



Energy research Centre of the Netherlands

Pushing membrane stability boundaries with HybSi[®] pervaporation membranes

**Jaap Vente, Robert Kreiter, Henk van Veen, Donough Shanahan,
Mariëlle Rietkerk, Hessel Castricum, Andre ten Elshof**

Presented at the DSTI Congres, Amersfoort, 25 June 2010

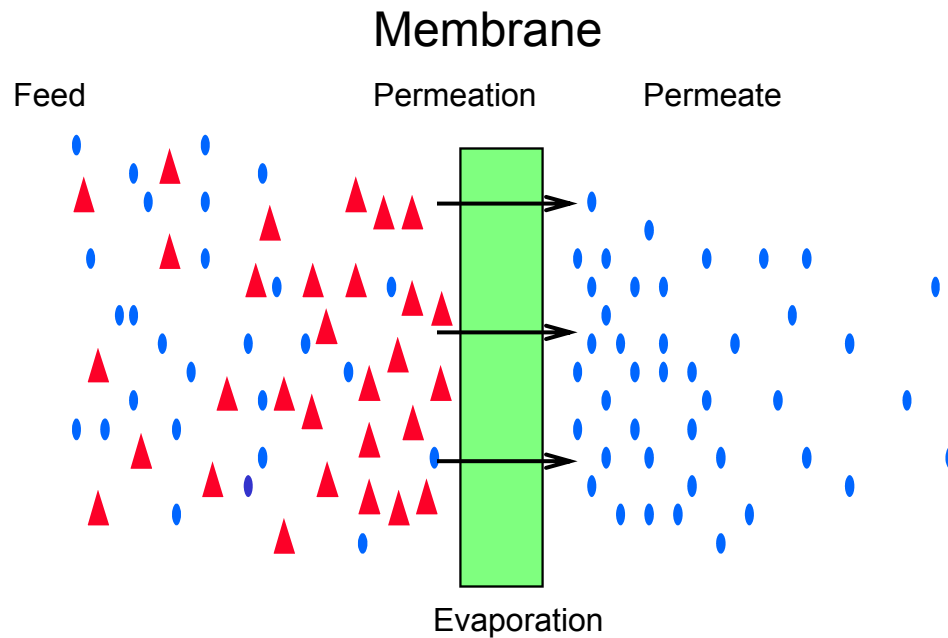
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What is pervaporation

- Selective evaporation via a membrane
- Much higher energy efficiency than distillation



Commercially available pervaporation membranes

- Polymers
 - PVA (Sulzer Chemtech)
 - Polyimide (Vaperma)
- Ceramics
 - Zeolite A (Mitsui, Mitsubishi, Inocermic, Zeolite Solutions)
 - SiO₂ (Pervatech)

Towards a generally accepted technology

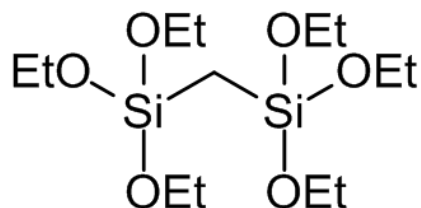
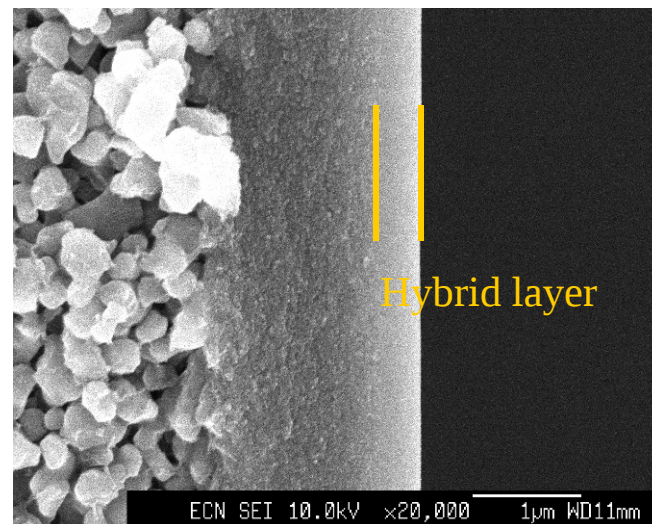
- Limitations currently perceived by the end-user
 - Limited stability
 - High risk option
 - Predictability has to improve (where is the predictive tool?)
 - Application window too small
- Current challenges
 - Higher application temperatures
 - Higher resistance against acids and alkalines
 - Higher stability in aggressive solvents
 - Larger application window w.r.t. water content
 - Effective methanol removal
 - Resistance against condensation

The answer: HybSi®

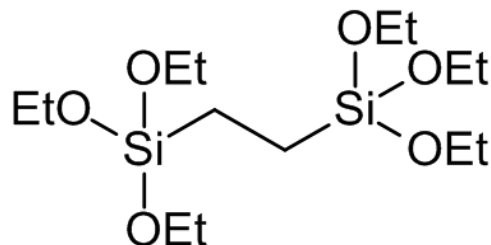
- **Strategy**

replace unstable Si—O—Si bonds in SiO_2
by stable $\text{Si—C}_m\text{H}_n\text{—Si}$ bonds

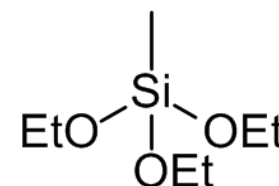
Precursors



Methane bridge
BTESM



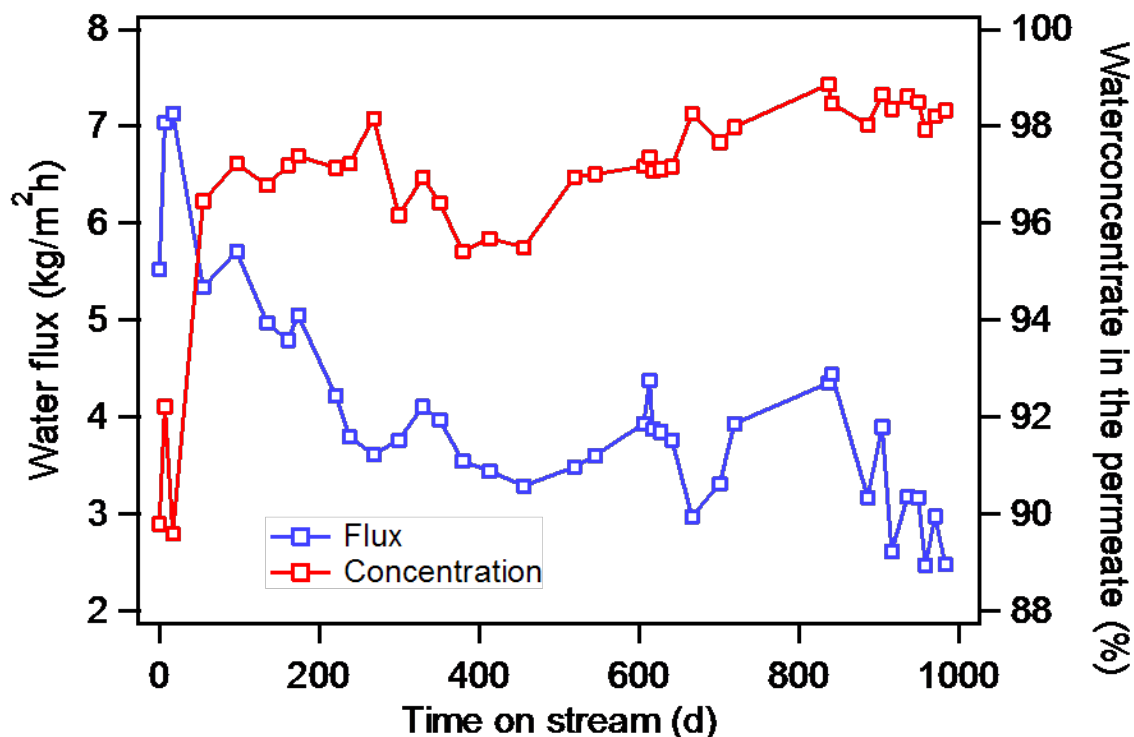
Ethane bridge
BTESE



Methyl terminating group
MTES

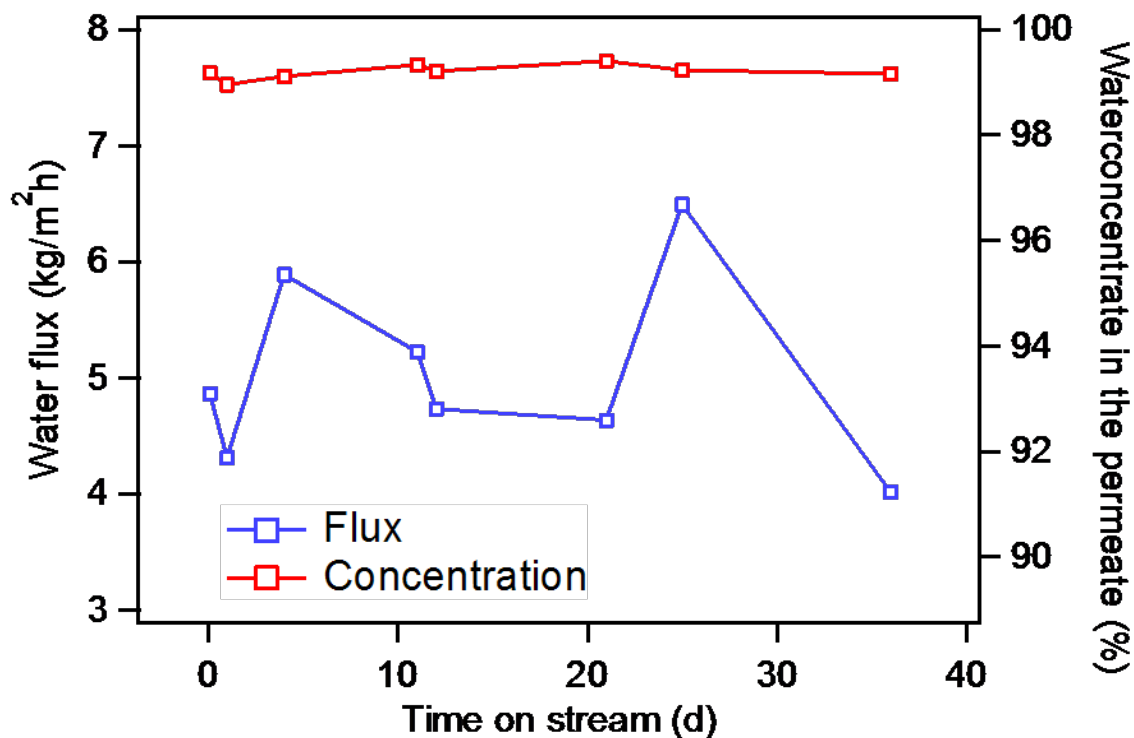
Long term performance

- BTESE – MTES
- 150°C
- 3% H₂O in BuOH
- Measurement stopped after 1000 days



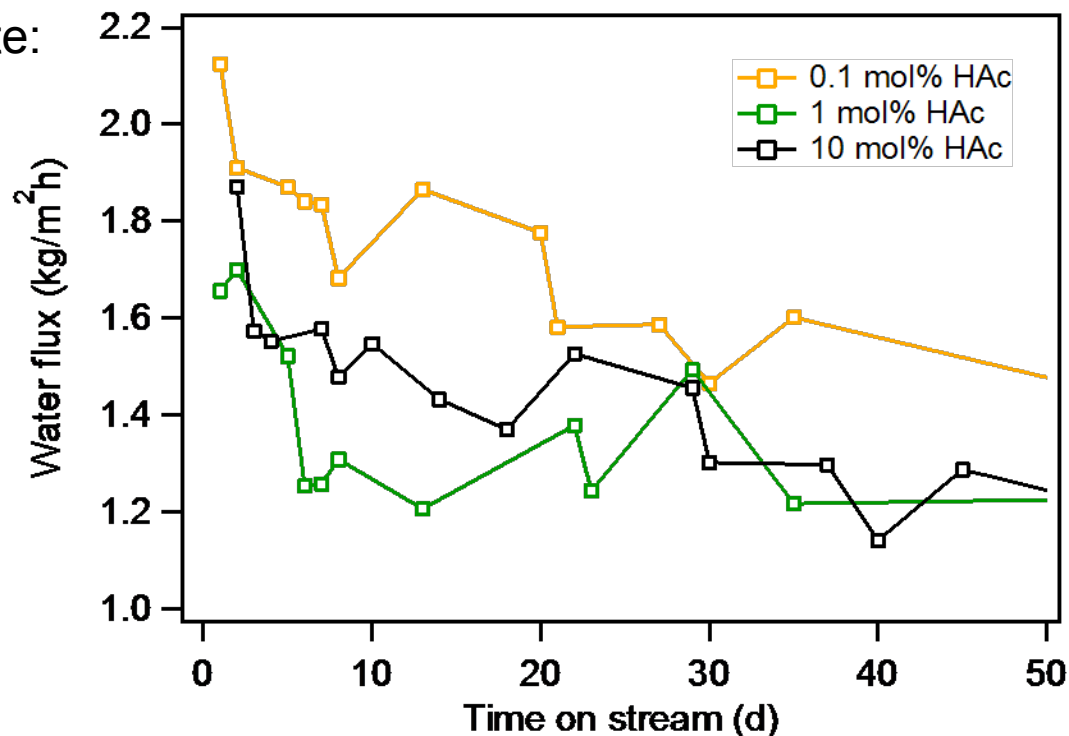
High temperature performance

- BTESE – MTES
- 190°C
- 3% H₂O in BuOH
- Measurement stopped after 35 days



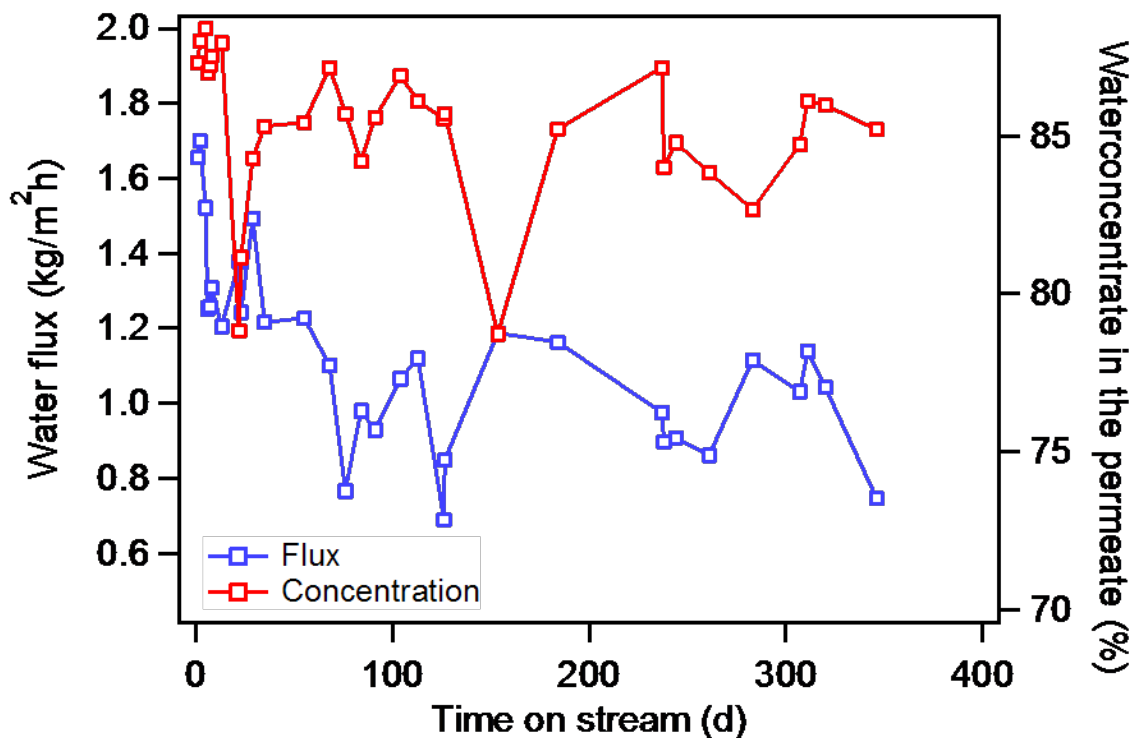
Acid resistance (HAc in EtOH)

- Various levels of HAc in EtOH
- BTESM
- 70°C
- 5% H₂O in EtOH
- Water content in permeate: >85%



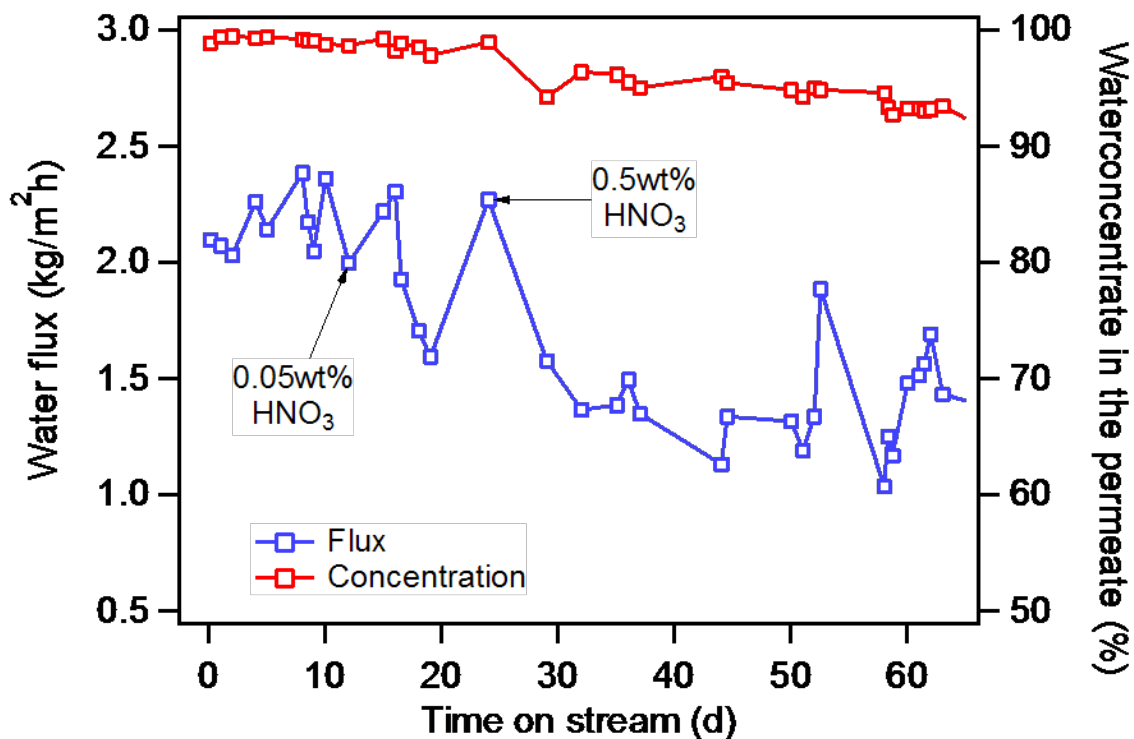
Long term behaviour in the presence of acid

- BTESM
- 70°C
- 5% H₂O in EtOH
- 1mol% HAc present



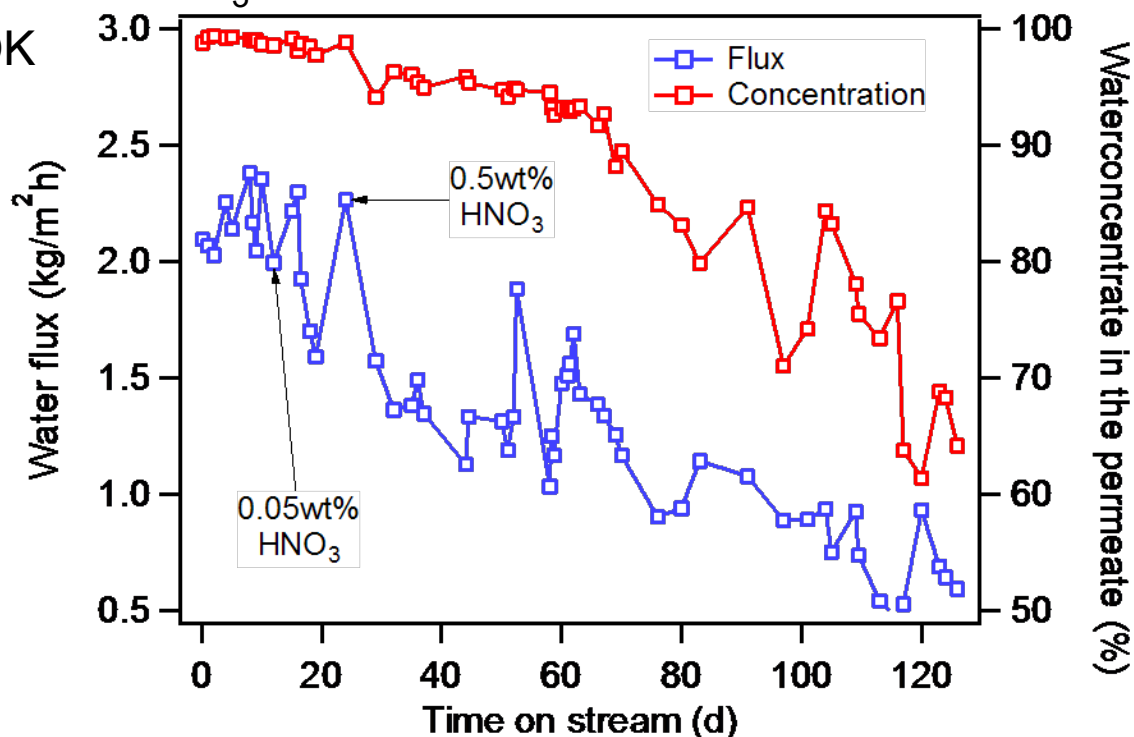
Acid resistance HNO₃ in BuOH

- BTESE
- 95°C
- 5% H₂O in BuOH



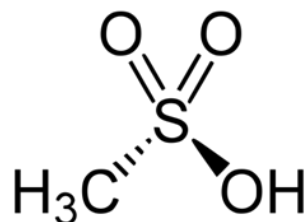
Acid resistance HNO_3 in BuOH

- BTESE
- 95°C
- 5% H_2O in BuOH
- Decrease of selectivity 0.5% HNO_3
- $\text{pH} \approx \sim 2$ seems to be OK

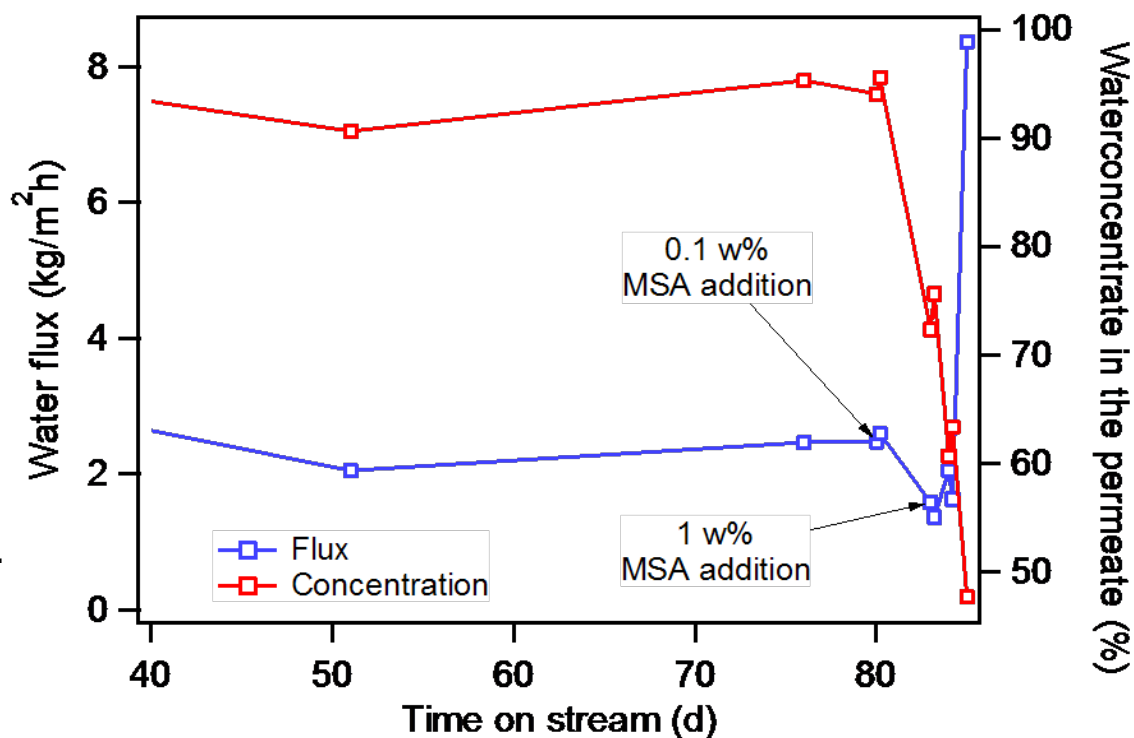


Limitations 1% MSA in BuOH

- Methysulfonic acid

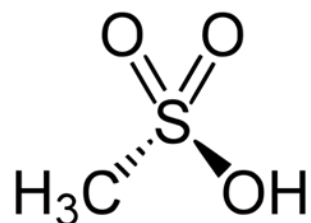


- BTESE
- 95°C
- 5% H₂O in BuOH
- 0.1 – 1 w% MSA added.

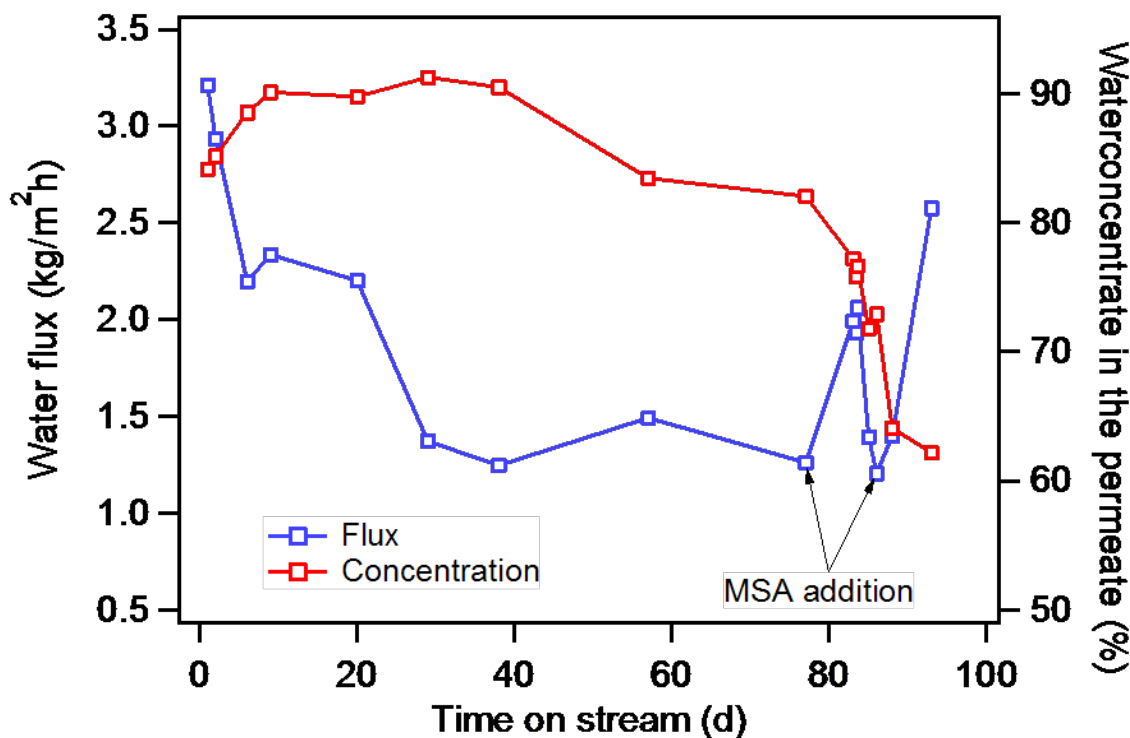


Limitations 0.1% MSA

- Methysulfonic acid

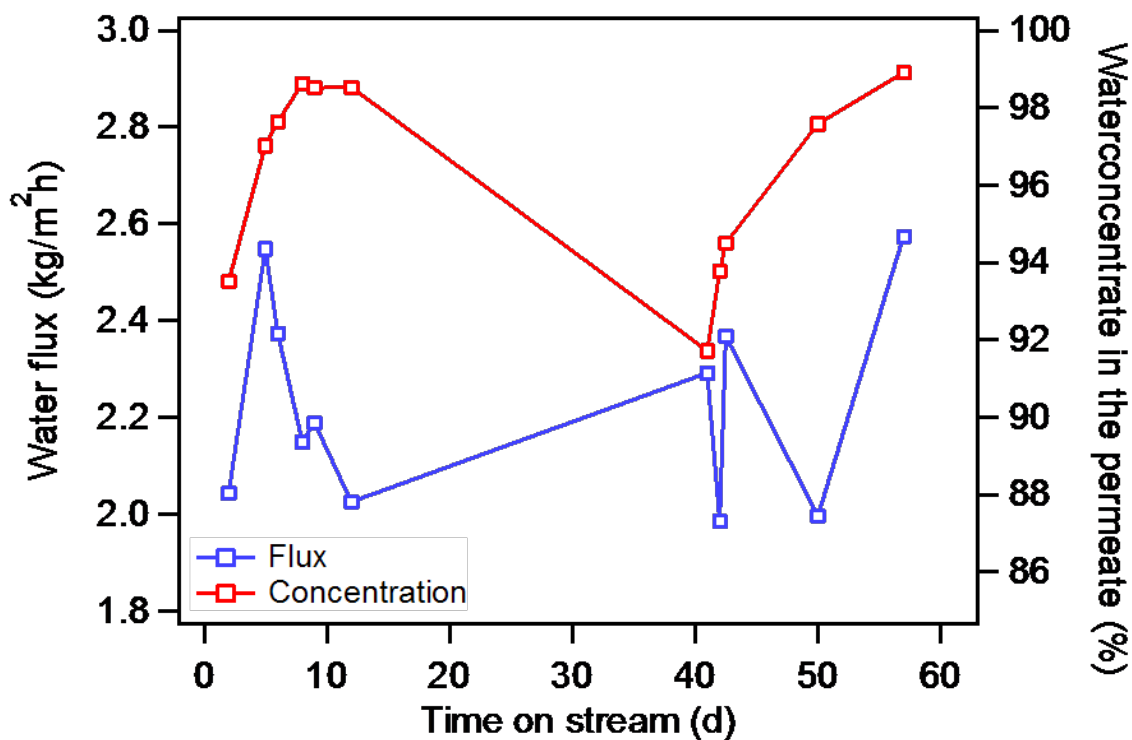


- BTESE – MTES
- 95°C
- 5% H₂O in BuOH
- 0.1w% MSA added



Acetic acid

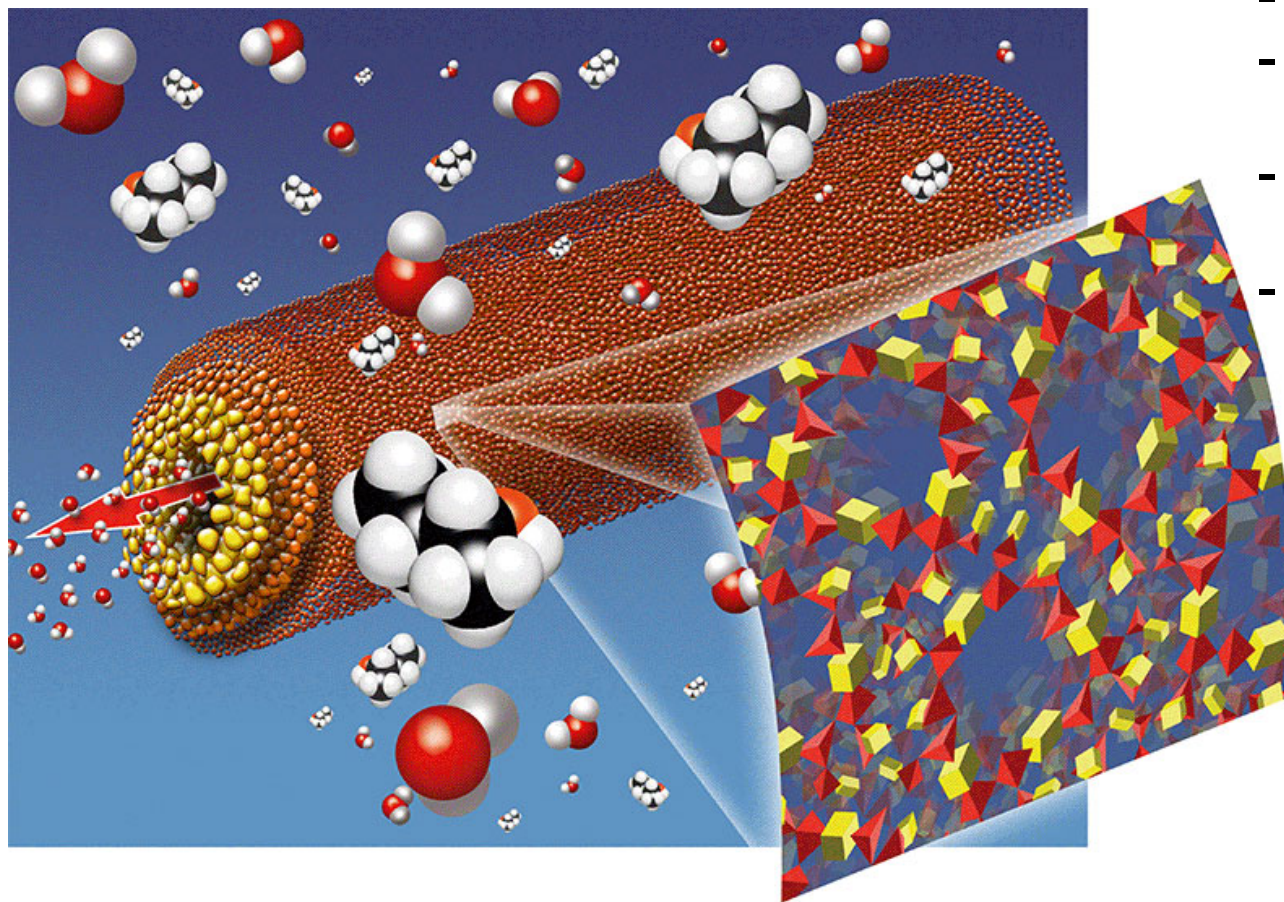
- BTESM
- 95°C
- 10% H₂O in HAc



HybSi advantages over commercial products

- Higher application temperatures
 - 190°C
- Higher resistance against acids and alkalines
 - $\sim 2 < \text{pH} < \sim 8$
- Higher stability in aggressive solvents
 - NMP, MEK
- Larger application window w.r.t. water content
 - Measurement up 30% performed
- Effective methanol removal
 - Feasibility shown
- Resistance against condensation
 - All liquid feed no issue

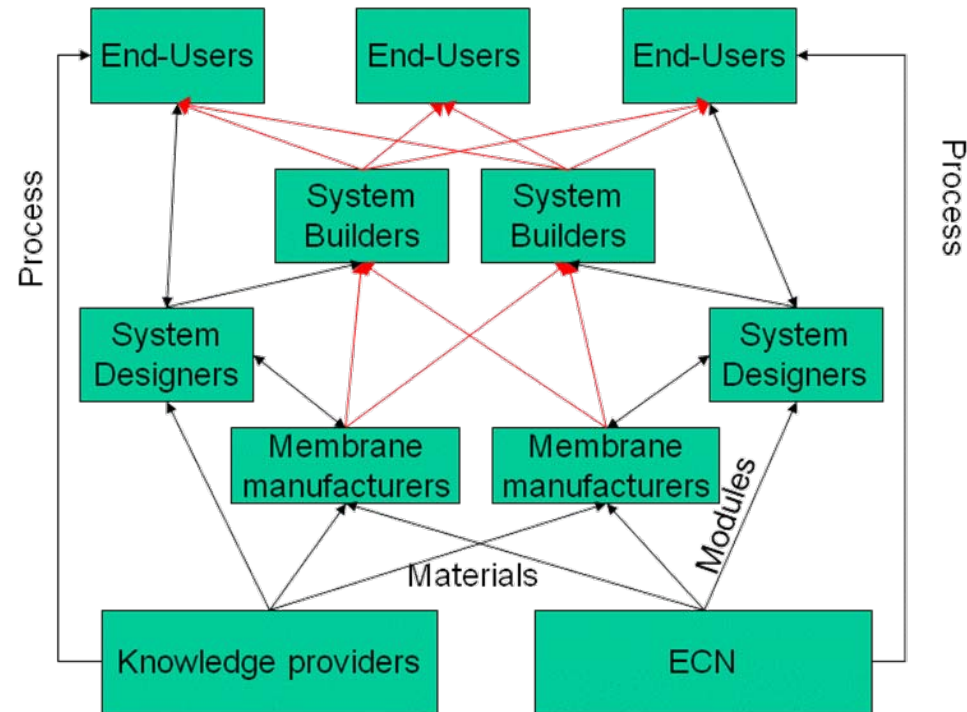
Origins of stability



- More stable bonds
- Higher crack propagation energy
- Lower surface diffusion coefficient
- Lower solubility

Moving to the market

- Commitment from **end users**
 - Tests & module sales
 - Process analyses
- Interest from **OEM**
 - Letters of interests
 - Active participation



- Contract with **manufacturers**
 - First licence granted to Pervatech
 - Letters of intent for joined developments with others



Lab scale testing for the industry

Targeted application tests for DSTI partners

- Bulk Chemicals sector (about to finish)
 - Sabic
 - Huntsman
- Technoproject (about to start)
 - DSTI in collaboration with NL-GUTS
 - Huntsman
 - DSM

Industrial pilot test

- Consortium:
 - Trion Partners, Air Products, Sulzer Chemtech, and Deltalinqs
- 30m³ of end of pipe fuel
- from 30-35% to ~2% water
- 1m² membrane area
- July – September 2010
- First result promising!



Acknowledgements

- Industrial collaborators
 - Sabic
 - Huntsman
 - Air products
 - DSM
 - Sulzer Chemtec
 - Pervatech
 - Trion partners
- Financial support
 - STW
 - AgentschapNL
 - DSTI

- Knowledge network
 - University of Twente
 - University of Amsterdam
 - TNO



Membrane Technology Group
www.ecn.nl/memtech

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Patent: WO2007081212; WO2010008283



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