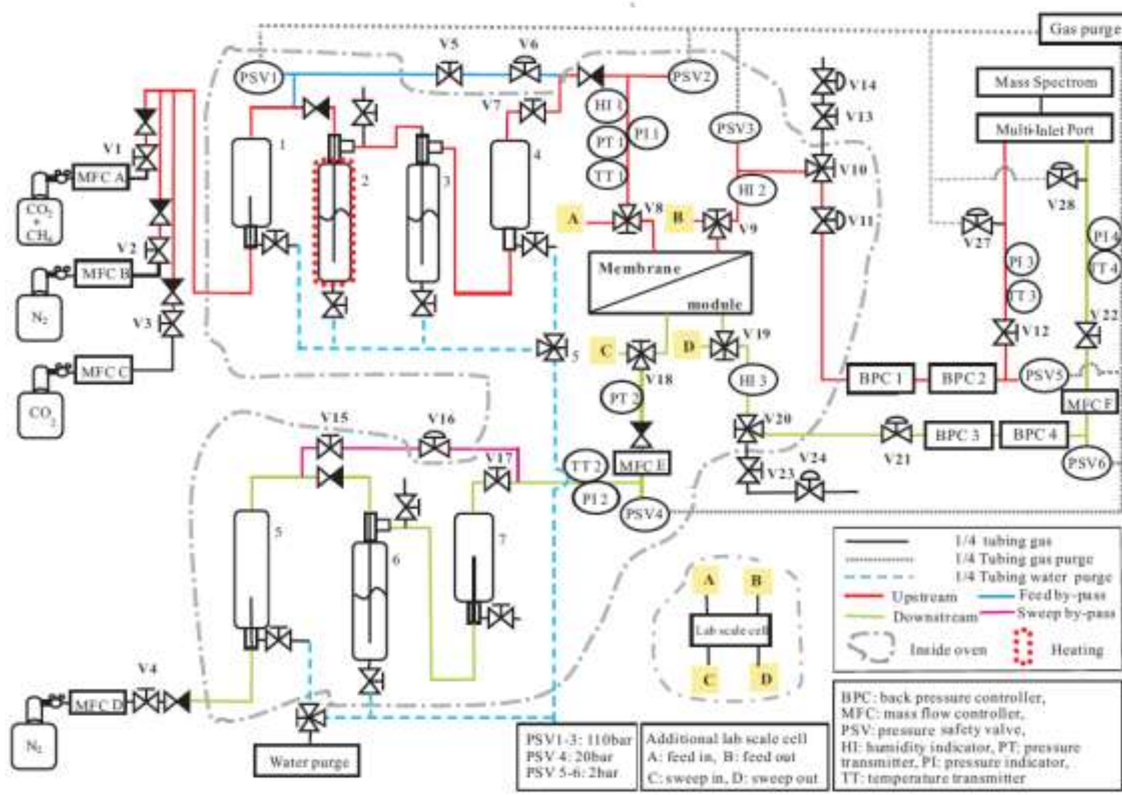
PSf 20K flat-sheet

cutting

110 cm^2

30cm×30cm

High pressure module and permeation rig



110~330 cm^2

Design pressure up to 100 bar

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Investigation of process operating parameters
- Feed pressure & feed composition

Membrane performance	Feed CO_2 composition	Feed pressure, bar			
		10	20	30	40
CO_2 permeance, m^3 (STP) / (m^2.h.bar) *	10%	0.218	0.162	0.113	0.084
	50%	0.143	0.088	0.055	0.033
CO_2 / CH_4 selectivity	10%	34.7	27.4	22.0	17.9
	50%	28.0	24.6	18.2	11.0

*: simulation basis

Membrane area: 110 cm^2
Tested at 30 °C with a feed flow 3000 Nml/min, no sweep gas

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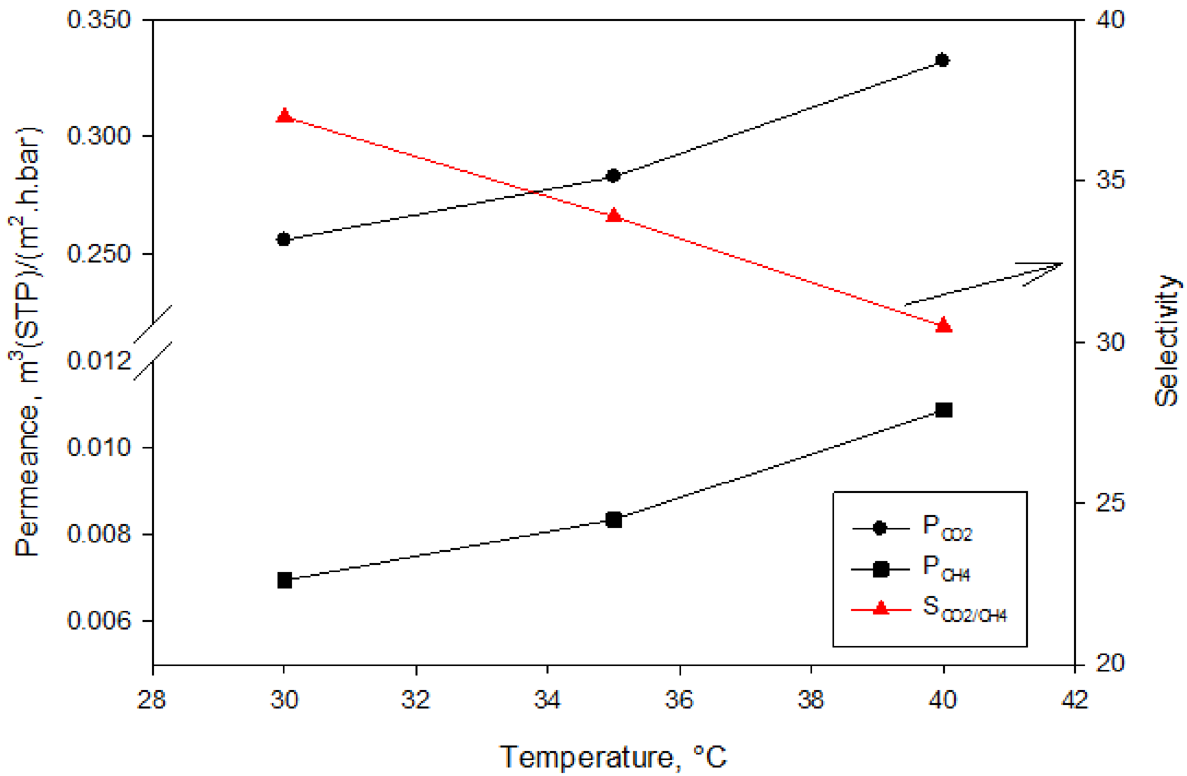
Investigation of process operating parameters
- Temperature



Higher temperature, higher water vapor content in a gas stream

Membrane area: 110 cm^2 , 10%CO_2/90% CH_4

Tested at 30°C and 10bar with a feed flow 3000 Nml/min, no sweep gas

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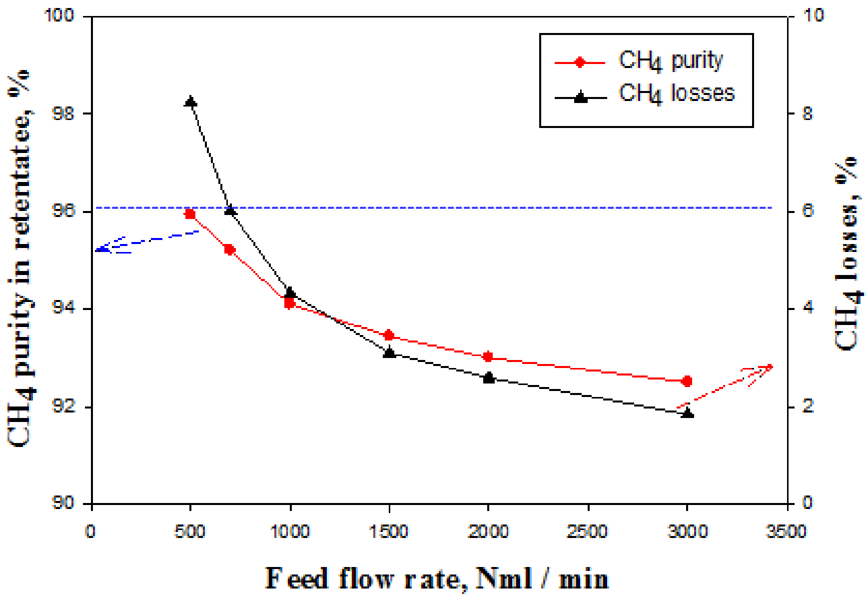
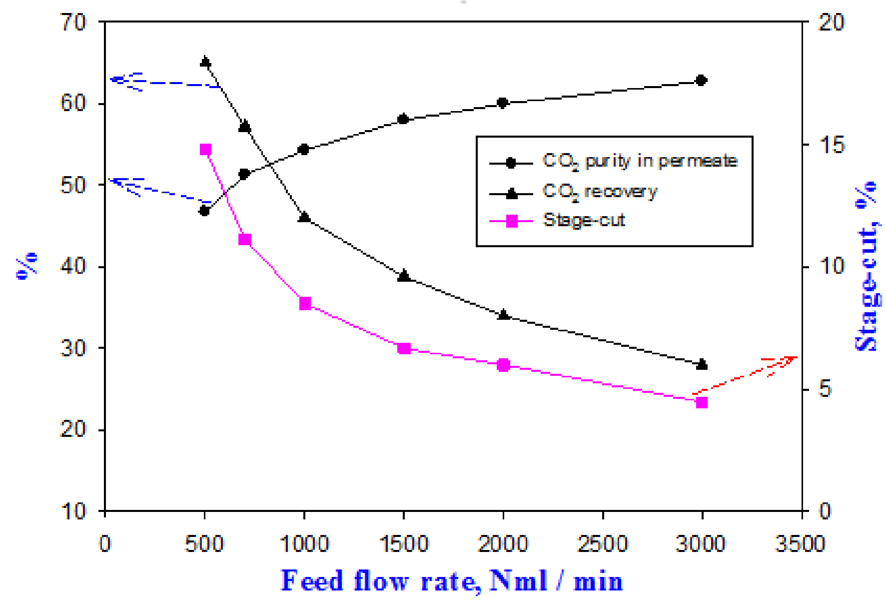
Investigation of process operating parameters - Feed flow & stage-cut





- CH_4 purity can reach 96% at a high stage-cut (15%), but CH_4 loss is high, which needs to be partly recovered from the permeate stream using a second stage membrane unit
- CO_2 purity can only achieve 50-60%, thus, further purification is required for storage or re-injection back to gas wells

Membrane area: 330 cm^2 , tested at 30 °C and 30bar, no sweep gas, 10%CO_2/90% CH_4

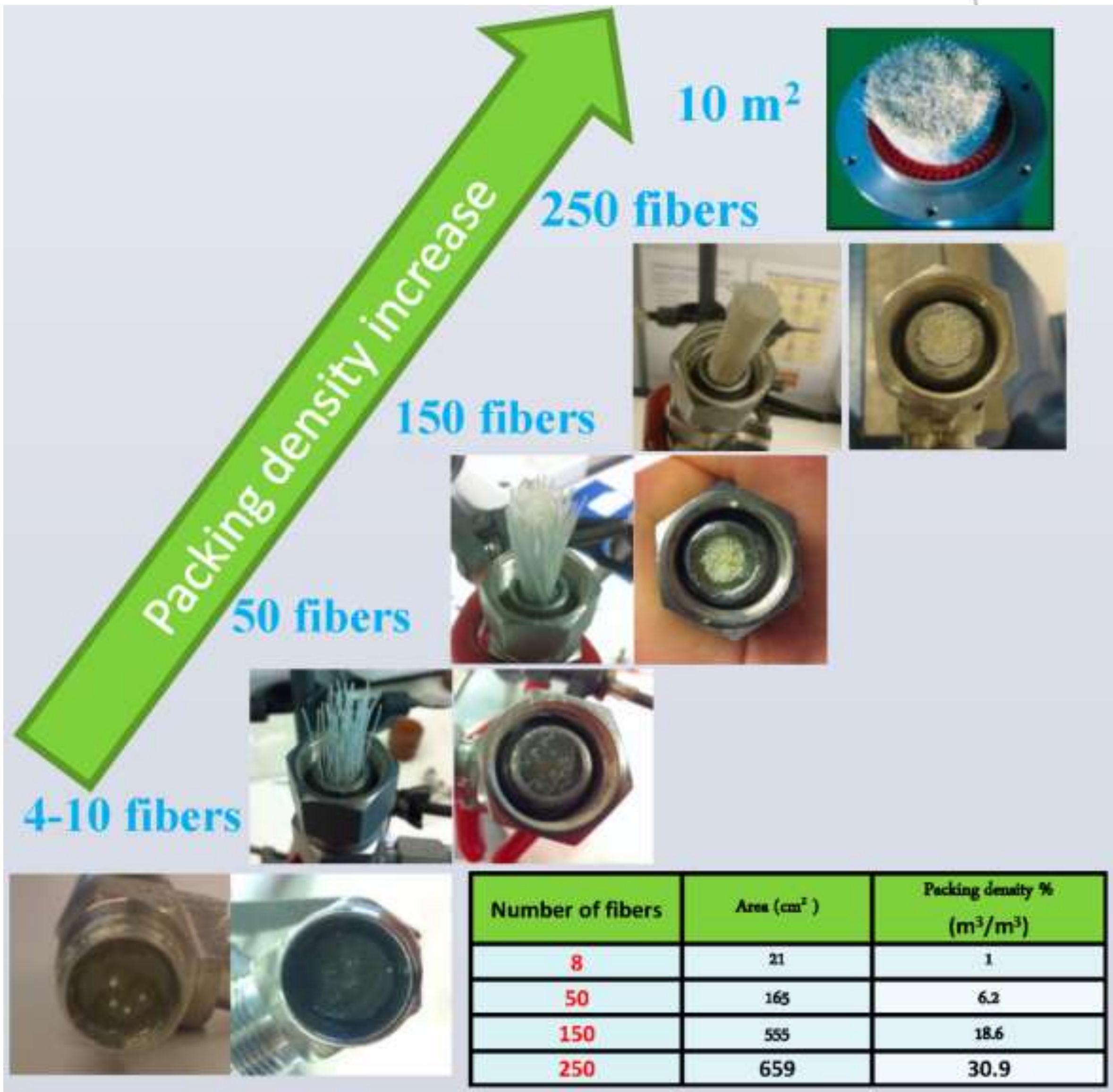
Challenges for up-scaling

Pilot demonstration

Process simulation

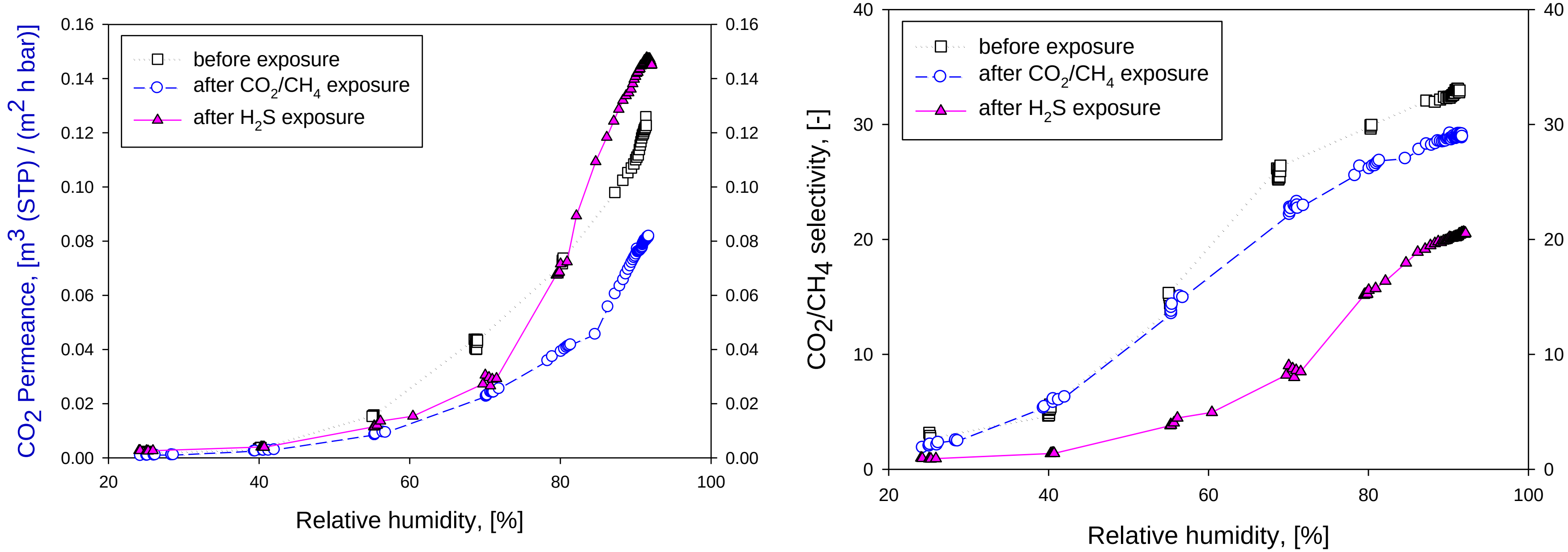
Parameters	Lab-scale	Industrial scale	Challenges
Module	Plate-and- frame / low packing density module	Spiral wound /high packing density module	Good flow pattern/ high performance
Impurities	No/less	Complex	Durability/ high performance
Testing period	Short (hours-days)	Long (months-years)	Long lifetime/ low replacement cost
Driving force	Pressurized from gas bottles	Compressor/blower /vacuum pump	Low capital and operating cost
Membrane cost	-	low	Low capital cost
Membrane Stage	Single/two	Two-/multi-	High CH_4 purity
Stage-cut	Very low (e.g., <1 %)	High (>15-20 %)	High CO_2 capture ratio
Recycling	No	Yes	Low methane loss

From flat-sheet to Hollow fibers



Number of fibers	Area (cm^2)	Packing density % (m^3/m^3)
8	21	1
50	165	6.2
150	555	18.6
250	659	30.9

Long-term static durability test



Exposed to 1.02 % H_2S, 10.0 % CO_2 and balance CH_4 at 10 bar and ca.60 °C for 3360 hours (20 weeks)

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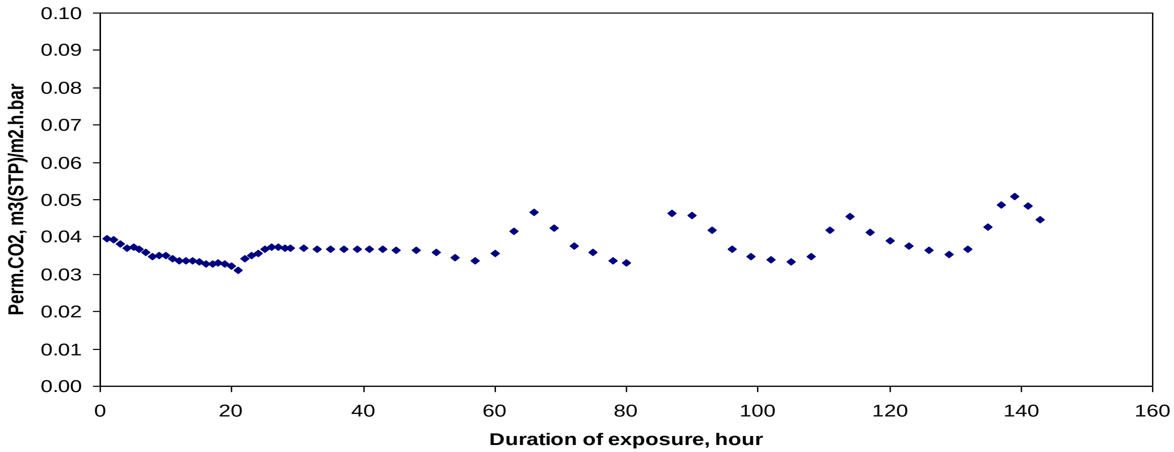
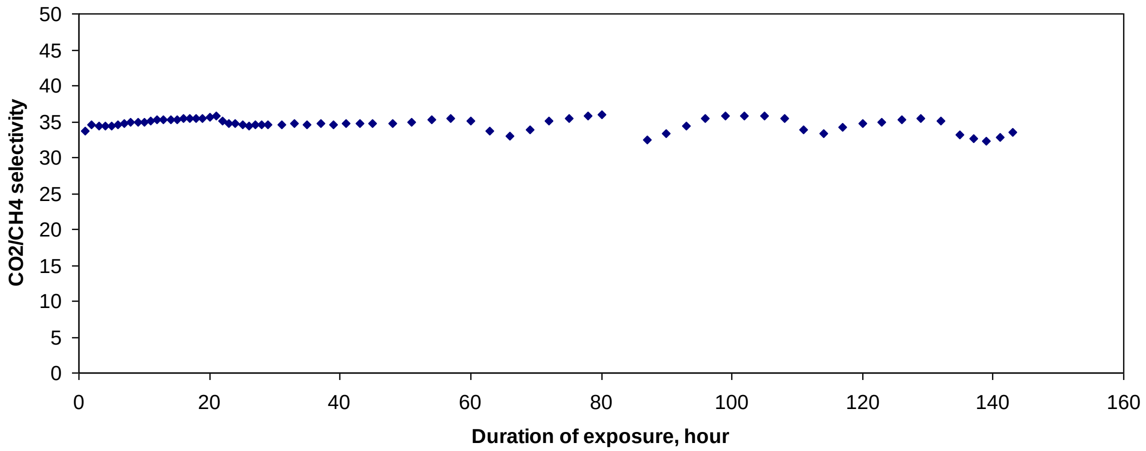
Dynamic durability test





0.5% iso-butane, 0.05 % n-butane, 10 % CO_2 and bal. CH_4
400 Nml/min, 30 bars, 30 °C, 6 days

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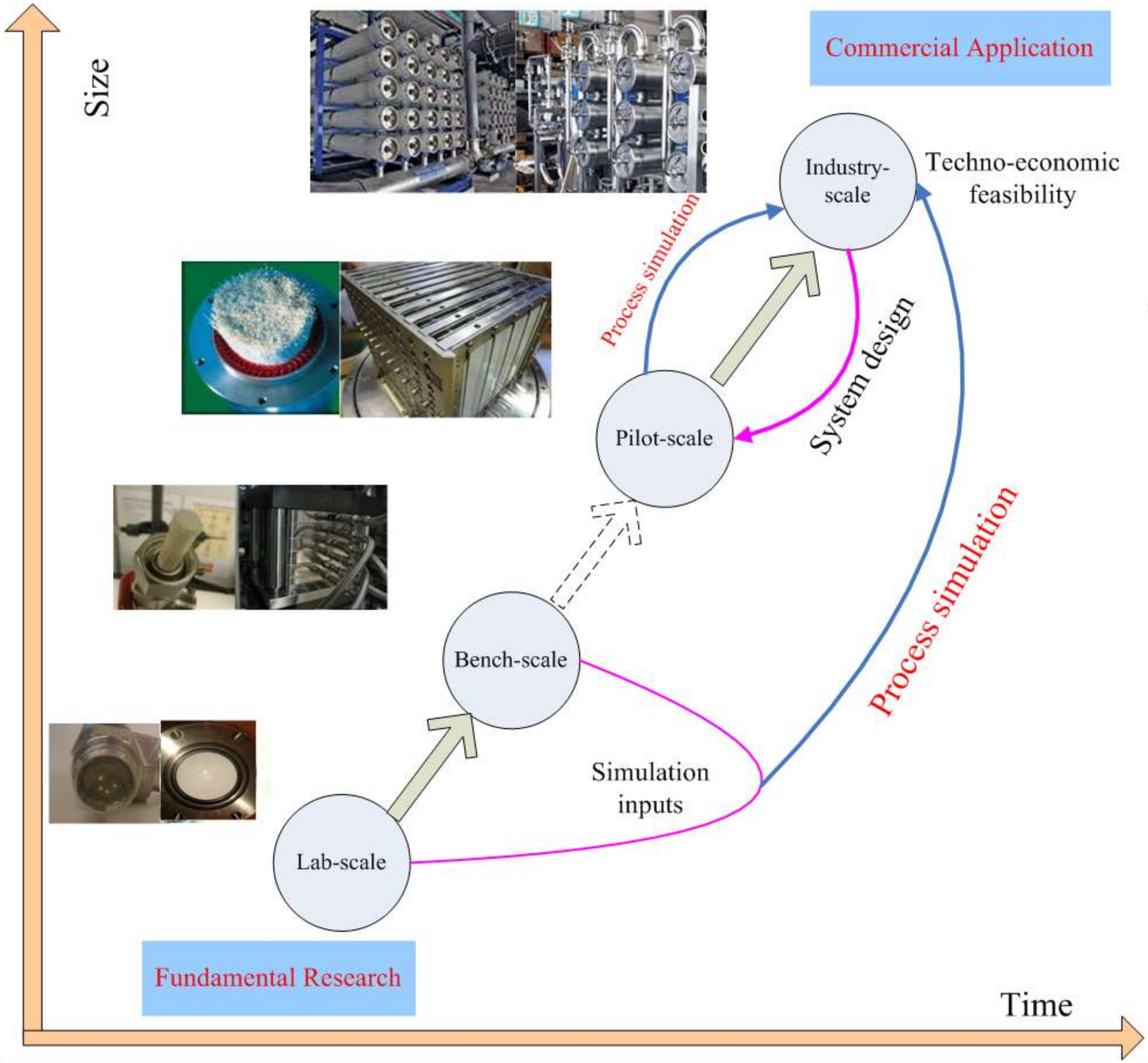
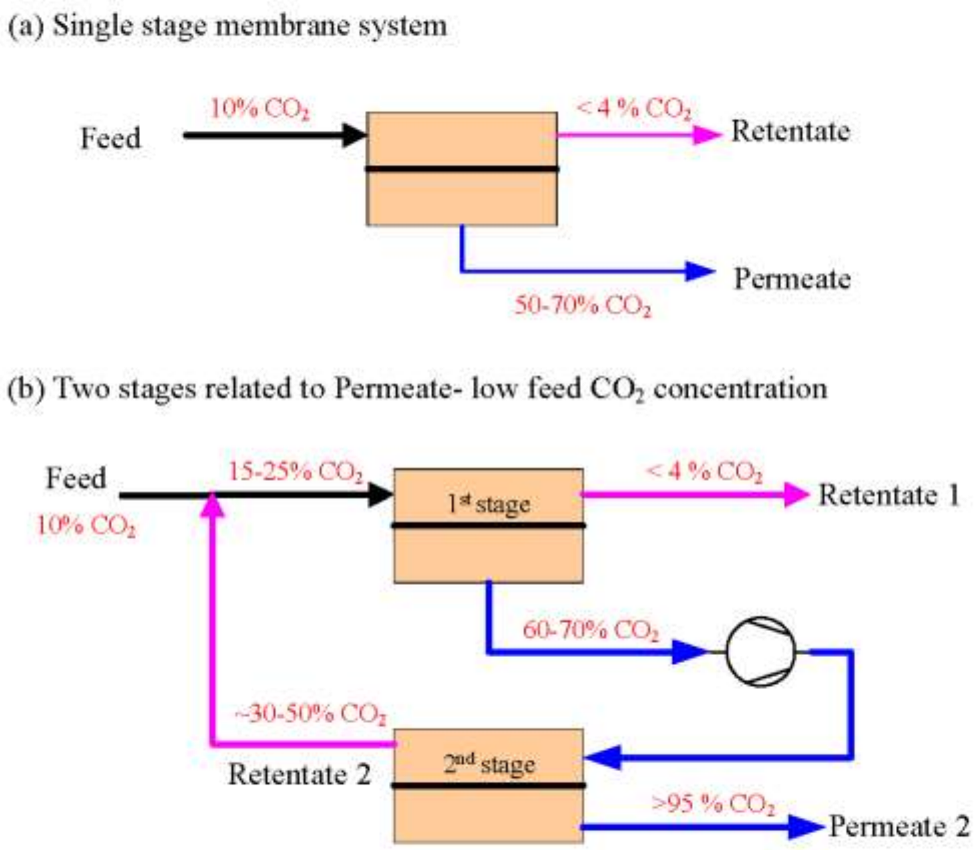
The importance of process simulation



Process simulation and feasibility analysis

Process design



CH_4 purity, >96%
CH_4 loss is high

CH_4 purity, >96%
CH_4 loss is low, <2%
High CO_2 purity

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Simulation basis

Process operating parameter	value	Separation requirement	value
Feed flow (Nm^3/h)	5E+5	CH_4 purity, %	>96
Feed CO_2 composition	10%	CH_4 losses, %	<2
1st stage Feed pressure, bar	40	CO_2 purity, %	>90
2nd stage Feed pressure, bar	10~40, optimized	CO_2 compression*, bar	110
Permeate pressure, bar	1		
Feed temperature, °C	30		
CO_2 and CH_4 permeance	Experimental data		

*: compress to 75bar and pump to 110bar

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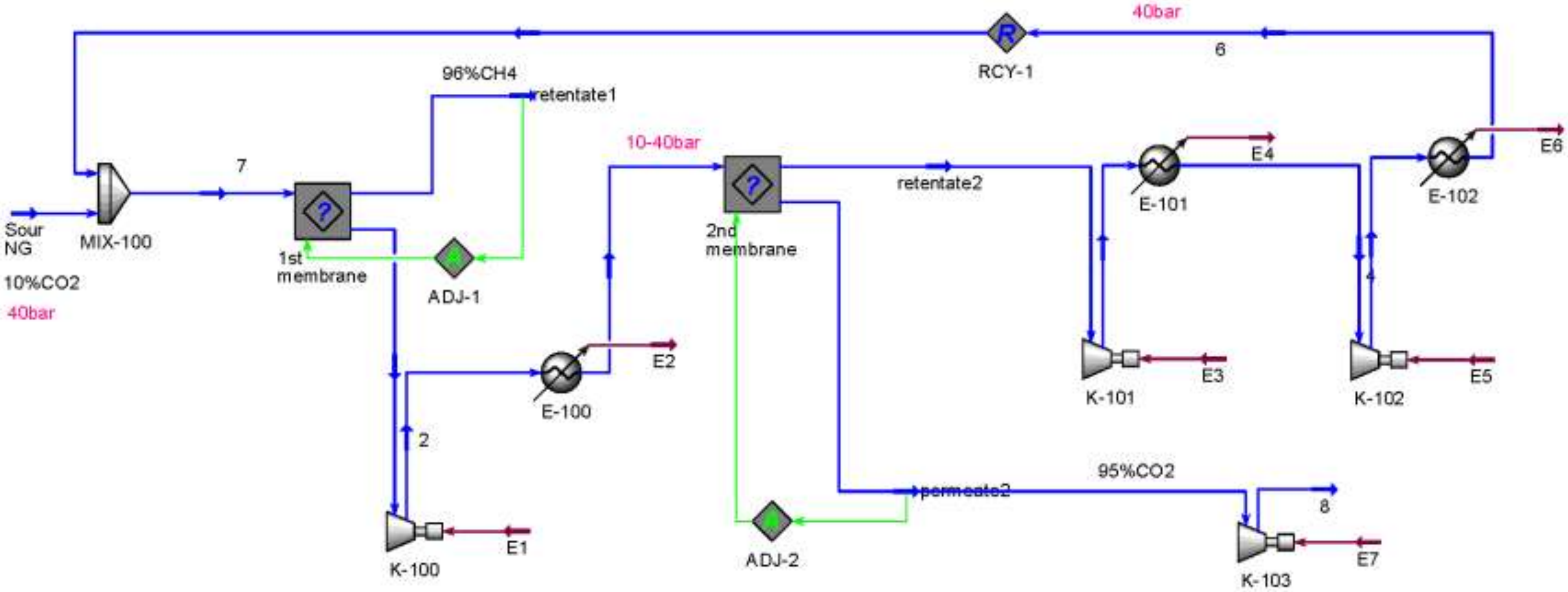
Process simulation



- HYSYS simulation integrated with ChemBrane unit (developed by Memfo group at NTNU)
- Counter-current configuration
- Feed pressure of the 2nd stage is optimized on the basis of cost minimization

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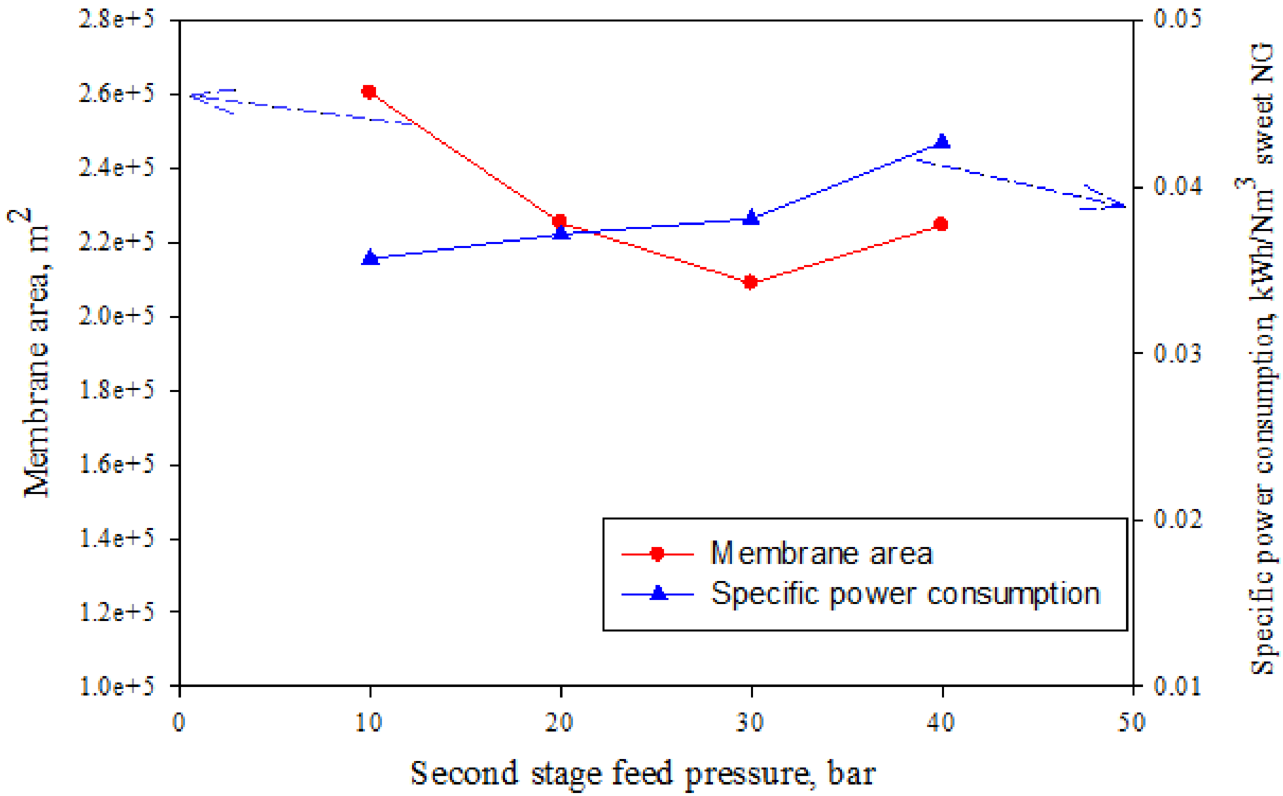
Process optimization-2nd stage feed pressure



- Specific power consumption increases with the 2nd stage feed pressure
- Increase of driving force may decrease the required membrane area
- Optimization based on cost estimation

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Cost estimation model

Category	Parameter	Value
Capital expenditure (CAPEX)	Membrane skid cost ($C_{BM, M}$)	35 $\$/m^2$
	Compressor, pump cost ($C_{BM,i}$)	CAPCOST 2012 §
	Total capital cost (C_{TM})	$C_{TM} = 1.18\sum_{i=1}^{n} C_{BM,i}$
Annual operating expenditure (OPEX)	Labor cost (LC)	15 $/hr
	Electricity cost (EC)	0.07 $/kWh
	OPEX	LC + EC
Annual capital related cost (CRC)#	$0.2 \times C_{TM}$	
NG sweetening cost*	(CRC+OPEX) / annual sweet NG production, $\$/m^3$ sweet NG	
Other assumptions	Membrane lifetime	5 year
	Project lifetime	25 year
	Operating time	7500 hrs/year
	Compressor and pump efficiency	85%

#: Covering depreciation, interest, and maintenance;

*: CH_4 losses cost is not included

§: Turton R., et al., Analysis, Synthesis, and Design of Chemical Processes, Fourth Edition, Pearson Education, Upper Saddle River, NJ, 2013

Economic feasibility analysis

Parameters	Simulation results	
Sweet NG productivity, Nm^3/h	4.67E+05	4.57E+5
CH_4 purity in sweet NG, %	96.08	98.02
CH_4 losses, %	0.35	0.54
CO_2 purity, %	95.01	94.41
CO_2 recovery, %	63.65	81.75
Specific power consumption, kWh/Nm^3 sweet NG	3.63E-02	5.62E-2
Total membrane area, m^2	2.62E+05	4.36E+5
NG sweetening cost, $\$/Nm^3$ sweet NG	5.73E-03	7.95E-3

A typical amine absorption: 6.4E-3 $\$/Nm^3$ sweet NG produced[§]
10bar of 2nd stage feed pressure is used

§: Peters L, et al., Chem Eng J. 2011;172(2–3):952-60

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Summary

- The developed FSC membranes show an good separation performance for CO_2/CH_4 separation at high pressure, and relatively good durability exposed to the impurities of H_2S, HHC

- Experimental results shows that single stage membrane system cannot achieve a high methane purity and low methane loss simultaneously. Two- or multi-stage system may be needed

- HYSYS simulation results showed that developed FSC membranes could be a promising candidate for CO_2 removal from high pressure natura gas sweetening

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Thank you for your attention!

Acknowledgements:

PETROBRAS

Statoil

The Research Council of Norway

NTNU
Det skapende universitet

Dr. M. Washim Uddin
Dr. Maria Teresa Guzman Gutierrez
Dr. Taek-Joong Kim (Sintef)
Dr. Marius Sandru (Sintef)

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