Lab and pilot scale pervaporation process for the purification of DiMethyl Carbonate

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Lab and pilot scale pervaporation process for the purification of dimethyl carbonate

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The separation of dimethyl carbonate (DMC) from methanol is of great industrial interest, as DMC can be prepared from urea (made from captured CO_2 and ammonia) and methanol with methanol also acting as a solvent for the reaction. As a result relative low levels of DMC in methanol can be obtained. The purification is a very energy intensive process with the base case being a pressure swing distillation method. The use of polymeric membranes for this purpose is not recommended as the driving forces for the transport of methanol are fairly low, which asks for high operating temperatures of over 120°C. These conditions call for a ceramic membrane. Zeolitic membranes are typically not suited for the transportation of methanol and polymeric membranes are not stable under these conditions. Hybrid silica membranes, such HybSi® can combine high operation temperatures, with sufficient high selectivities and high permeances.

In the current study, we have performed process simulations to assess the potential reduction in CAPEX and OPEX when a HybSi® membrane is included in the process. The costs of the separation of DMC from methanol has been assessed by Aspen Plus flow sheeting using the by ECN developed Pervatool to simulate the behavior of the membrane pervaporation process. The calculations were based on actual lab scale membrane performance data and vapor-liquid-equilibrium data originating from internal and published sources. To facilitate a transparent comparison, the total costs of the purification were calculated per ton of DMC produced. The cost saving is as high as 45% when a hybrid process is being used that combines membranes and distillation as compared to the base case with pressure swing distillation, see Table 1. Cost reductions can be found in both the OPEX and the CAPEX and range from 25 to 55%. The OPEX savings can be ascribed to a strongly reduced energy consumption, while the CAPEX reduction is ascribed to a much more compact design with smaller distillation columns. The values are dependent on the way of calculation, e.g. absolute numbers or relative to the amount of DMC produced, and on technical factors such as the DMC content in the methanol recycle and various process conditions throughout the separation train.

These simulations have been supported by long term measurements at lab scale as well as a pilot testing in a fully specialized plant using about 0.7 m^2 of membrane area. In the presentation all the relevant results will be discussed of the process simulations and the lab and pilot scale testing.

Table 1: Purification costs per ton DMC produced taking into account both CAPEX and OPEX

	Relative purification costs per ton DMC produced	Relative cost reduction
Base case with high purity recycle	100	
Base case with low purity recycle	96	4%
Membrane case with high purity recycle	72	28%
Membrane case with low purity recycle	55	45%

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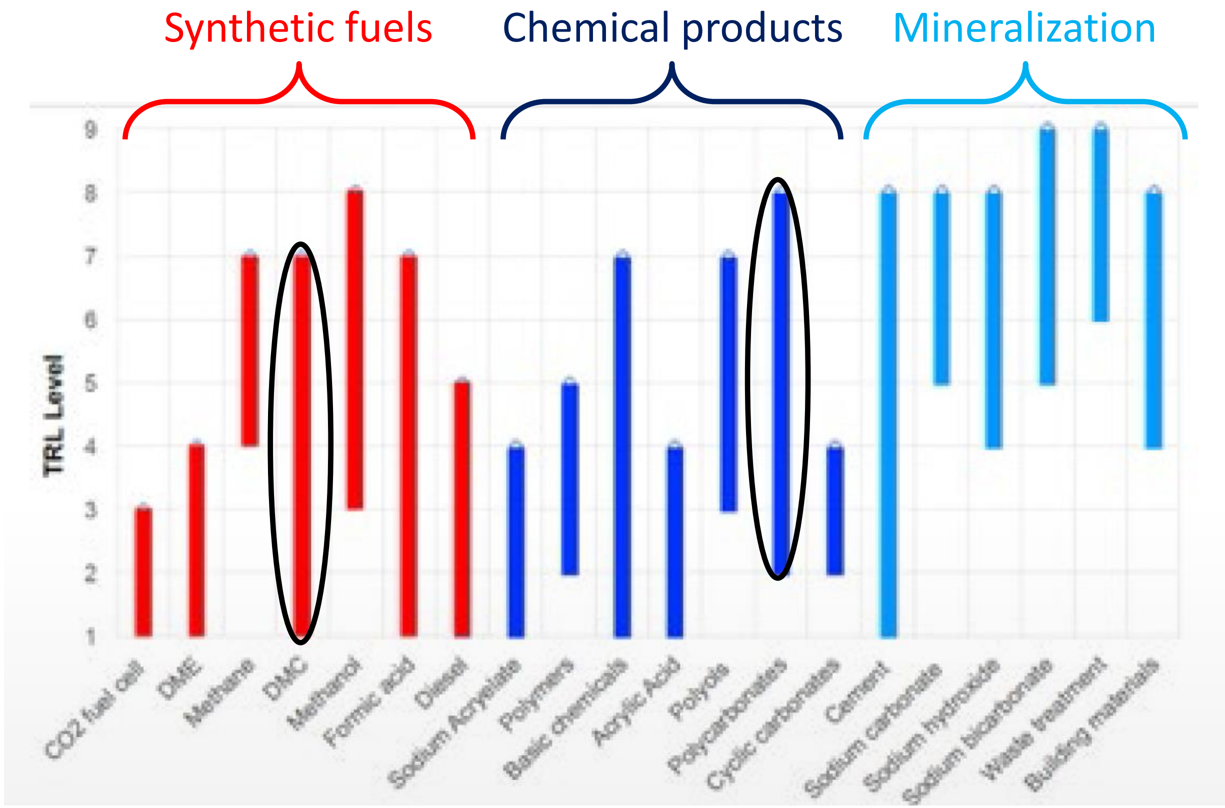
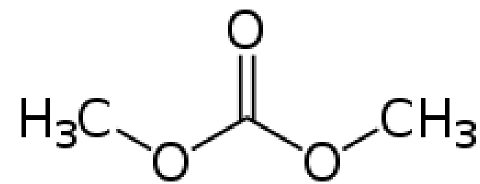
CO_2 reuse an upcoming field

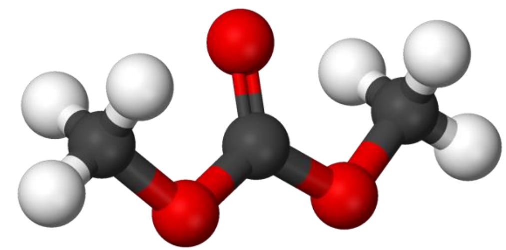


Source SCOT: Smart CO2 Transformation (http://scotproject.org/)

DMC use

- Basis for polycarbonate (~50%)
- Solvent, replacing MEK and others also in paints
- Fuel additive
- Market size (mainly Asia and Europe)
  - >1Mton/y





Manufacture

Historical

- Phosgene with methanol

Modern routes

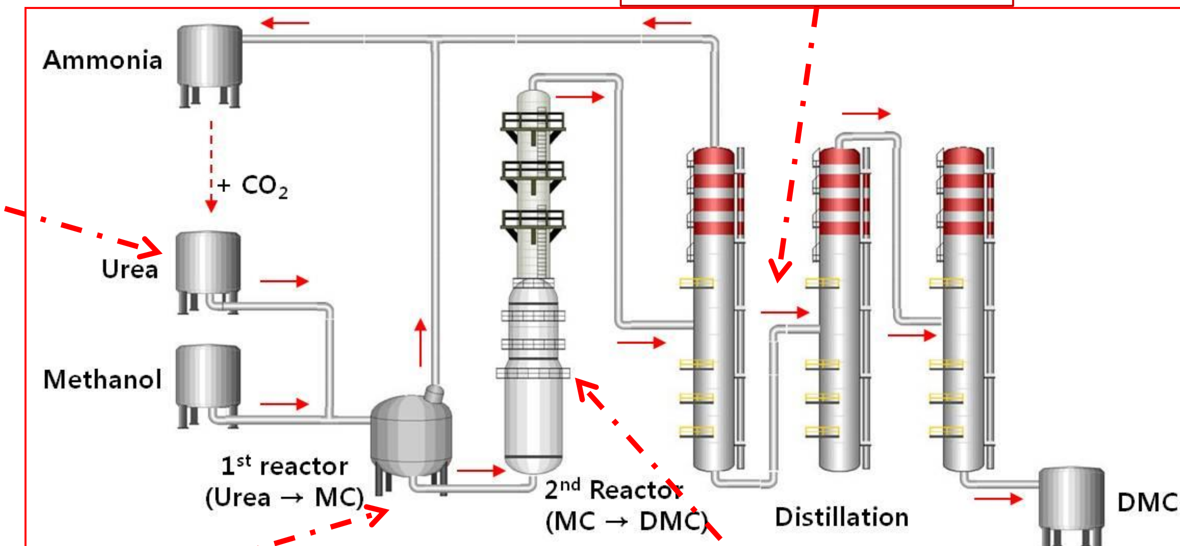
- Transesterification of ethylene carbonate and methanol
- Carbon monoxide, methanol and oxygen

Upcoming routes

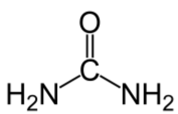
- CO_2 and methanol with urea as intermediate
- Direct conversion of CO_2 and methanol

Production via Urea

DMC/MeOH
mixture 25/75%



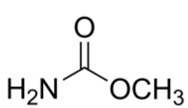
$CO_2 + 2NH_3$
$\rightarrow (NH_2)_2CO + H_2O$



urea

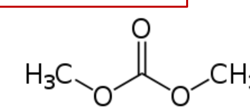
$(NH_2)_2CO + CH_3OH$
$\rightarrow (CH_3)(NH_2)CO_2 + NH_3$

$(CH_3)(NH_2)CO_2 + CH_3OH$
$\rightarrow (CH_3)_2CO_3 + NH_3$

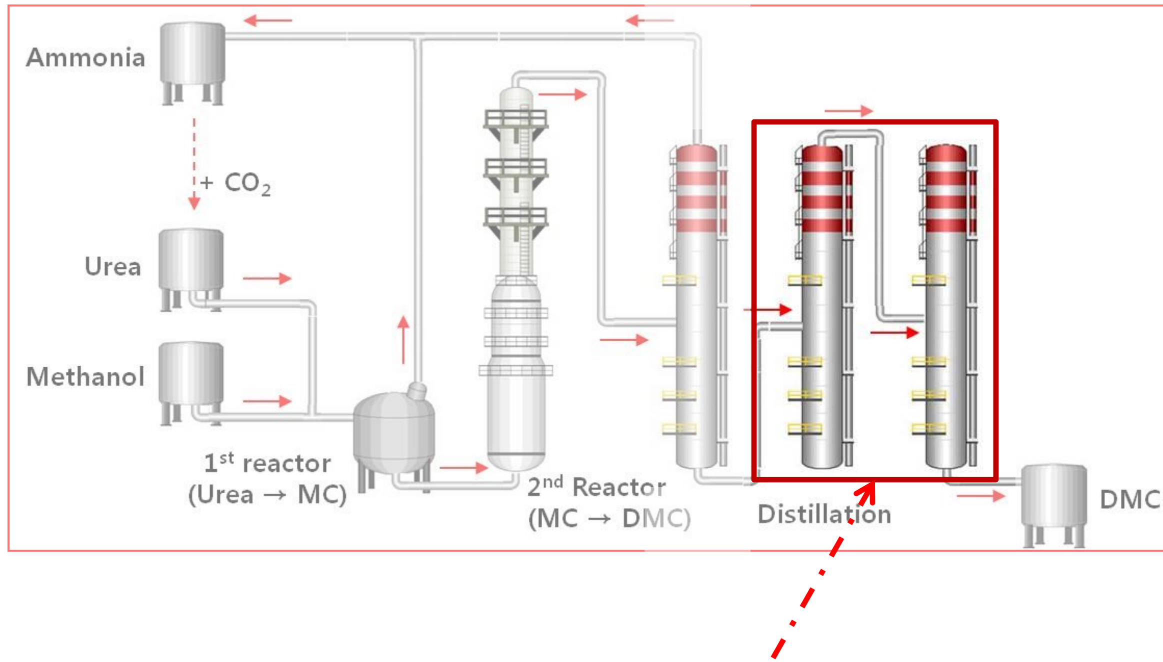


Methyl Carbamate

DiMethyl Carbonate



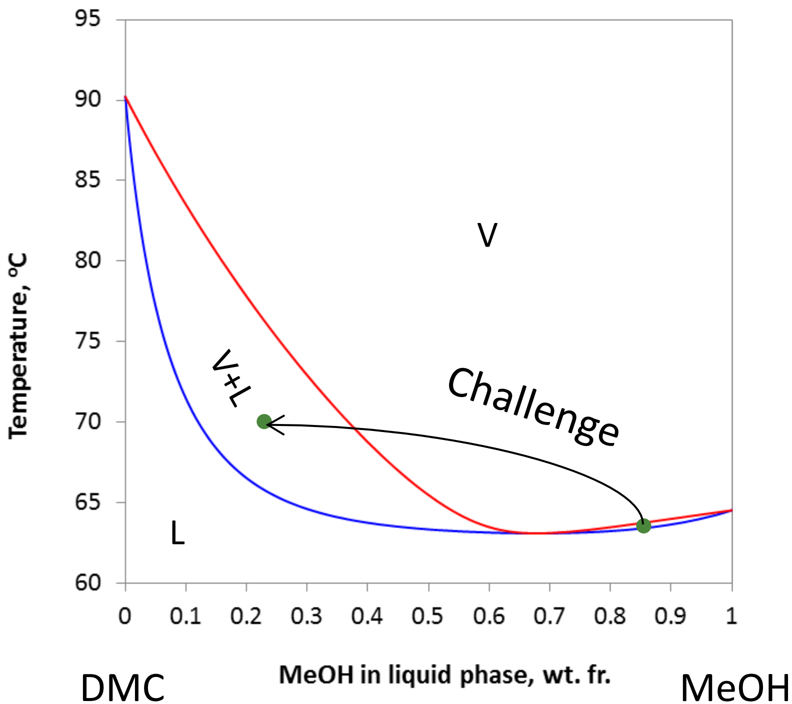
DMC/MeOH separation

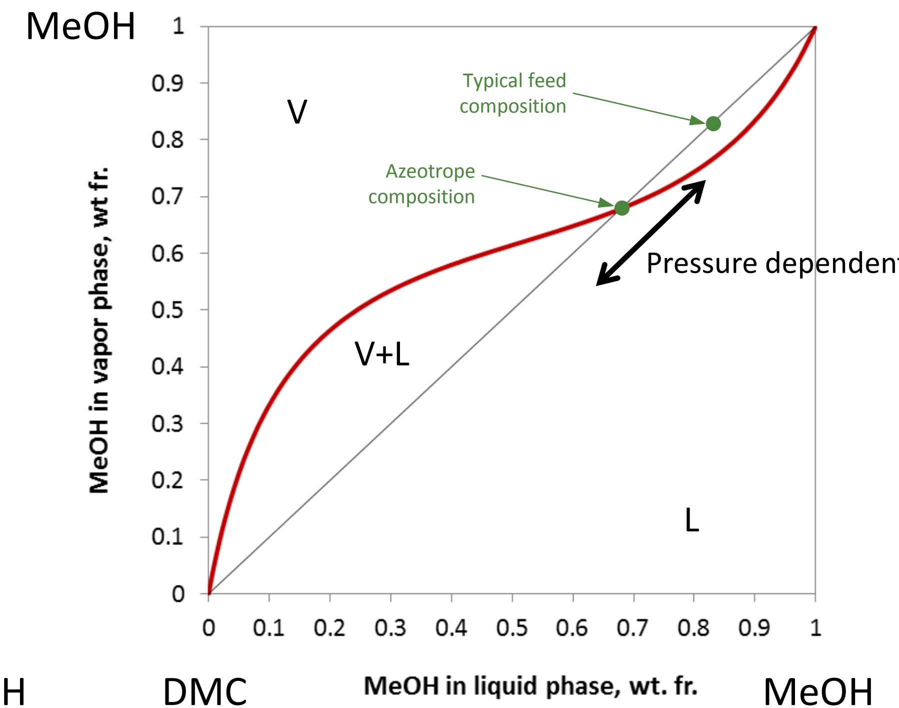


Focus of today's talk:
cost and energy efficient MeOH/DMC separation

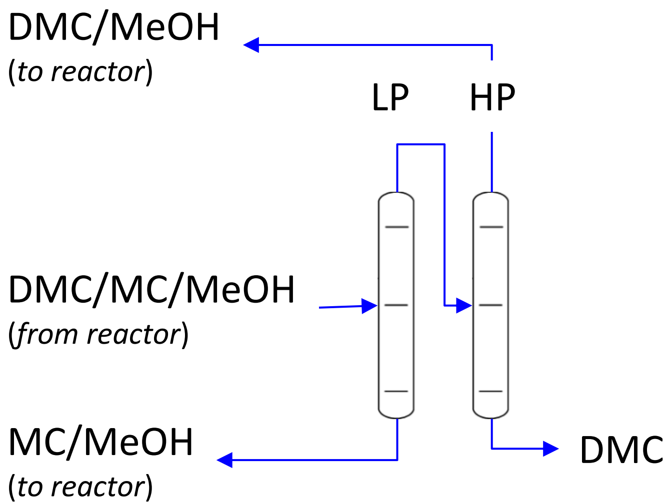
VLE diagram MeOH/DMC

Azeotrope formation is at ~ 70 wt% MeOH (1 bar)

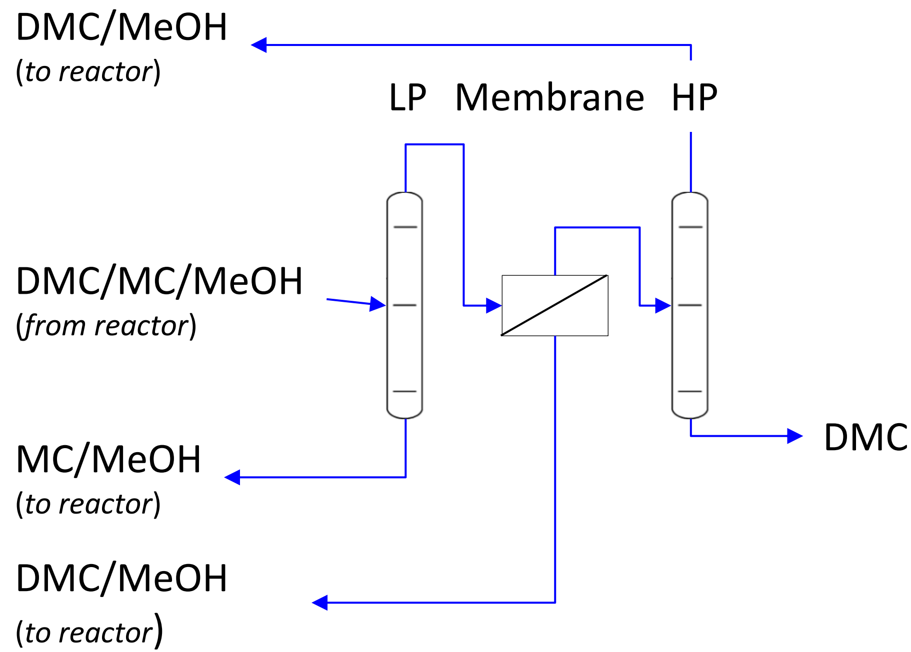




Breaking the azeotrope



Base case
Pressure swing

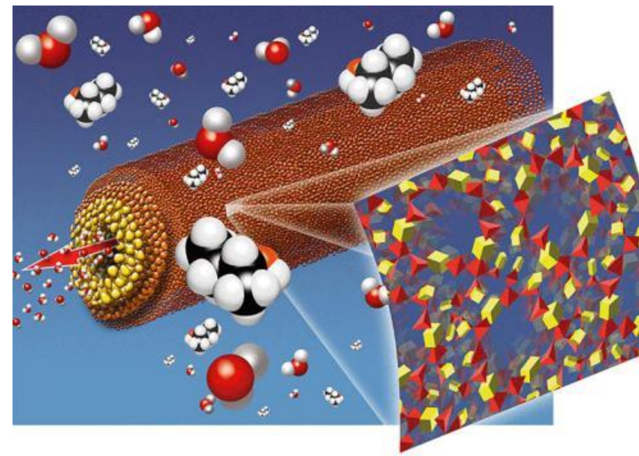


Membrane case

HybSi® Membrane in MeOH/DMC Separation

What is so special about HybSi®?

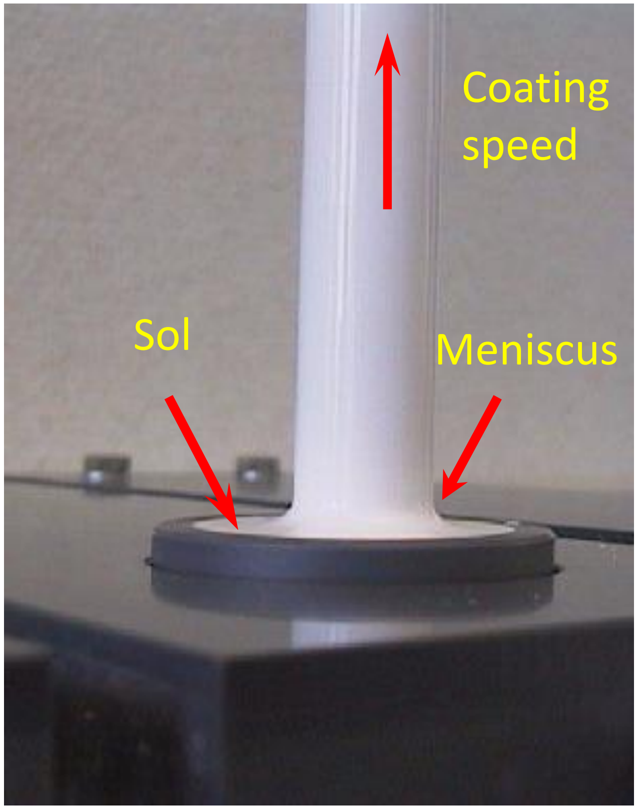
- Organic – inorganic hybrid silica with exceptional stability cf. competition

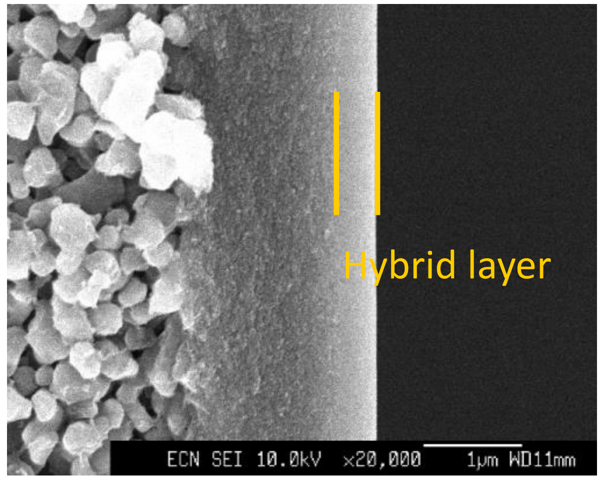


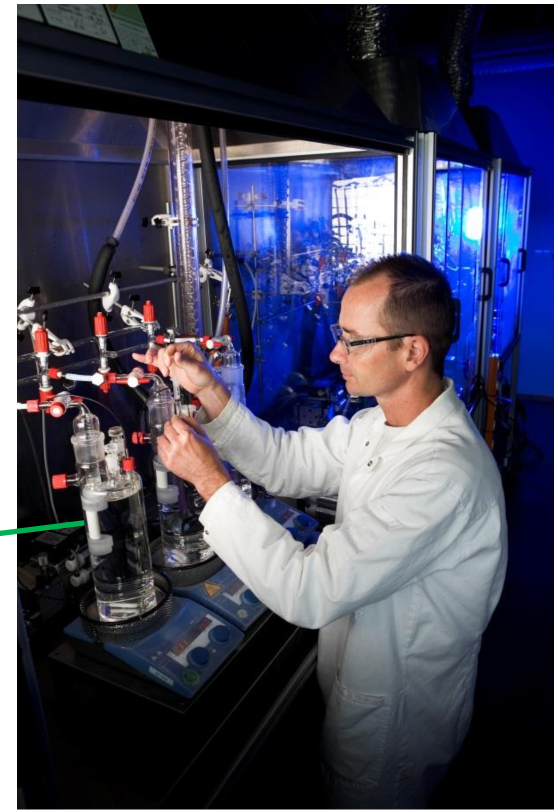
- High application temperature (up to 190°C)
- Good resistance against acids (~ 0 < pH < ~8)
- Stable in aggressive solvents (NMP, MEK)
- Stable in water: up to at least 60%
- Feasibility of effective methanol removal shown
- Resistance against condensation

HybSi® Pervaporation Membranes

Membrane fabrication and testing

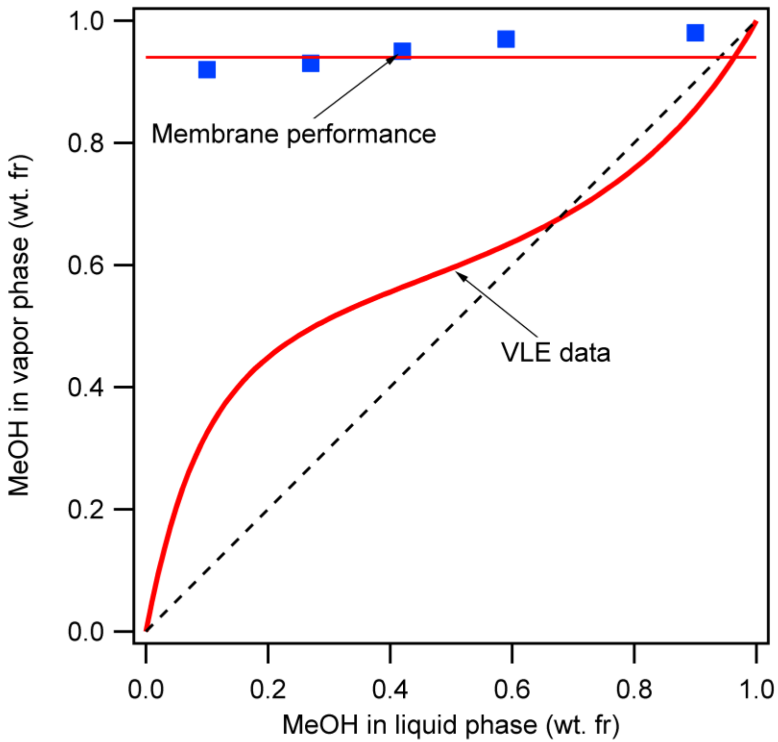


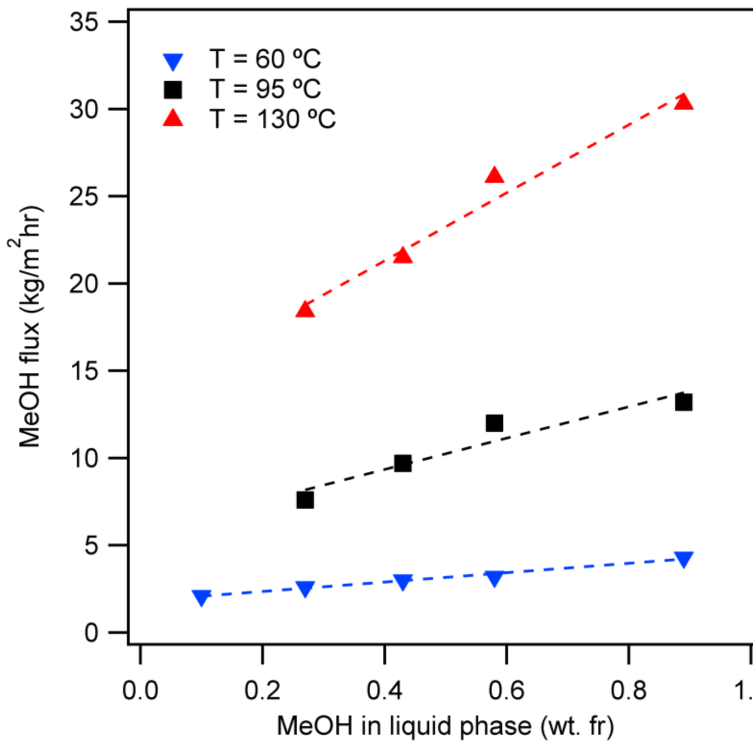




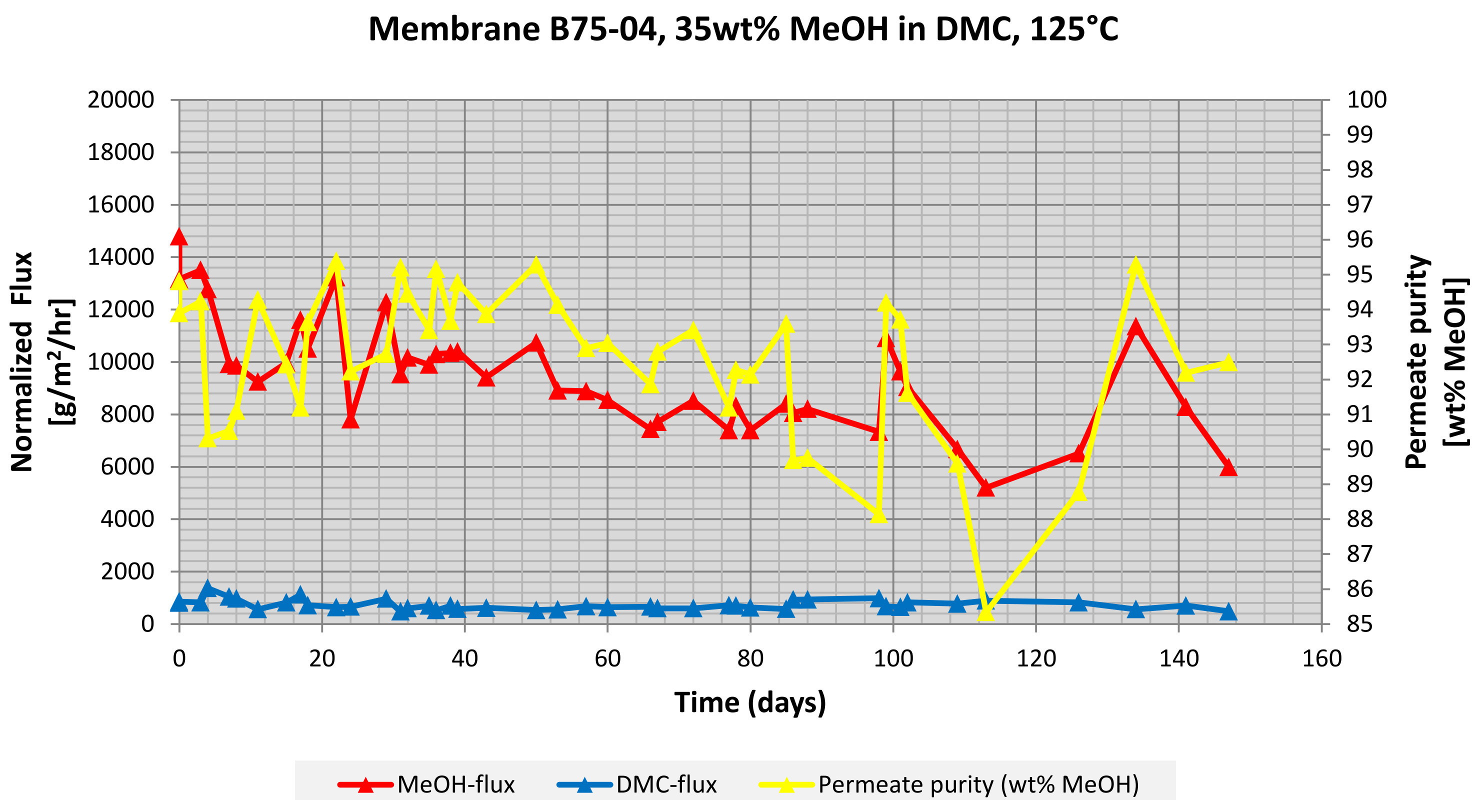
HybSi® membrane in lab scale pervaporation test

Membrane performance MeOH/DMC: lab scale

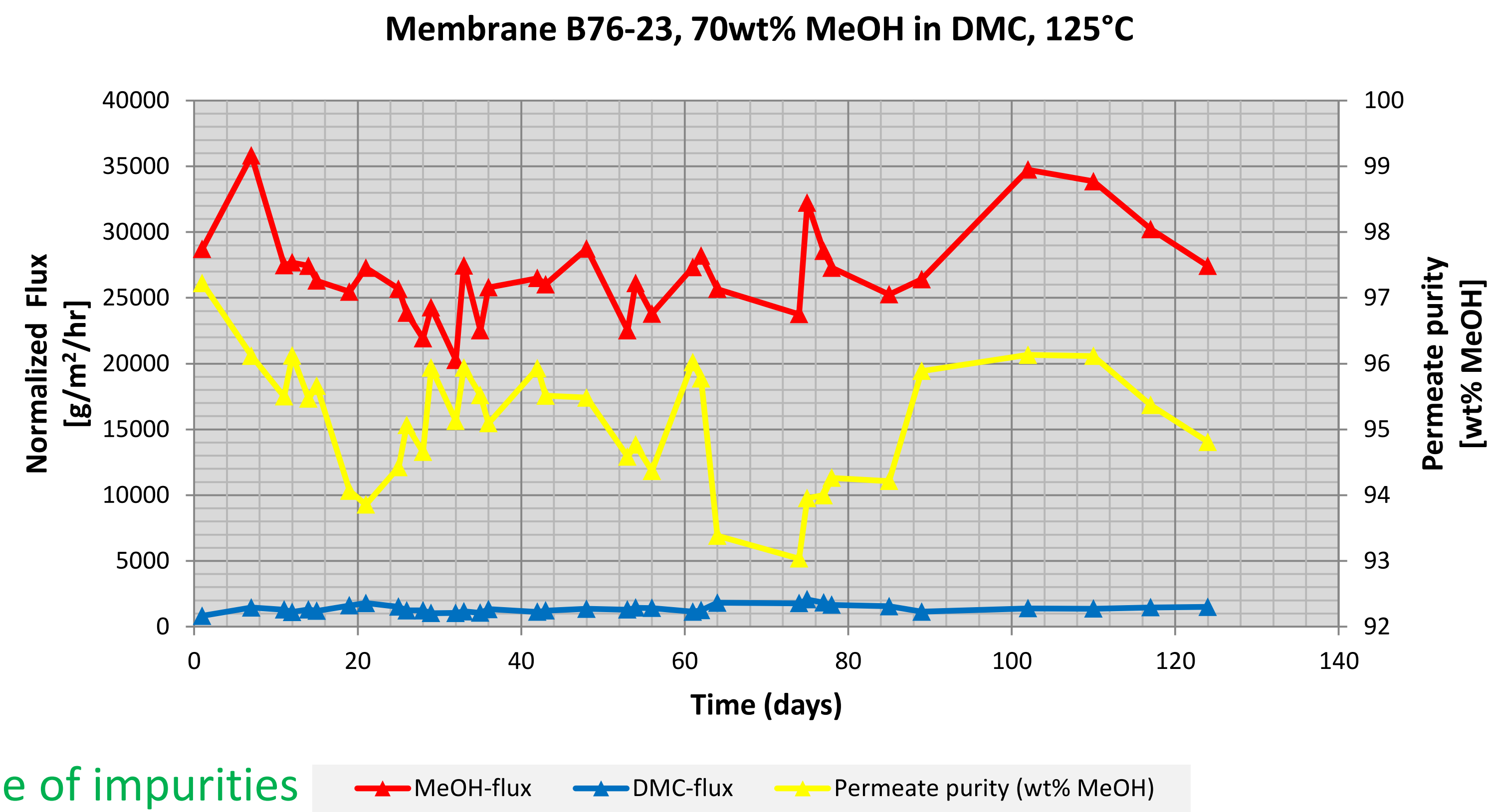




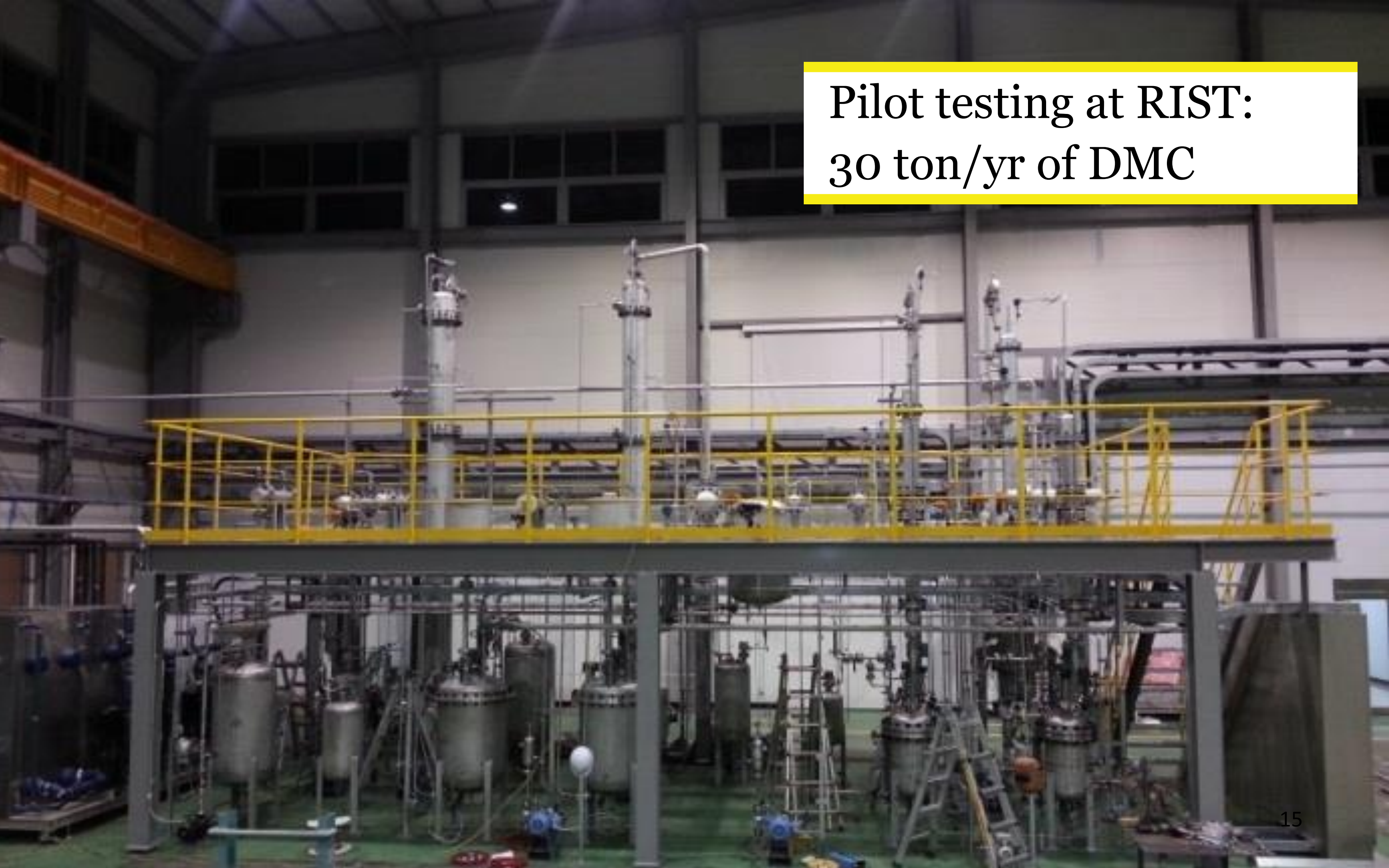
Long term behavior lab scale (1)



Long term behavior lab scale (2)

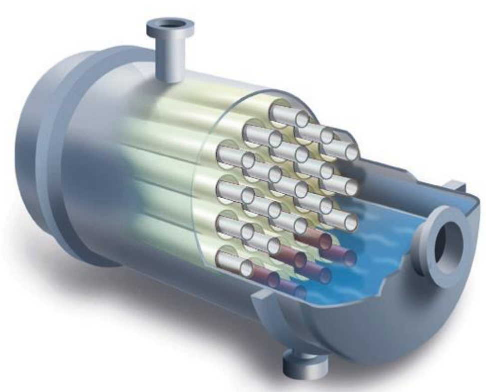


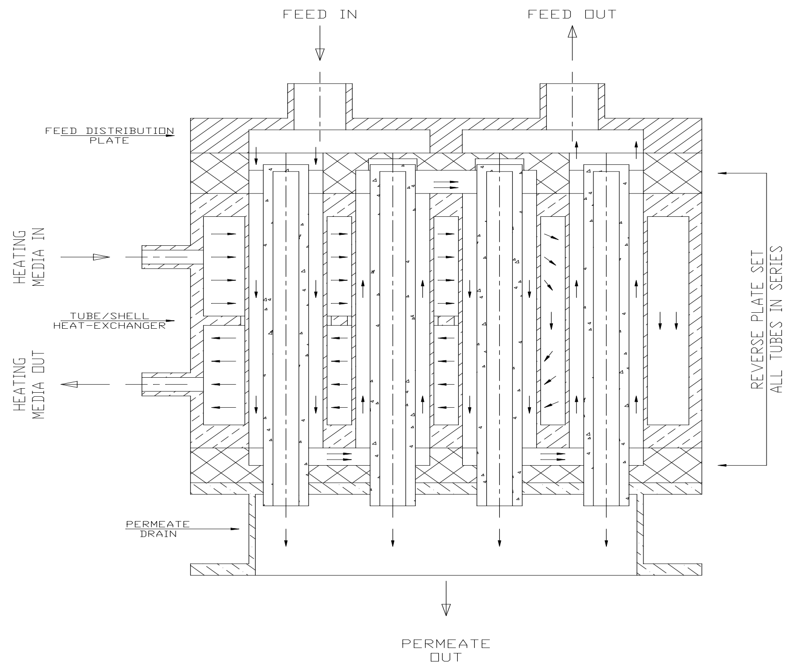
No influence of impurities NH_3 and triethylamine


Pilot testing at RIST:
30 ton/yr of DMC

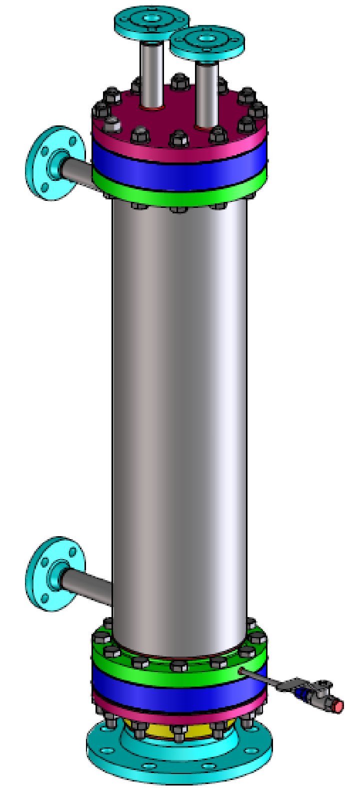
Membranes and Module

- Isothermal configuration
  - Very suitable for high fluxes → high energy demand
- Maximum 1m^2 of membrane surface area





ISOTHERMAL FILTER UNIT

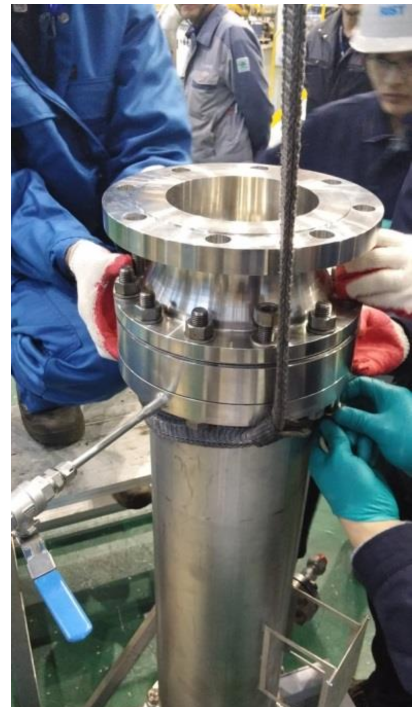


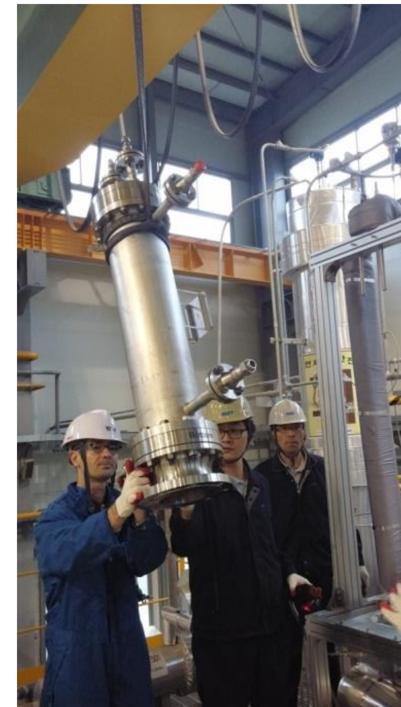
Membranes and Module

ECN, Petten, Netherlands

ECN

Membranes and Module



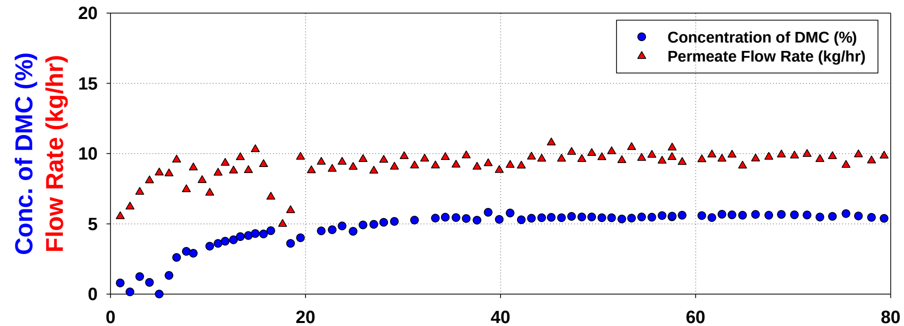


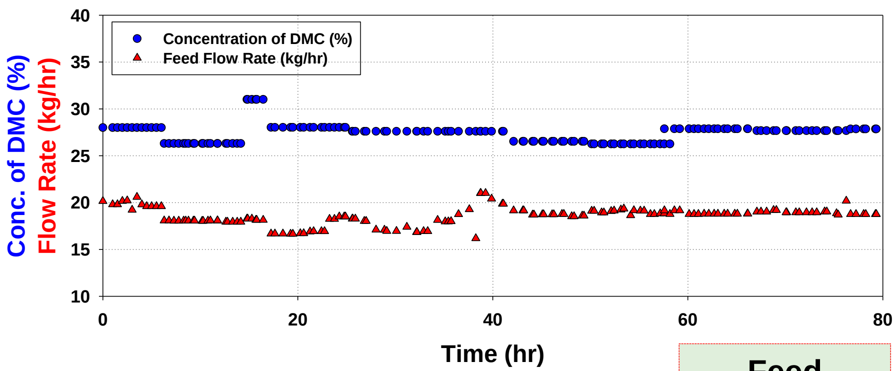
RIST, Pohang, Korea

Pilot test results

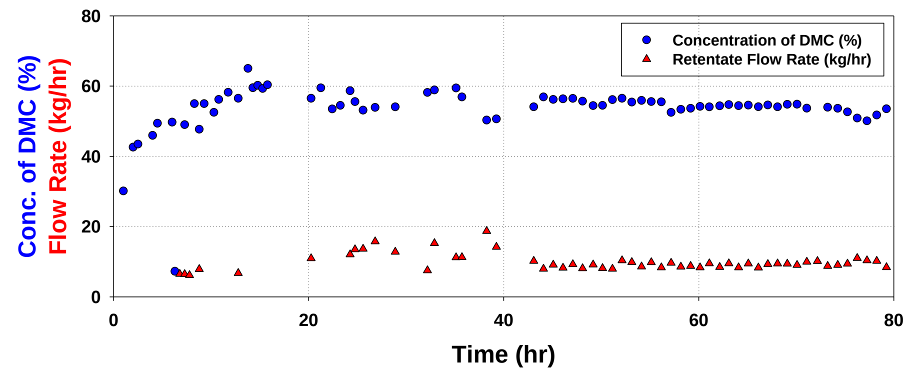
Variations in temperature, permeate pressure, feed flow and feed composition

Permeate





Feed



Retentate

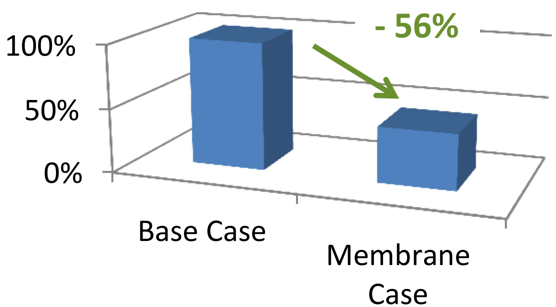
<u>General membrane performance:</u>

Flux = 15 kg/m^{2}hr @ 105°C @ 8 bar @ 600 mbar

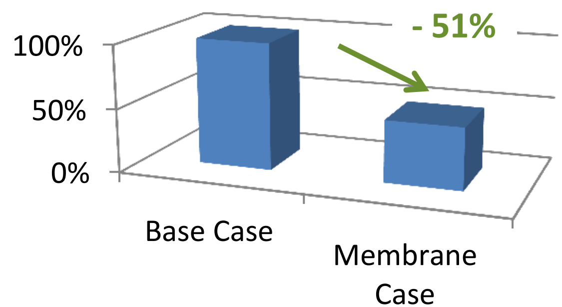
Celebrating the fruitful collaboration and a successful pilot test

Economics

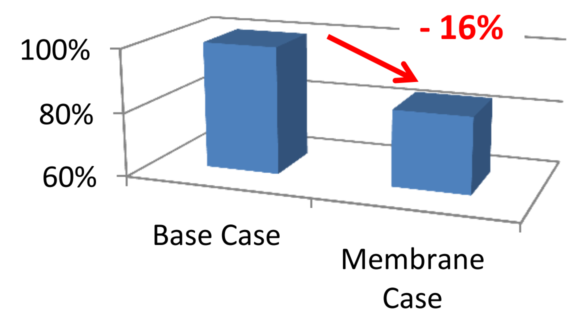
CAPEX



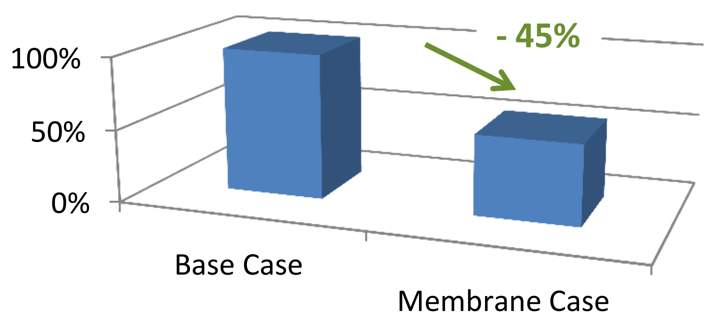
OPEX



DME production rate



Purification cost per ton DME



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