Development of HybSi Membranes for Esterification Reaction

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Membrane Winter School
Eindhoven, Netherlands

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Dutch Organization for Applied Scientific Research TNO

Roadmaps

Sustainable Subsurface
Home to the Geological Survey of the Netherlands. Levering knowledge of the subsurface for the energy transition.

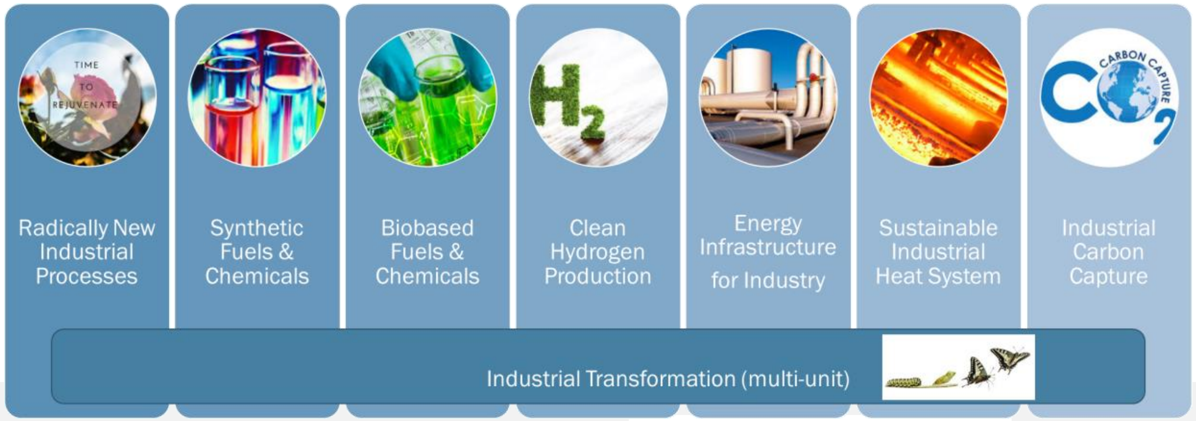
Renewable Electricity
Developing and deploying expertise in wind and solar energy.

System Transition
Enabling a just and socially inclusive energy transition.

CO_2 Neutral Industry
Developing services and technologies for a sustainable industrial sector.

MEASURED

Locations in Netherlands



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TNO innovation for life

A Glance at STIP
Increasing the CO_2 Neutrality of Energy-Intensive Industry

TECHNOLOGY DEVELOPMENT AND UP SCALING

- In-process CO_2 capture and use
- Sustainable industrial heat systems
- Production of green hydrogen

- **We develop crucial technologies enabling industrial transformation and contributing to a reliable sustainable energy system**

KEY KNOWLEDGE AND EXPERTISE

- Separation enhanced synthesis
- Membrane technology
- Process intensification
- Heat pumps
- Electrolysis
- Engineering for piloting & up scaling

- **Cutting edge knowledge and expertise enable us to innovate and scale-up technologies and have tangible impact on industrial transformation**

STATE OF THE ART RESEARCH FACILITIES

- Chatelier lab
- Nollet lab
- Carnot lab
- Mollier lab
- Faraday lab
- Field Lab Industrial Electrification

- **Our research facilities open up new possibilities to fast-track innovations to a higher TRL level**

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Conversion and Separation Technologies (ConSepT)
Membrane Separation Technology

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- Development of (hybrid) ceramic membranes:
  - Ceramic supports providing high chemical and thermal stability
  - Intermediate layer between ceramic support and top-layer.
  - Top layer for selective separation:

1. Sol-gel (hybrid) chemistry: patented HybSi® membrane
2. Polymer top layer

HybSi®
Pervaporation Membranes

- Development of Pd-based membranes:
  - Hydrogen purification from a mixture of gases (HySep)
  - Membrane-enhanced ammonia cracking in a membrane reactor

- See www.hybsi.com
- See www.hysep.com

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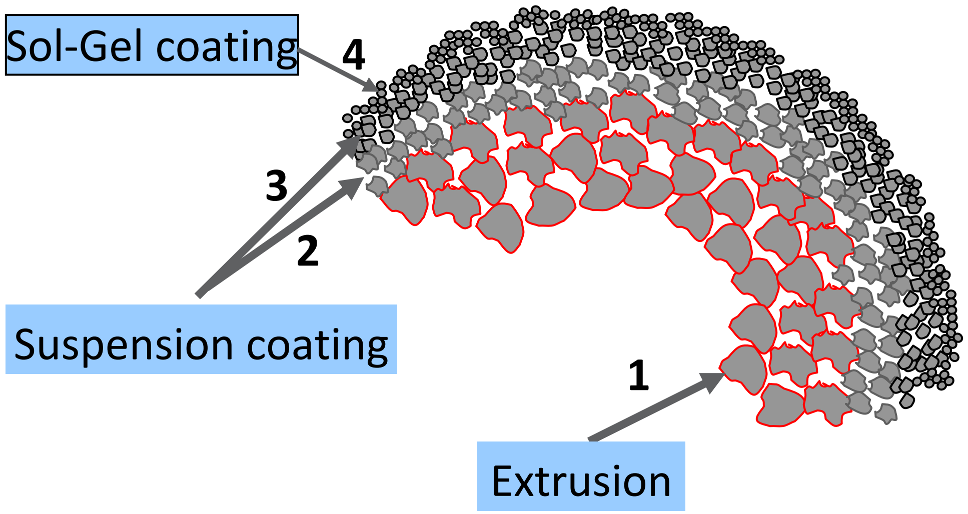
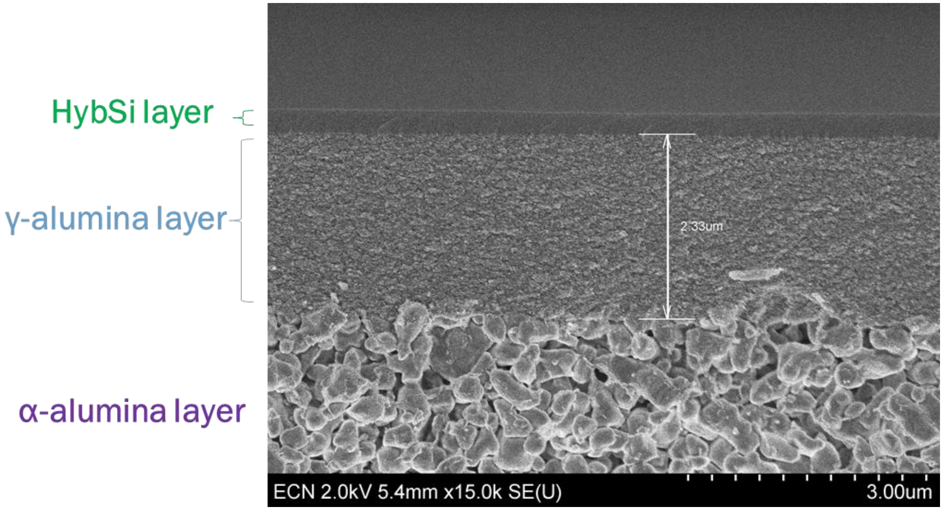
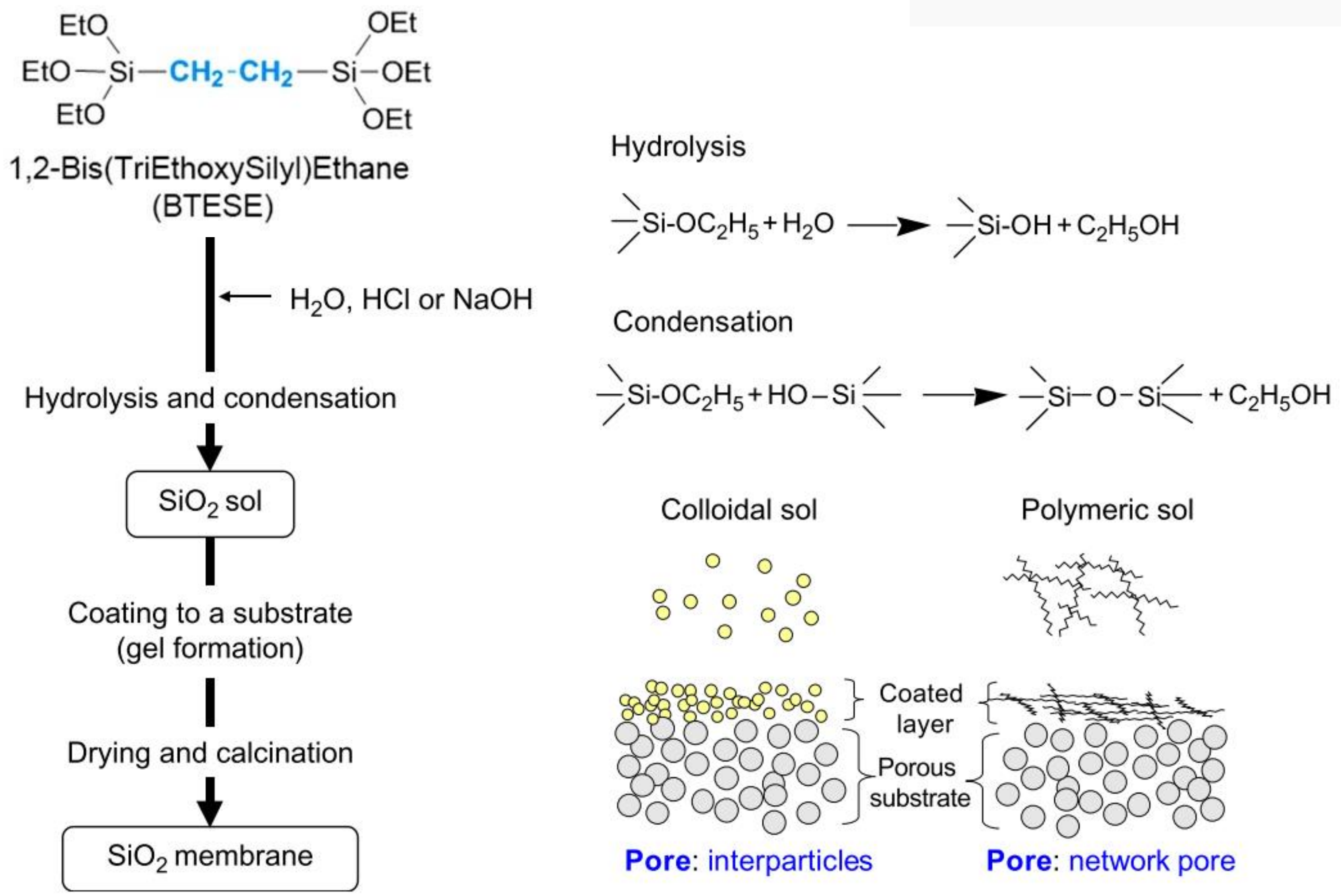
Hybrid Silica (HybSi) Membrane Preparation







Silica Membrane Application for Pervaporation Process, http://dx.doi.org/10.1016/B978-0-444-63866-3.00009-1

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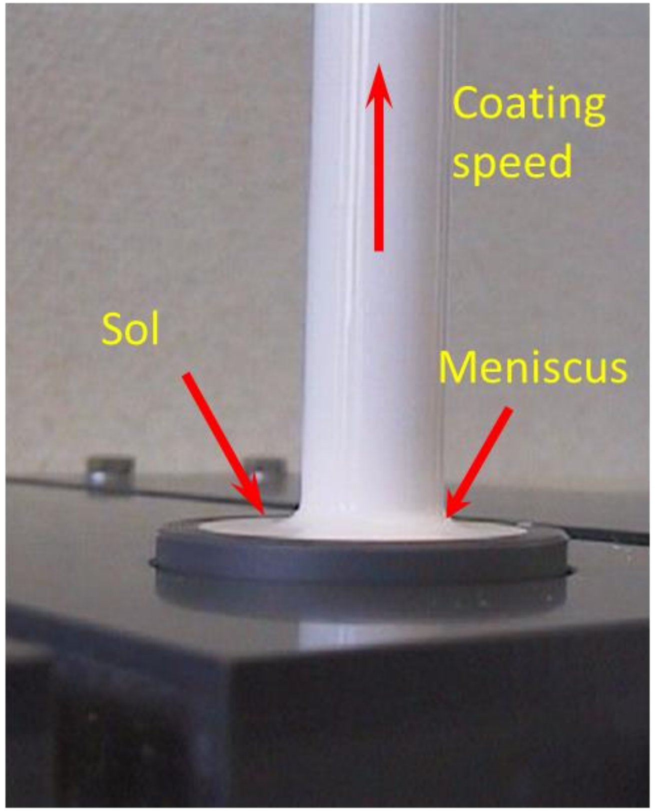
Hybrid Silica (HybSi) Membrane Preparation

Coating procedure



- Coating outside tubular support
- 1 m length, OD: 14 mm, ID: 10 mm

- Stainless steel caps

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Pervaporation Using HybSi Membrane

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Pervaporation (with a hydrophilic membrane):

= Permeation + Evaporation

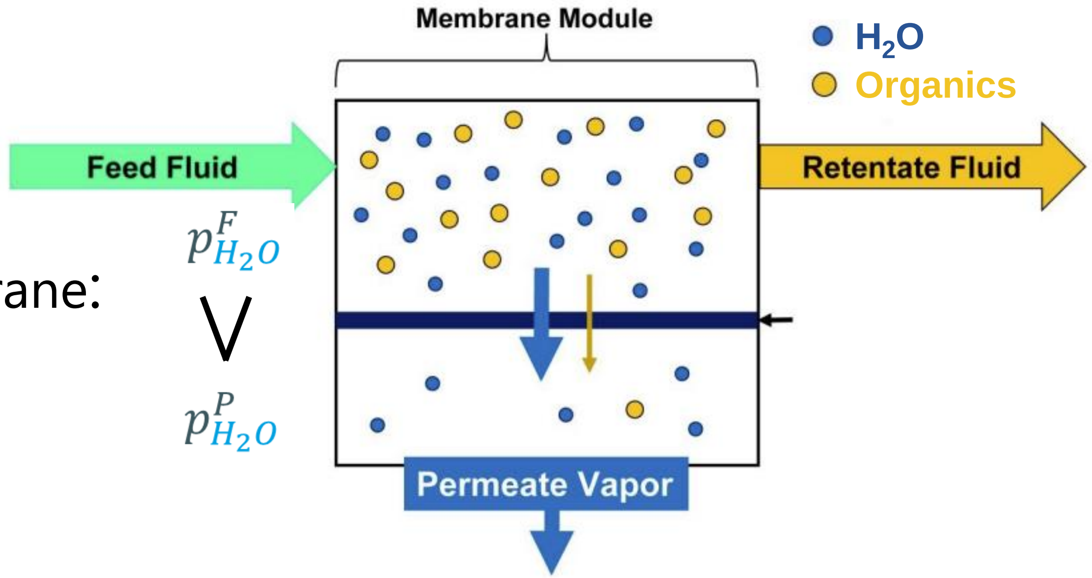
= Water selectively permeates through HybSi®

= Driving force is partial pressure gradient across membrane:

$$\Delta p_{H_2O} = p^F_{H_2O} - p^P_{H_2O} > 0$$

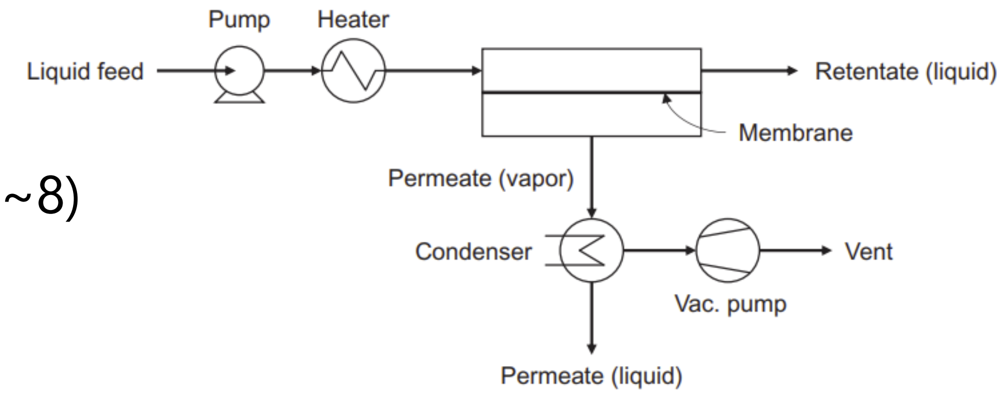
= More energy efficient than distillation

= Breaking azeotropes



HybSi® separation of water from organic fluids

- Very high stability, operating up to 200°C
- Operating under harsh process conditions (~ 2 < pH < ~8)
- Reduced operating costs in industrial processes



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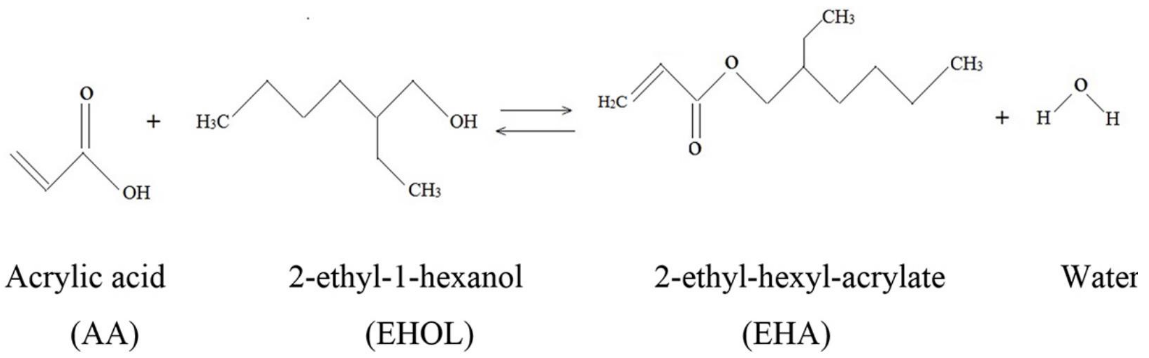
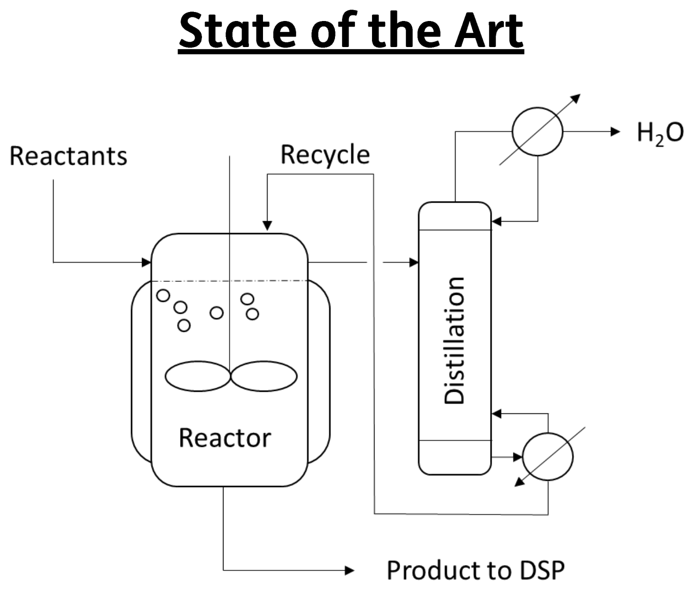
Esterification Reaction of Arkema

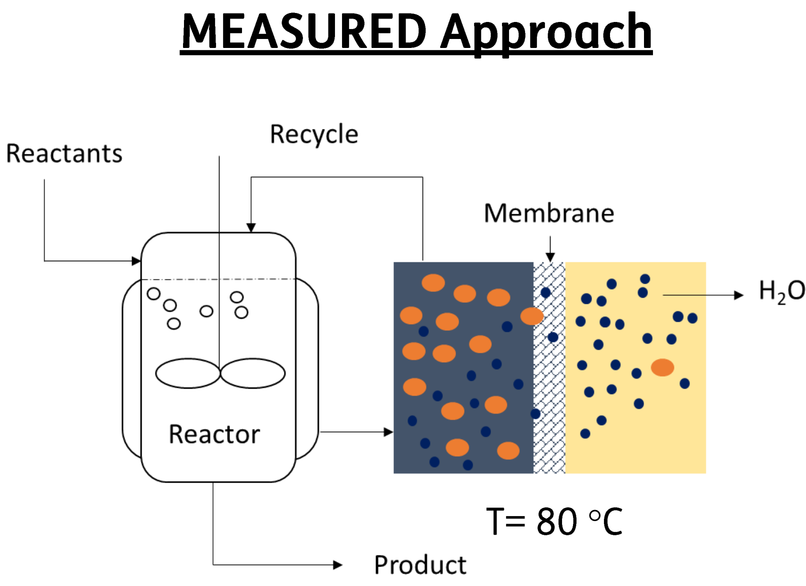


Potential advantages pervaporation:

- Pervaporation is less energy intensive compared to distillation
- Lower temperature => decrease polymerization and blocking of equipment
- Faster water removal => decrease undesired byproducts and higher feedstock efficiencies

- Reaction temperature: 80-100 °C
- Water content: 1-2 wt.%
- Acrylic acid content: 5-10 wt.%
- pH= 4
- Boiling point of the mixture= 160 °C
- Distillation T> 120 °C
- Pervaporation T= 80 °C





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Objectives of the MEASURED

- Development of an Acid Resistant HybSi membrane for esterification reaction
- Scaling up the HybSi membrane from tubular mono-channel to mutil-channel geometry

- Coating on outer surface
- L: 1 m, OD:14mm, ID: 10 mm
- 24 Tubes to get 1 m^2 area

Higher area per volume
Membrane cost reduction

- Coating inside 7 channels
- 1.2 m length, OD:25 mm ID: 6 mm
- 7 Tubes to get 1 m^2 area

- Demonstration in pilot-scale with 3 m2 membrane area for 3 months
- Cleaning in Place (CIP)

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Experimental Protocol

1. N_2 permeation measurement test at 3 bars
   - To check if the selective HybSi layer is defect-free
2. Pervaporation dehydration of n-butanol/water (5 wt.% water)
   - Selectivity (water concentration in permeate)
   - Permeate Flux

$$J = \frac{m_p}{A \cdot t}$$

3. Dehydration of Arkema reaction mixture in pervaporation at 80 °C
4. Dehydration of n-butanol/water (5 wt.% water) in pervaporation at 80 °C
   - To check if the membrane performance changed after the main pervaporation test

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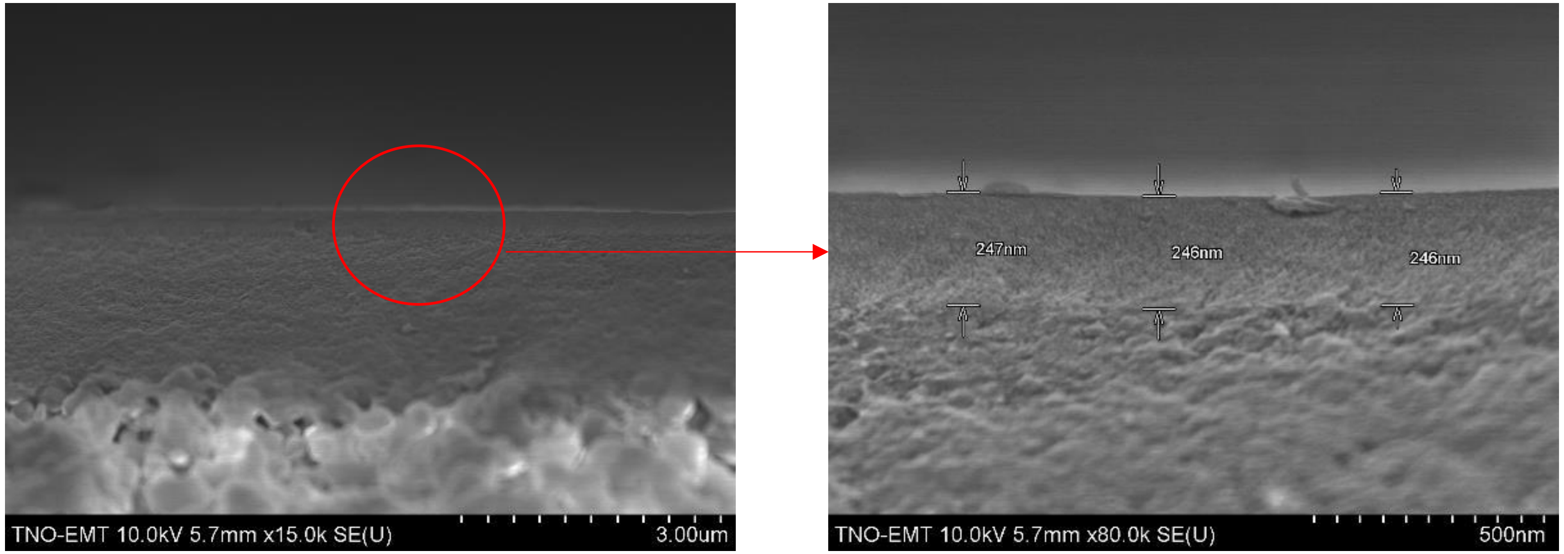
Preparation of 1st Generation of HybSi
HybSi Standard

- Tubular ceramic support (Pore size: 3 µm)
- 2 layers of α-alumina (200 nm)
- 1 layer of γ-alumina intermediate layer (3-5 nm)
- HybSi layer (0.5-0.8 nm)



HybSi Standard, Thickness: 250 nm

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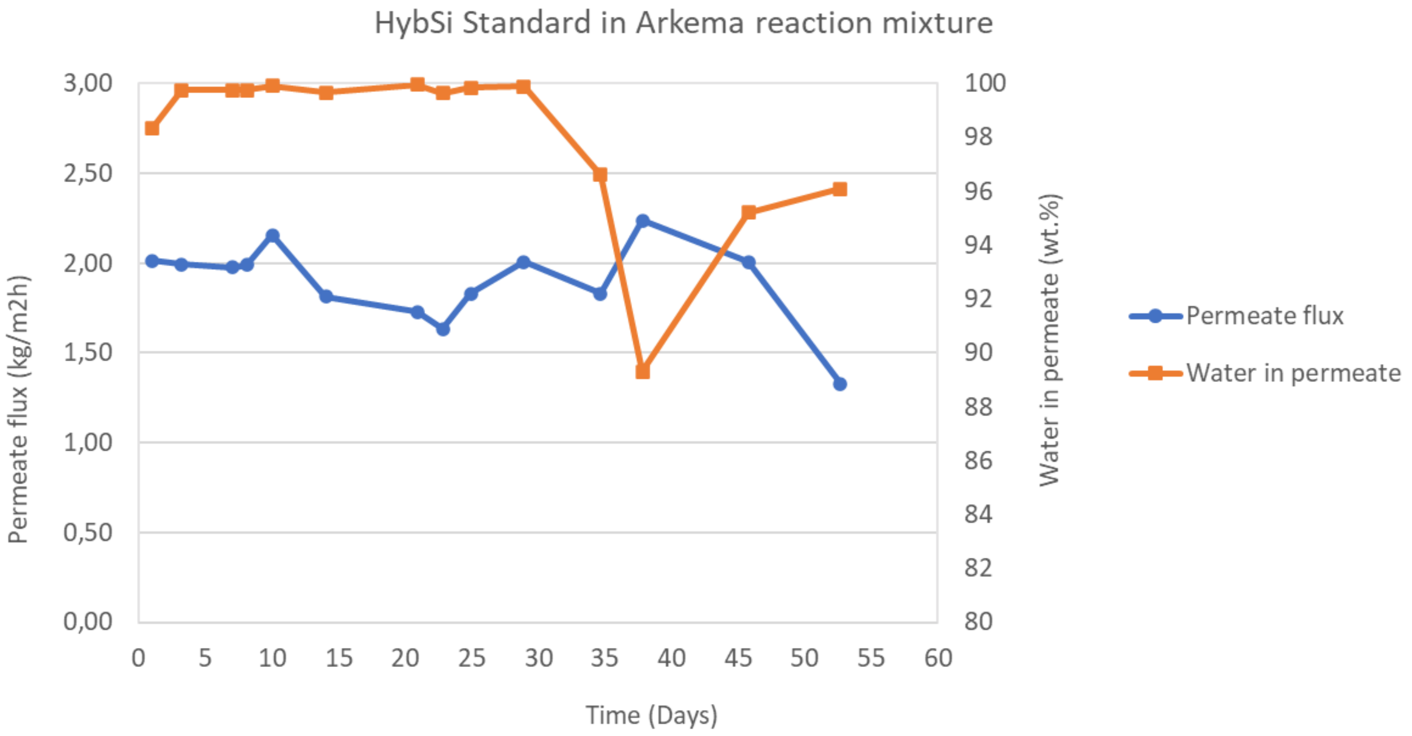
1st Generation of HybSi
Pervaporation Stability Test with HybSi Standard

- Arkema mixture: 2 wt.% water, 2EHA (60%), 2EHOH (28%), AA (10%) and Tempo (0.06%)
- T= 80 °C
- Permeate P= 10 mbar
- Flow rate= 160 L/h

- Stable for almost a month
  - Flux= 2 kg/m^{2}h
  - Water in permeat= 99.9 wt.%

- Selectivity dropped from Day 29
- Other components also permeated through the membrane
- Membrane affected by acid attack



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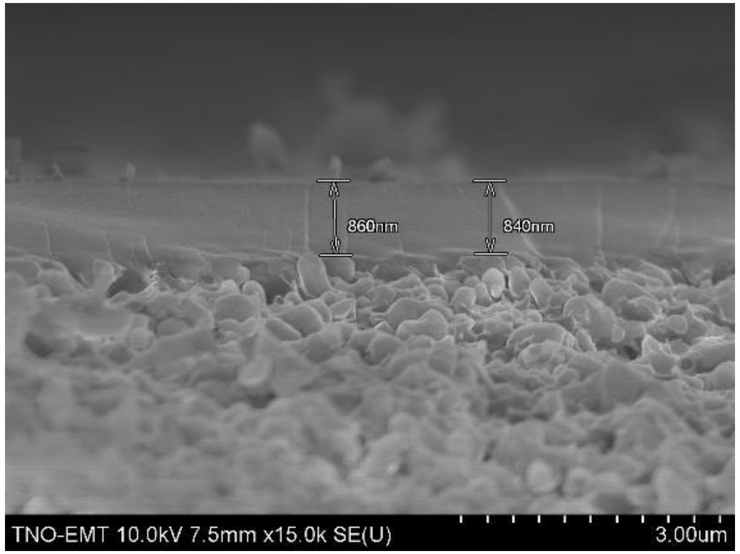
Preparation of 2nd Generation of HybSi
HybSi Acid Resistant (AR)

- Gamma-alumina sublayer is the weakest link for acid stability in the HybSi Standard.
- Gamma-alumina intermediate layer is eliminated. (TNO Route)
- HybSi sol is directly coated on alpha-alumina layer with sequential coating method
- A thicker selective layer compared to HybSi St.



HybSi AR, Thickness: 850 nm

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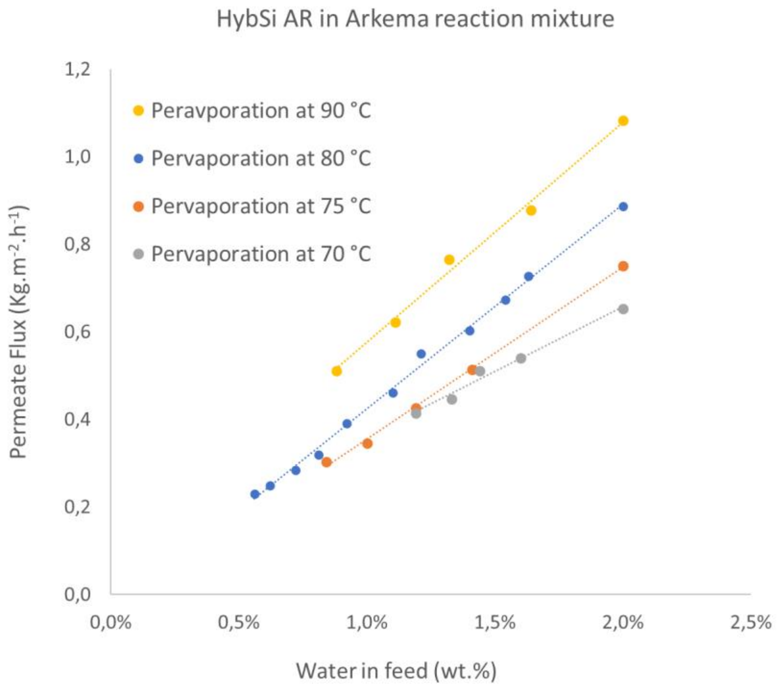
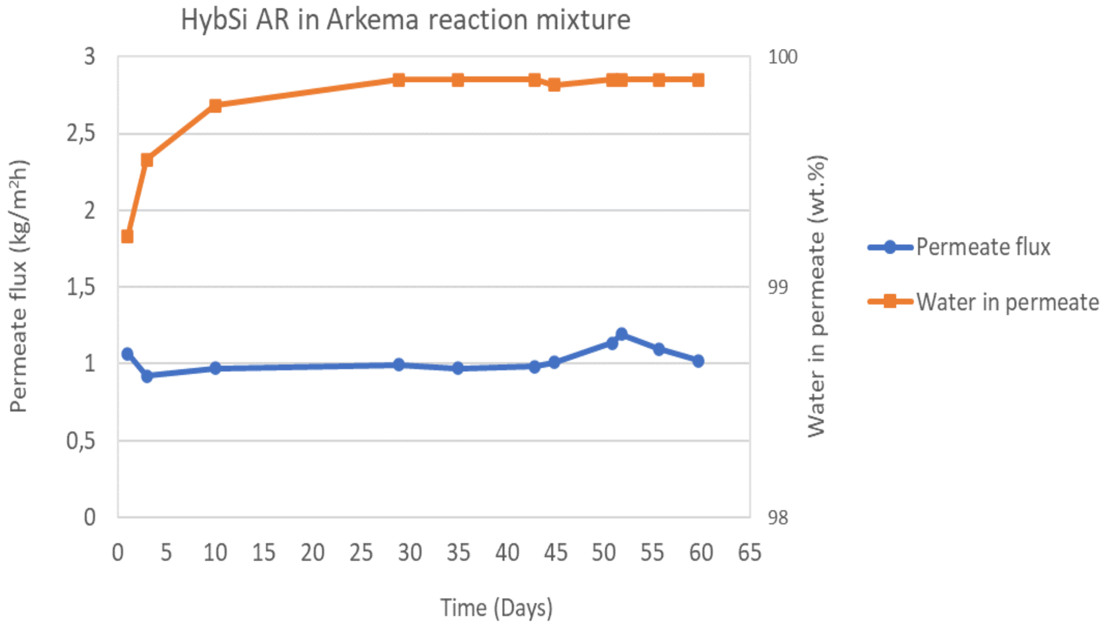
2nd Generation of HybSi
Pervaporation Tests with HybSi AR

- Feed: 2 wt.% water in EHA (60%), EHOL (28%), AA (10%) and Tempo (0.06%)
- T= 80 °C, Permeate pressure = 10 mbar, Flow rate= 160 L/h



Short-term test at different temperatures
Water in permeate > 99.5 wt.%



Long-term stability test for 2 months
Stable performance throughout 2 months of test
Water in permeate> 99 wt.%; Permeate flux = 1 kg/m^2h

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Preparation of 3rd Generation of HybSi Multi-Channel HybSi Acid Resistant (AR)

- Sequential coating **inside** multi-channel CTI supports **ID: 6 mm**
  - Different CTI MC supports
  - Different coating speeds
  - Different Sol dilutions
  - Intermittent drying

L= 250 mm OD: 25 mm, ID: 6 mm, 7 Channels,

- Multiple coating steps are required
- Challenge: After calcination formation of cracks in HybSi layer.
- Solution: Calcination in lower temperature

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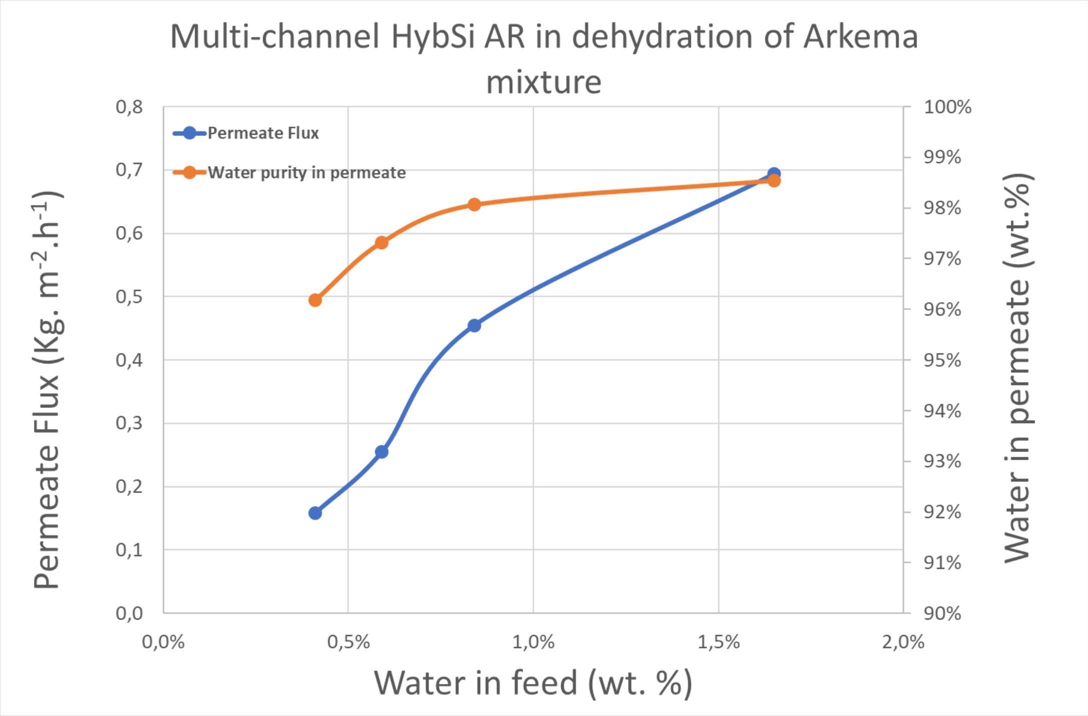
3rd Generation of HybSi
Pervaporation Tests with MC HybSi AR

- Feed: 2 wt.% water in EHA (60%), EHOL (28%), AA (10%) and Tempo (0.06%)
- T= 80 °C, Vacuum pressure = 10 mbar, Flow rate= 160 L/h
- In the end: water in feed= 0.27 wt.%



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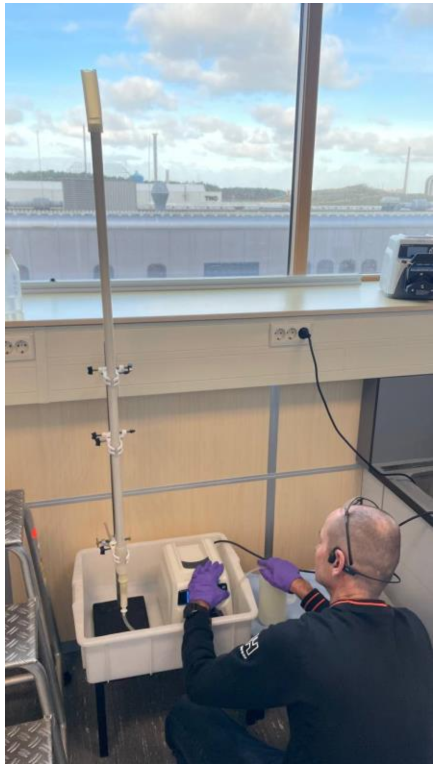
Scaling up of 3rd Generation of HybSi MC HybSi AR with industrial size

- Multi-Channel CTI supports: L= 1.2 m, 7 Channels, Channels ID= 6 mm
- Sequential coating method is applied to get desired N_2 permeance
- Testing is scheduled in Feb 2025



Conclusions and Next Steps

- 3 Generations of HybSi membrane were developed by TNO.
- The 1st Generation was not acid resistant, and the 2nd Generation was on a tubular support.
- The membrane showed a stable performance in pervaporation dehydration of acid-containing Arkema esterification reaction mixture for 2 months.
- The 3rd Generation of HybSi was prepared inside MC CTI supports based on 2nd generation approach.
- MC HybSi AR membrane showed also a comparable results with good permeability and selectivity
- Upscaling of MC HybSi AR membrane is ongoing on industrial size CTI supports (1.2 m) and will be tested in pervaporation.
- Either of HybSi AR membranes develoted by TNO or CTI will be produced for demonstration phase.

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