Pushing membrane stability boundaries with HybSi® pervaporation membranes

H.M. van Veen

R. Kreiter

D.P. Shanahan

M.D.A. Rietkerk

M.M.A. van Tuel

H.L Castricum (Univ. Twente)

J.E. ten Elshof (Univ. Twente)

Jaap Vente

Presented at NAMS-ICIM 2010 (North American Membrane Society - Int. Conference on Inorganic Membranes 2010),July 17-22, 2010, Washington, D.C., USA

ECN-M--10-064 August 2010

ECN

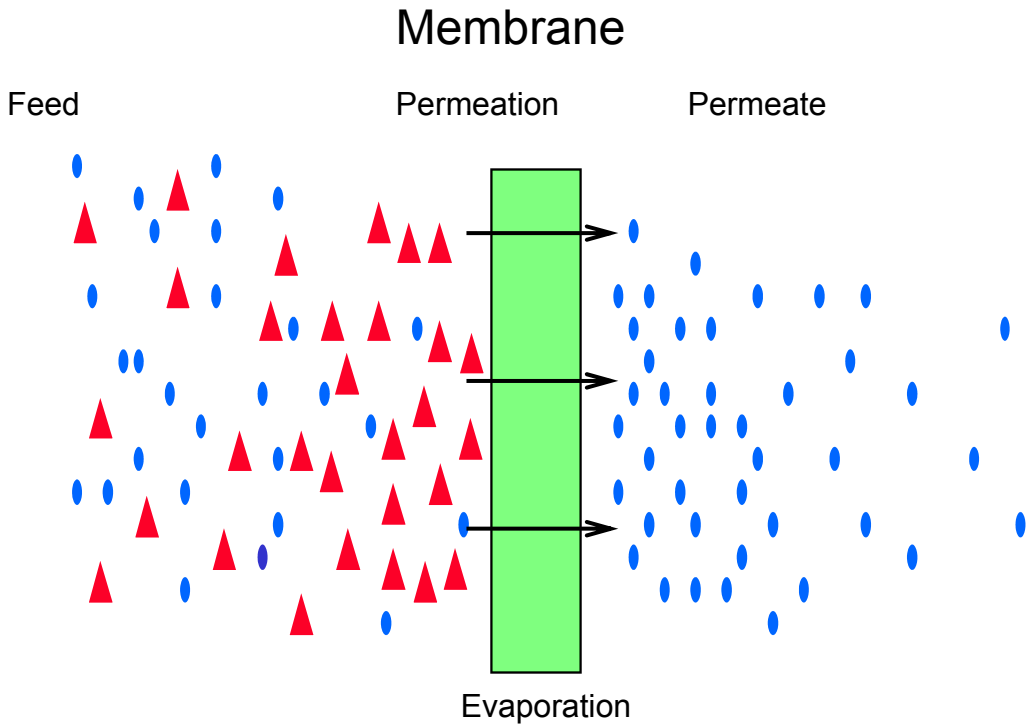
Energy research Centre of the Netherlands

Pushing membrane stability boundaries with HybSi® pervaporation membranes

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

What is pervaporation

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



Heating 1 kg water from 25 to 100°C: 314 kJ
Evaporation of 1 kg water: 2260 kJ

Commercially available pervaporation membranes

- Polymers
  - PVA (Sulzer Chemtech)
  - Polyimide (Vaperma)

- Ceramics
  - Zeolite A (Mitsui, Mitsubishi, Inocermic, Zeolite Solutions)
  - SiO_2 (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

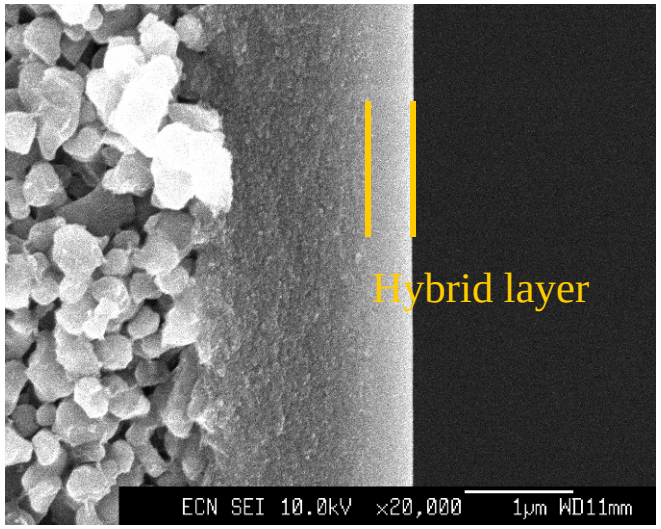
- Current challenges
  - Higher application temperatures
  - Higher resistance against acids and alkalines
  - Higher stability in aggressive solvents
  - Larger application window w.r.t. water content
  - Effective methanol removal
  - Resistance against condensation

The answer: HybSi®

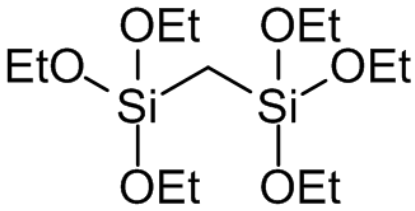
- Strategy

replace unstable Si—O—Si bonds in SiO_2

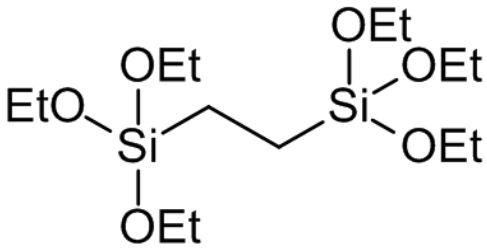
by stable Si—C_mH_n—Si bonds



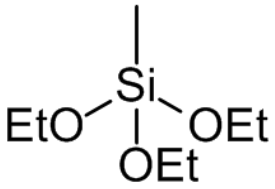
Precursors



Methane bridge
BTESM



Ethane bridge
BTESE

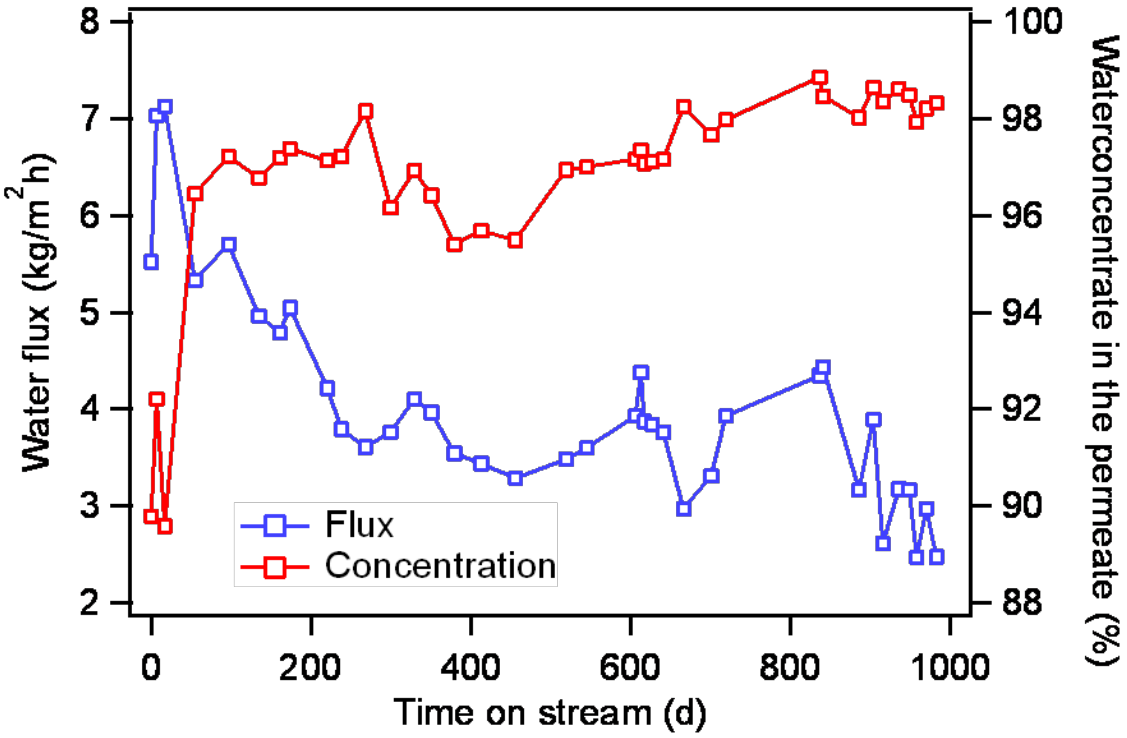


Methyl terminating group
MTES

Test results

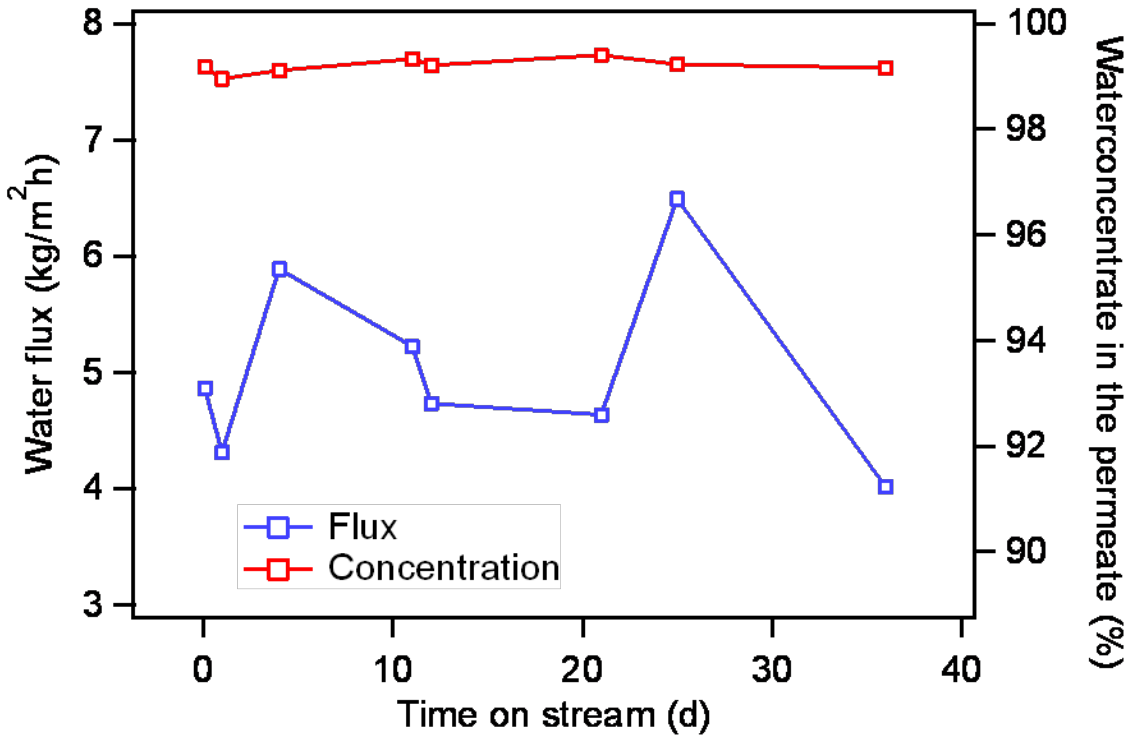
Long term and high temperature performance

- BTESE – MTES
- 150°C
- 3% H_2O in BuOH
- Measurement stopped after 1000 days



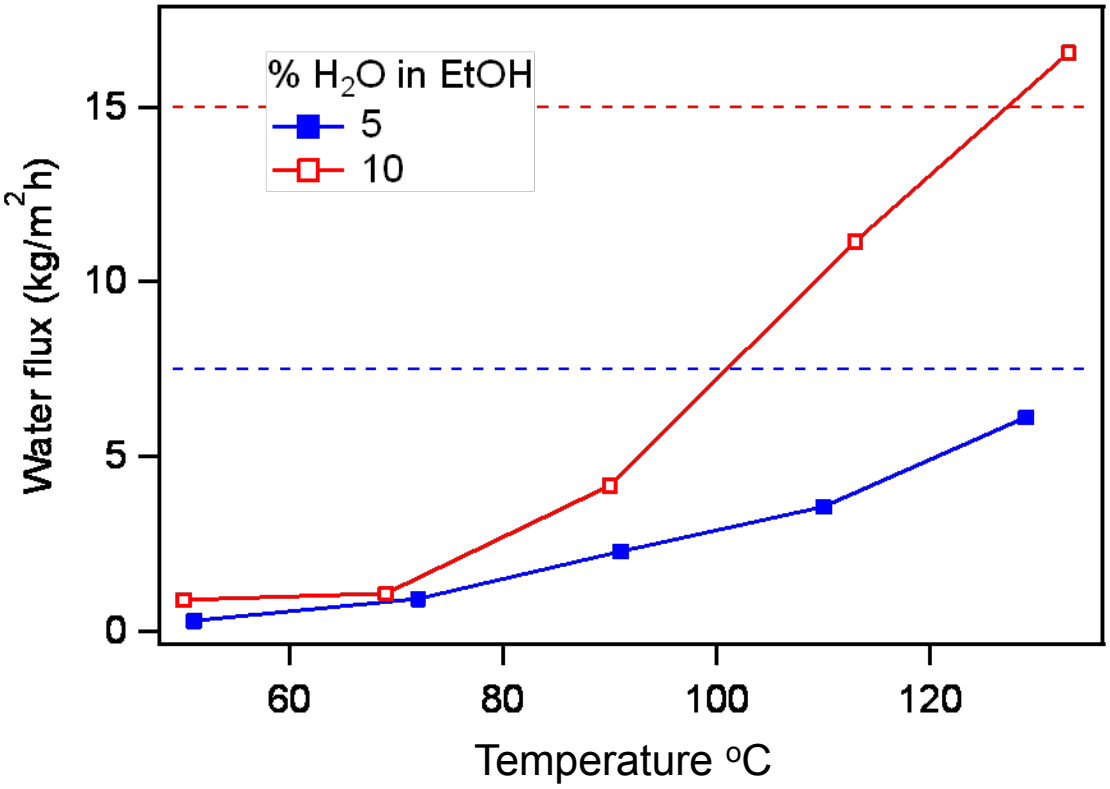
High temperature performance

- BTESE – MTES
- 190°C
- 3% H_2O in BuOH
- Measurement stopped after 35 days



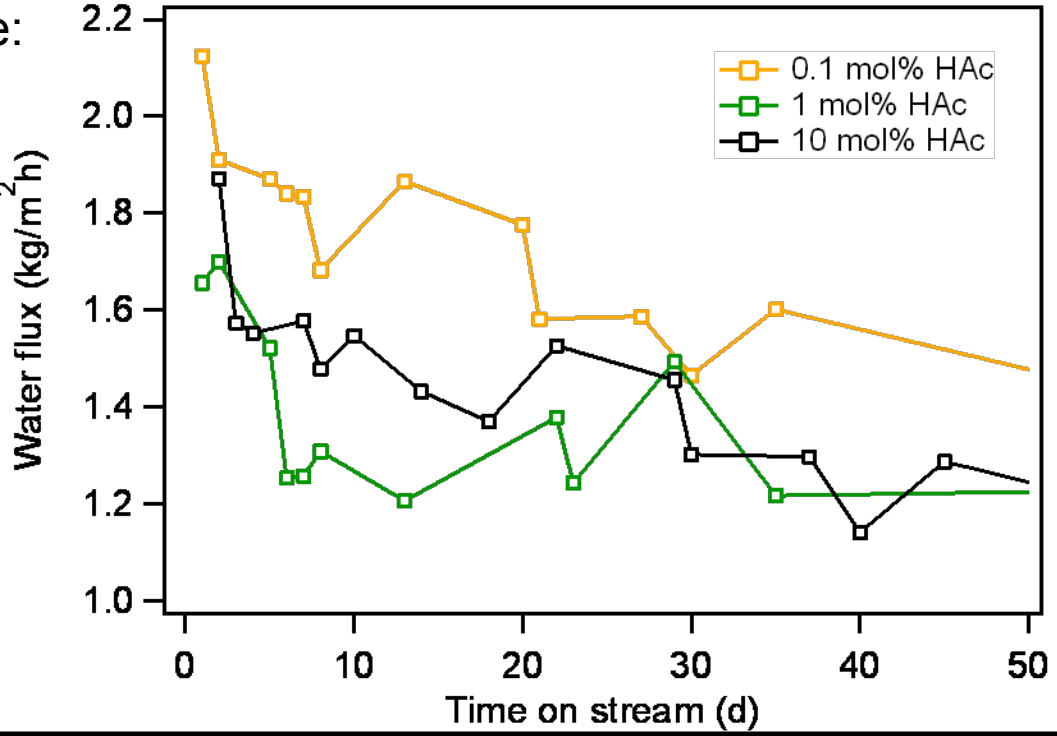
High temperature performance

- BTESM
- Ethanol dehydration
- 5 or 10% H_2O in Ethanol



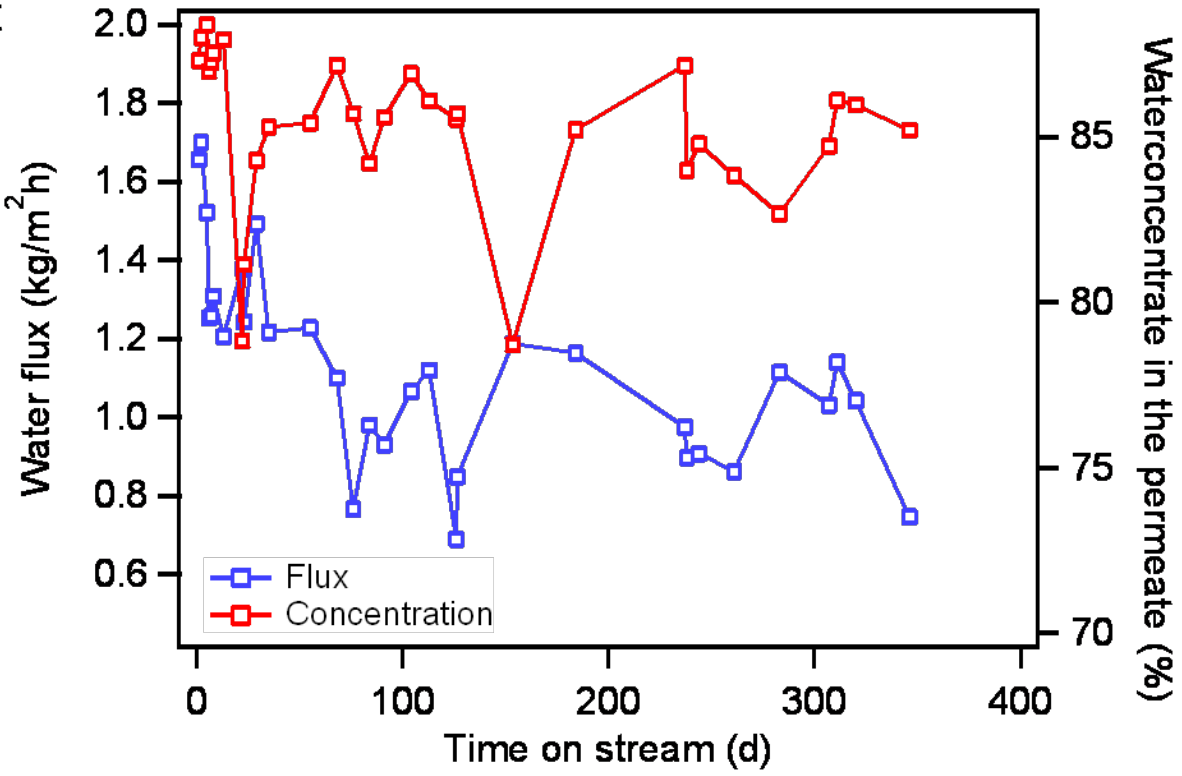
Acid resistance (HAc in EtOH)

- Various levels of HAc in EtOH
- BTESM
- 70°C
- 5% H_2O in EtOH
- Water content in permeate: >85%



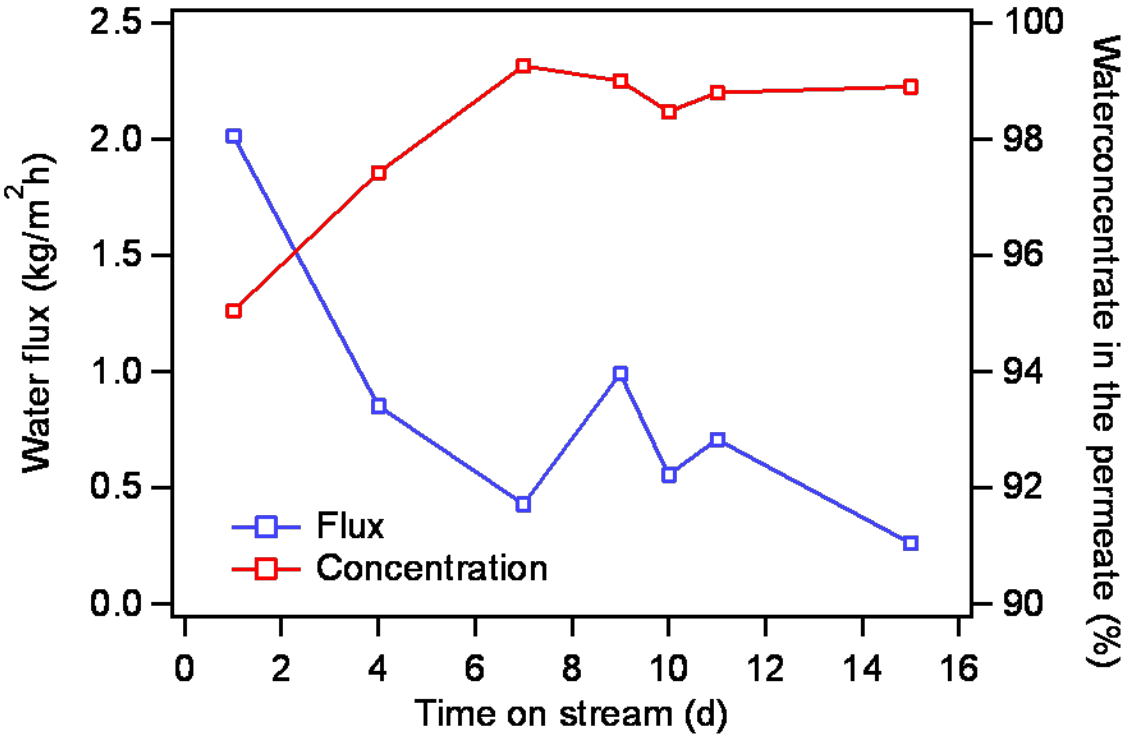
Long term behaviour in the presence of acid

- BTESM
- 70°C
- 5% H_2O in EtOH
- 1 mol% HAc present



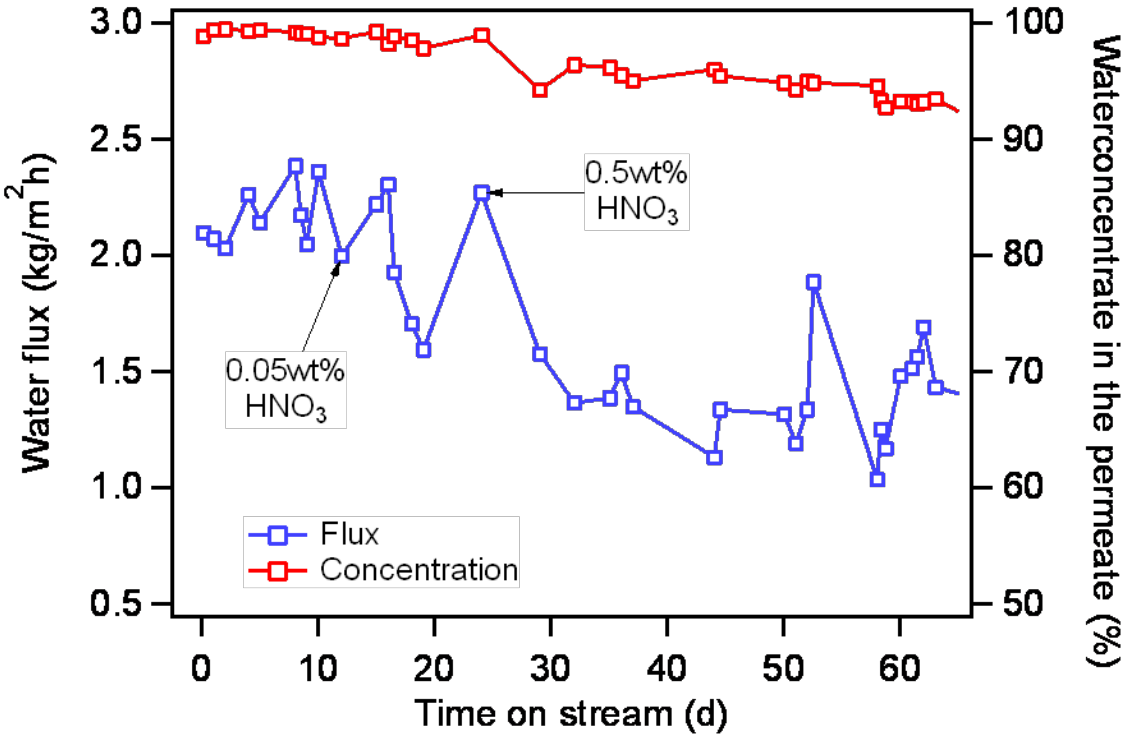
Acid resistance at higher temperature: glycol + HAc

- BTESM
- 130°C
- 5% H_2O in glycol
- 1 mol% HAc



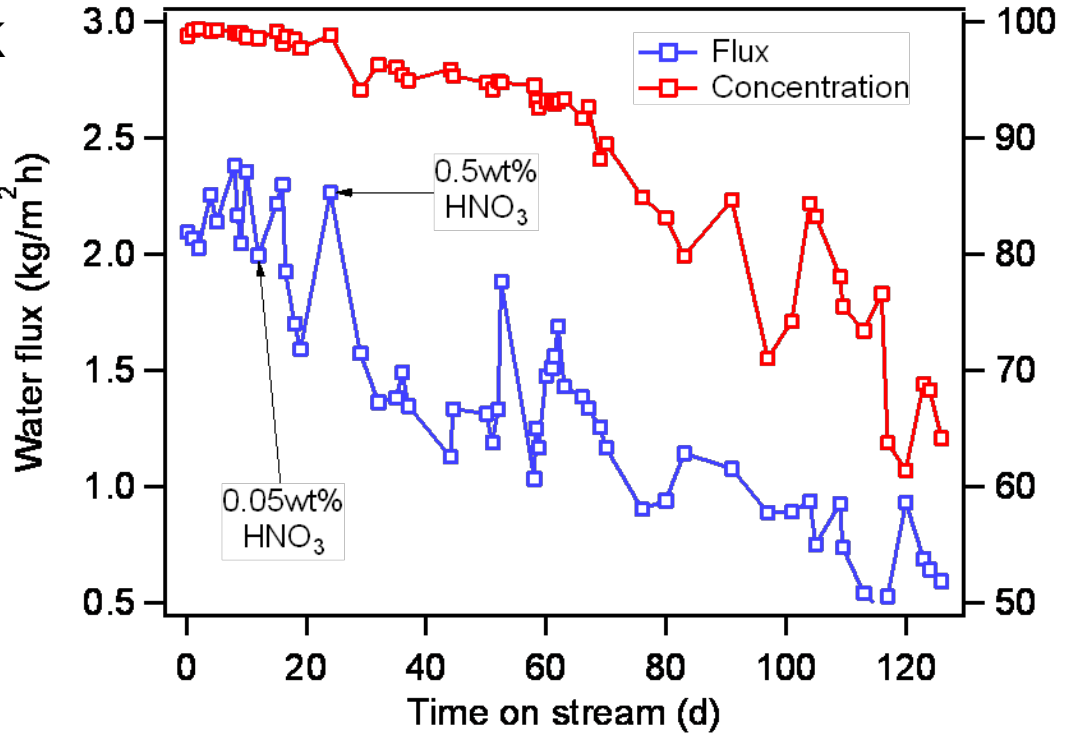
Acid resistance HNO_3 in BuOH

- BTESE
- 95°C
- 5% H_2O in BuOH
- Started with
  0.005 wt% HNO_3



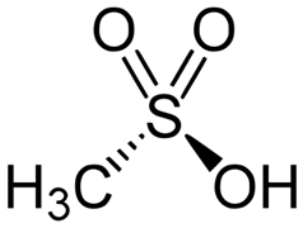
Acid resistance HNO_3 in BuOH

- BTESE
- 95°C
- 5% H_2O in BuOH
- Decrease of selectivity 0.5% HNO_3
- pH ≈ ~2 seems to be OK

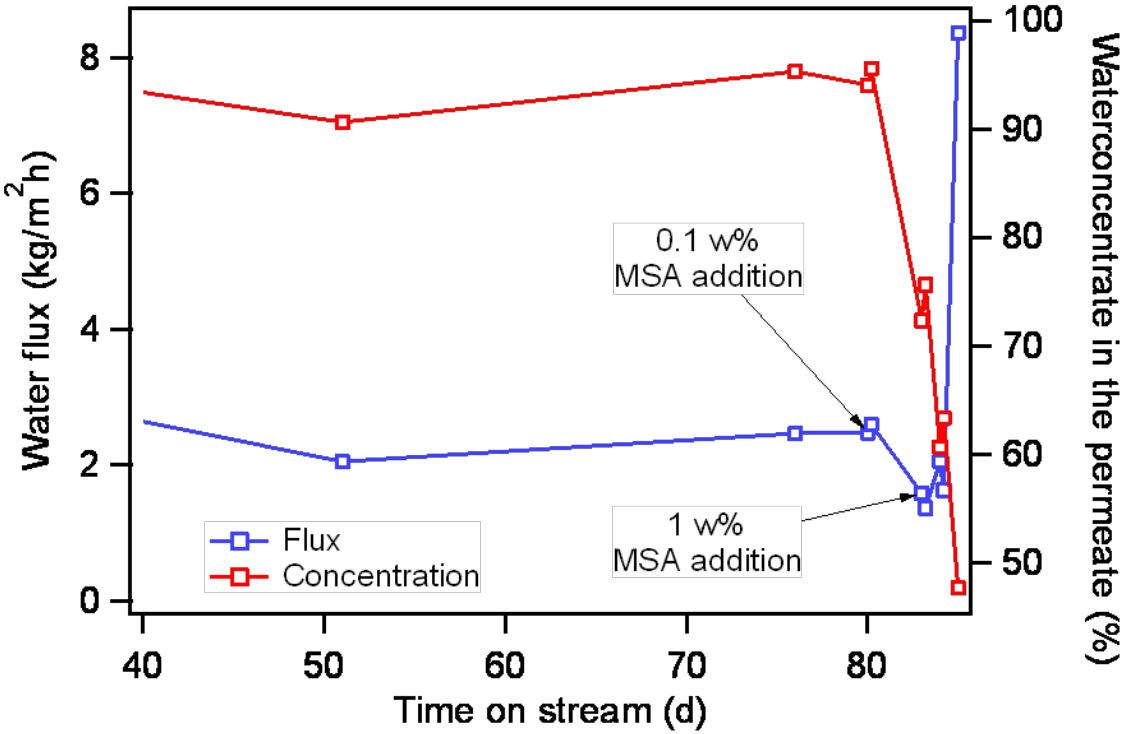


Limitations 1% MSA in BuOH

- Methylsulfonic acid

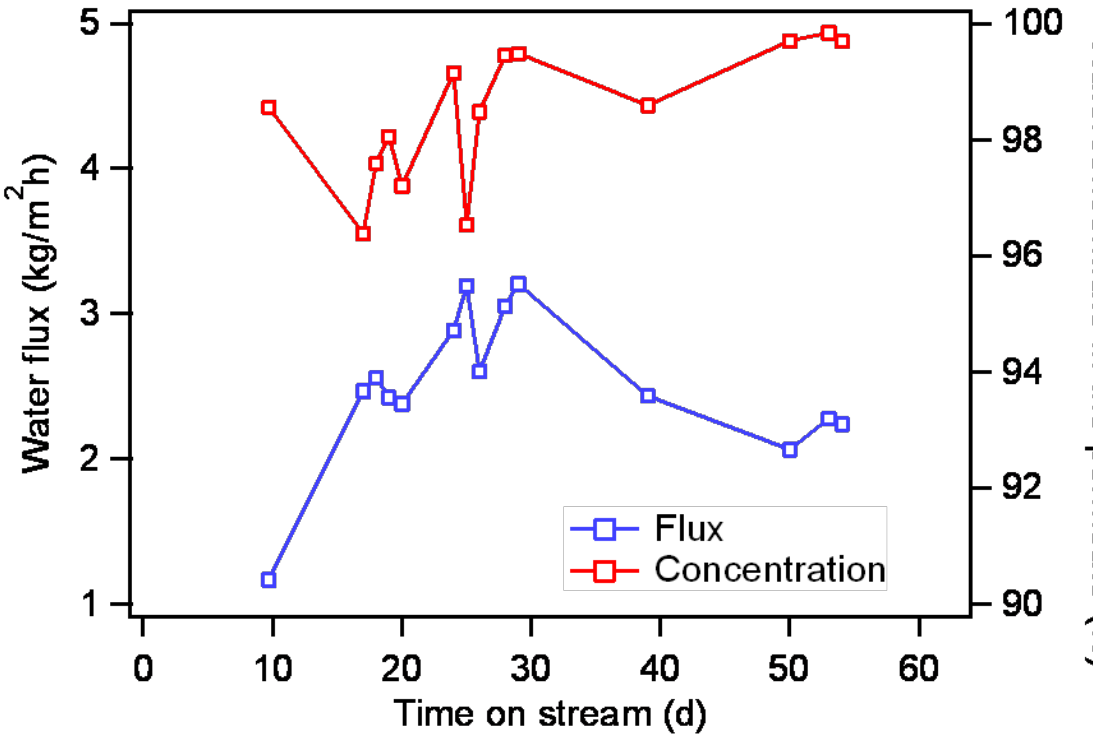


- BTESE
- 95°C
- 5% H_2O in BuOH
- 0.1 – 1 w% MSA added.



Long term behaviour in strong solvent

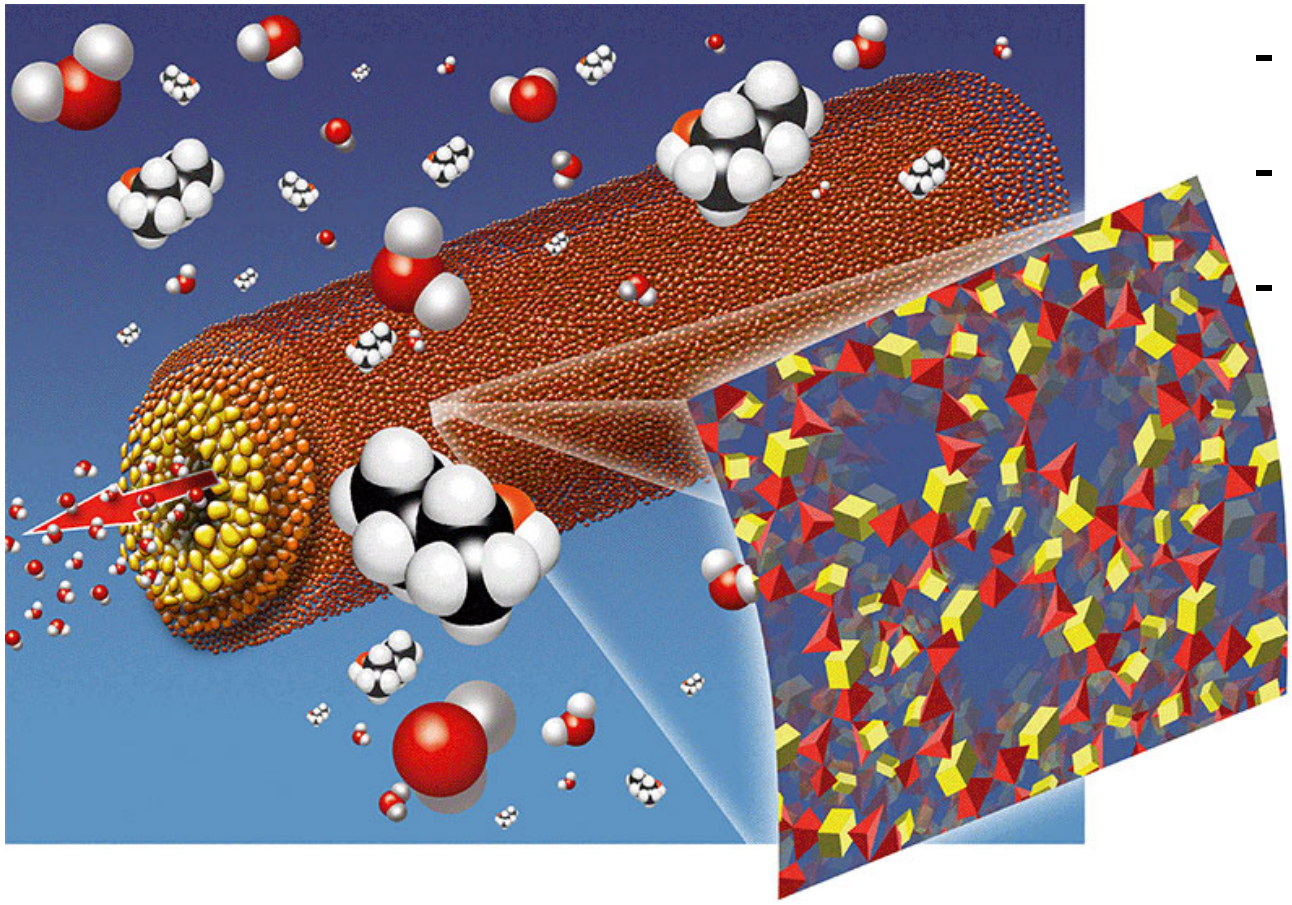
- BTESE
- 130°C
- 8% H_2O in NMP



HybSi advantages over commercial products

- Higher application temperatures
  - 190°C
- Higher resistance against acids and alkalines
  - ~ 2 < pH < ~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

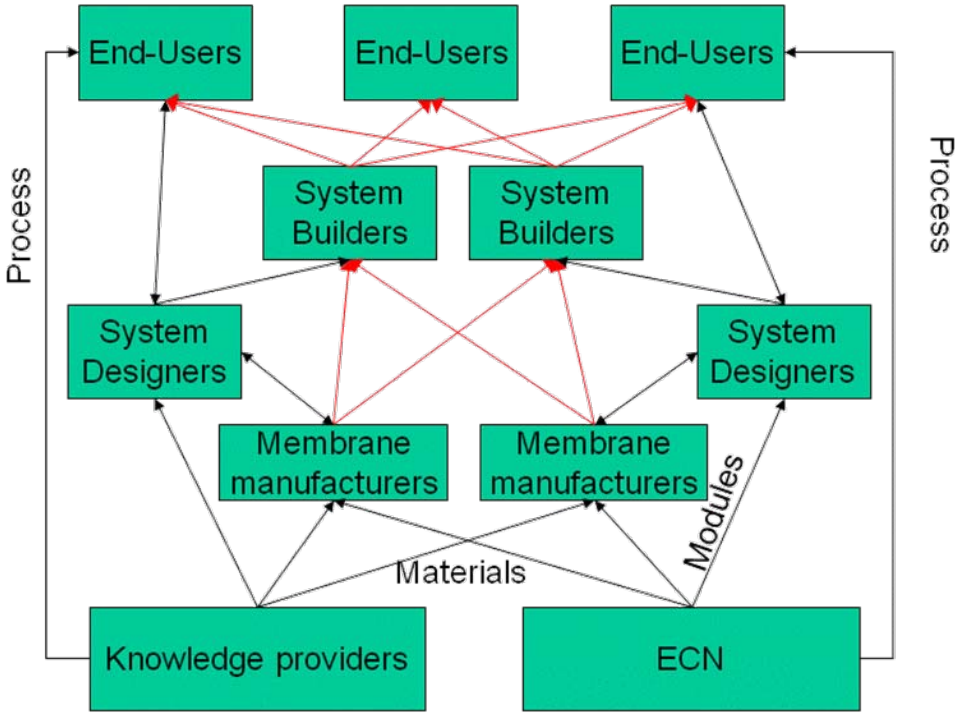


- More stable bonds
- Higher crack propagation energy
- Lower surface diffusion coefficient
- Lower solubility

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 IP
  - 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

- 30m^3 of end of pipe fuel
- from 30-35% to ~2% water
- 1m^2 membrane area
- August – October 2010

- First result promising!

Acknowledgements

- Industrial collaborators
  - Sabic IP
  - Huntsman
  - Air Products
  - DSM
  - Sulzer Chemtech
  - Pervatech
  - Trion partners

- Financial support
  - STW
  - AgentschapNL
  - DSTI

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

Membrane Technology Group
www.ecn.nl/memtech

Chem. Commun, 2008, 1103

J. Sol-Gel Sci. Techn, 2008, 48, 203-11

ChemSusChem, 2009, 2, 158-60

J. Mater. Chem, 2008, 18, 2150

J. Mem. Sci, 2008, 319, 126-32

J. Sol-Gel Sci. Techn, 2010, accepted

Patent: WO2007081212; WO2010008283

For more information:

vanveen@ecn.nl

+31 – 224 56 4606

www.hybsi.com