Hydrothermal stable pervaporation membranes

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HYDROTHERMAL STABLE PERVAPORATION MEMBRANES

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1 Abstract

Thermal separation processes like distillation consume a large amount of energy in the process industry. Replacing these processes by membrane pervaporation will lead to much lower energy consumption. The expected high chemical and thermal stability of inorganic membranes compared to polymer membranes has resulted in a growing research activity with the first aim of replacing polymer membranes with inorganic ones. The superior separation performance, i.e. selectivity and flux, of silica-based membranes in the dehydration of alcohols and solvents at elevated temperatures has raised the interest even further. The application depends on a reliable and good long-term performance. Unfortunately, information on this topic is still very limited. We have shown that silica and methylated silica membranes are not stable at temperatures above 100^{o}C and the application window of state-of-the-art Me-SiO_2 membranes for use in dehydration processes is limited to 95°C [1]. For methanol separation from organic solvents the Me-SiO_2 membranes can be used at higher temperatures [2].

Hybrid silica materials are expected to have a much higher hydrothermal stability than (methylated) silica. The superior separation performance, i.e. selectivity and flux, of these hybrid membranes in the dehydration of alcohols and solvents at elevated temperatures has raised the interest [3]. High flux performance is required to decrease the membrane area needed and thereby the price to become competitive against the well know distillation technique. It is proven that the required water flux of at least 3 kg/m^{2}h, for the dehydration of 5wt.% water in butanol as a representative standard application, can be achieved easily. The profitable application of the membranes depends on a reliable, stable long-term behaviour and the broad applicability especially at temperatures above 100°C. We will report on the development of organic/inorganic hybrid silica membranes with selectivities and fluxes, that are comparable with the silica based membranes in dehydration by pervaporation. Details of test results will be given in different dehydration applications up to 150°C including the dehydration of aprotic solvents. Further, results will be given on long term stability testing up to 150°C and up to 2 years of continuous operation in the dehydration of organic mixtures. The results show that a completely new class of hybrid materials is available that opens new markets for dehydration processes by pervaporation.

Acknowledgement

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References

[1] J. Campaniello, C.W.R. Engelen, W.G. Haije, P.P.A.C. Pex and J.F. Vente, Long-term performance of microporous methylated silica membranes, Chem.Comm. (2004), p.834-835.
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[3] H.L. Castricum, A. Sah, R. Kreiter, D.H.A. Blank, J.F. Vente and J.E. ten Elshof, Chem.Comm. (2008) 1103-1105, DOI:10.1039/B718082A.

ECN

Energy research Centre of the Netherlands

Hydrothermal stable pervaporation membranes

Development of hybrid silica - HybSi®

Henk van Veen, Rob Kreiter, Marielle Rietkerk, Charles Engelen, Hessel Castricum, Andre ten Elshof, and Jaap Vente

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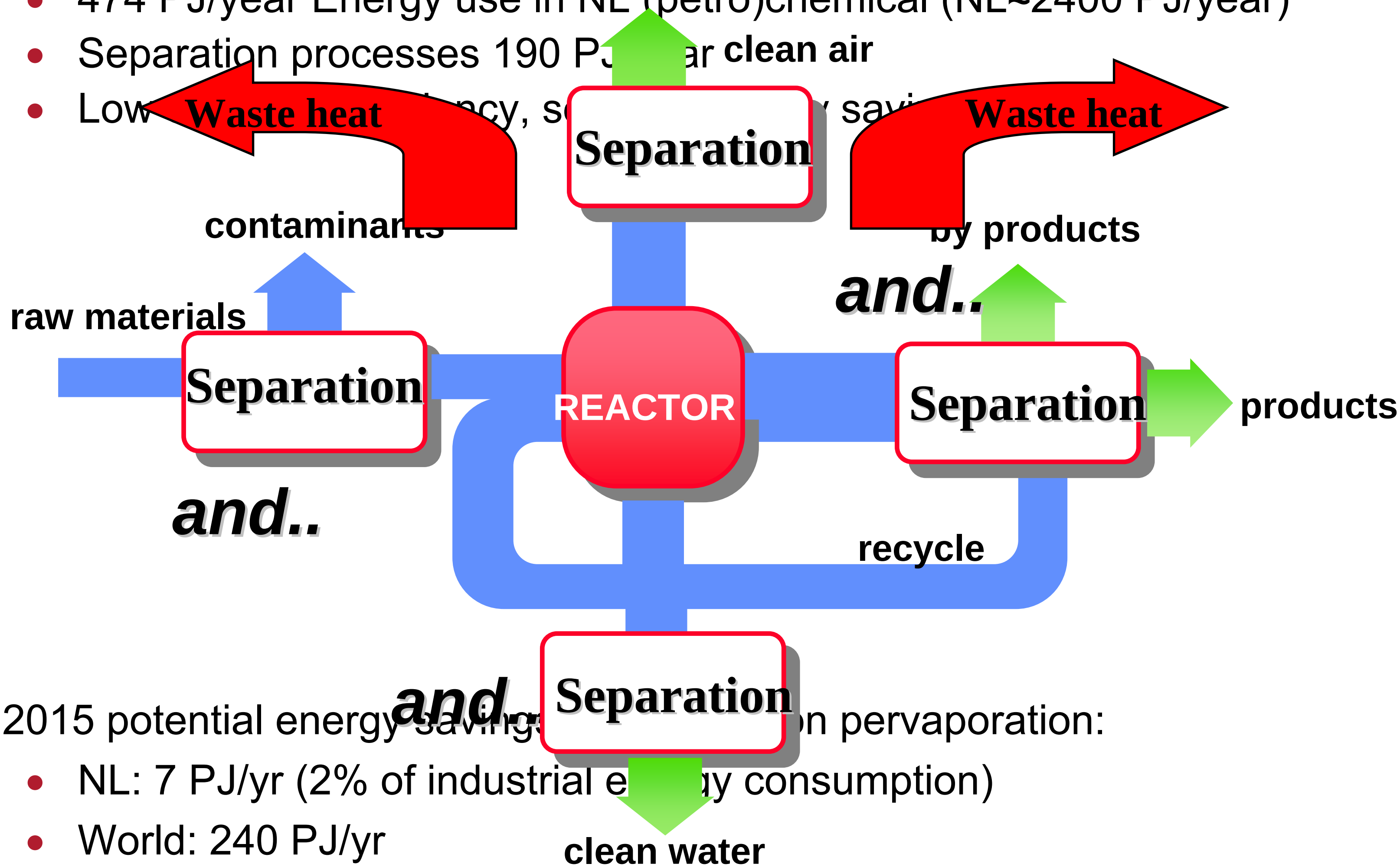
Introduction

- 474 PJ/year Energy use in NL (petro)chemical (NL≈2400 PJ/year)
- Separation processes 190 P… ar
- Low … ncy, s … y savi…



By 2015 potential energy savings … n pervaporation:

- NL: 7 PJ/yr (2% of industrial e… gy consumption)
- World: 240 PJ/yr

Introduction

BUT

Pervaporation membrane stability is limited with respect to:

- (Hydro) thermal conditions
- Solvent resistance
- Acids

Pervaporation membrane materials: goals set

Test conditions dehydration of organics by pervaporation:

1. Temperature: 150°C.
2. Mixture 5 wt.% water in n-butanol.
3. Acidity: pH 2-10.
4. Pressures and pressure differences up to 30 bar.

and the membrane process should meet the following industrial demands:

1. Water flux of 5 kg/m^2h.
2. Selectivity of at least 360 (feed 5 wt.% water → permeate 95 wt.% water).
3. Run time of 3 years = average maintenance time of a process.
4. Change of flux and selectivity of less than 10% per year.

Steps in the membrane production

Sol synthesis

⬇

Membrane coating

⬇

Drying

⬇

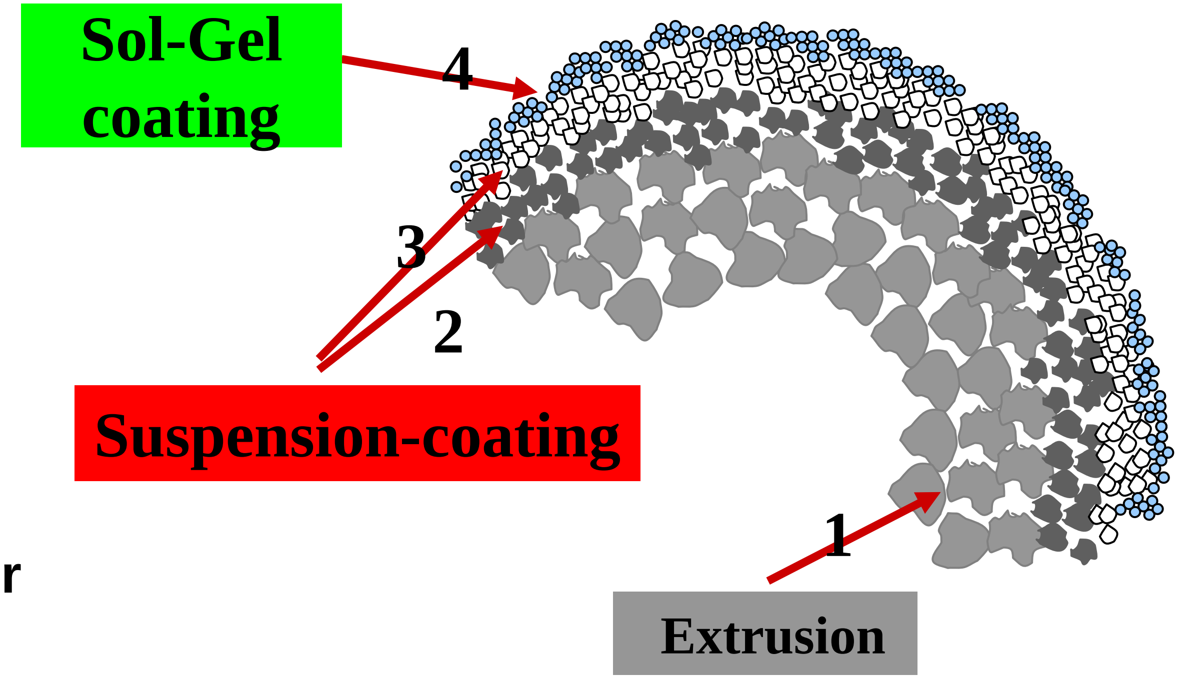
Firing

⬇

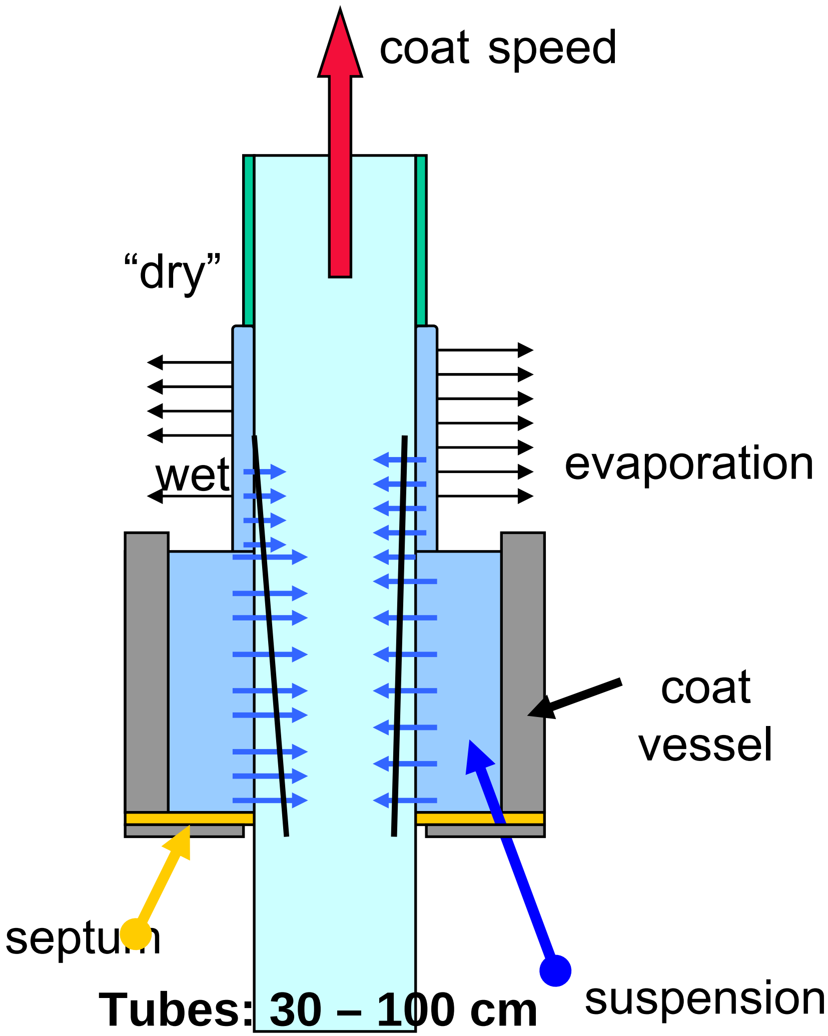
Ceramic membrane layer

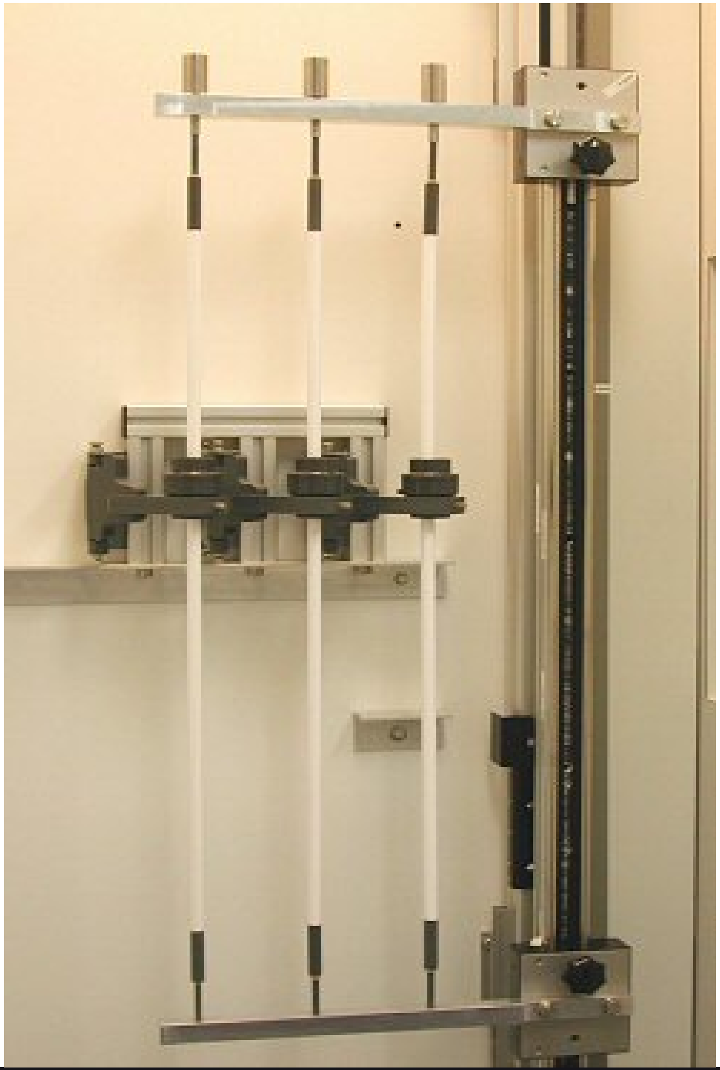
⬇

Membrane characterisation

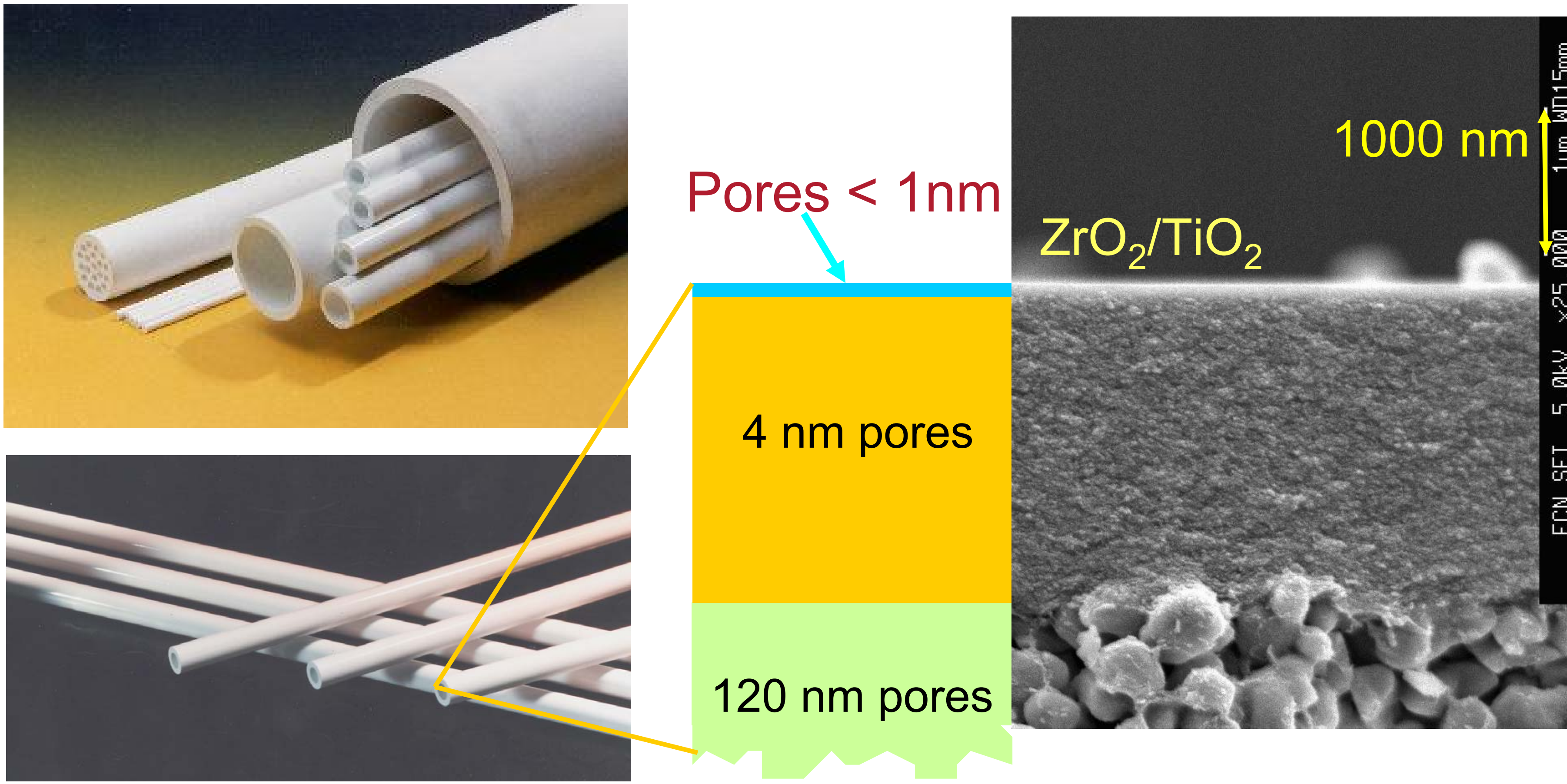


Preparation of the membranes





Tubular microporous membranes



Materials covered

Previous developments:

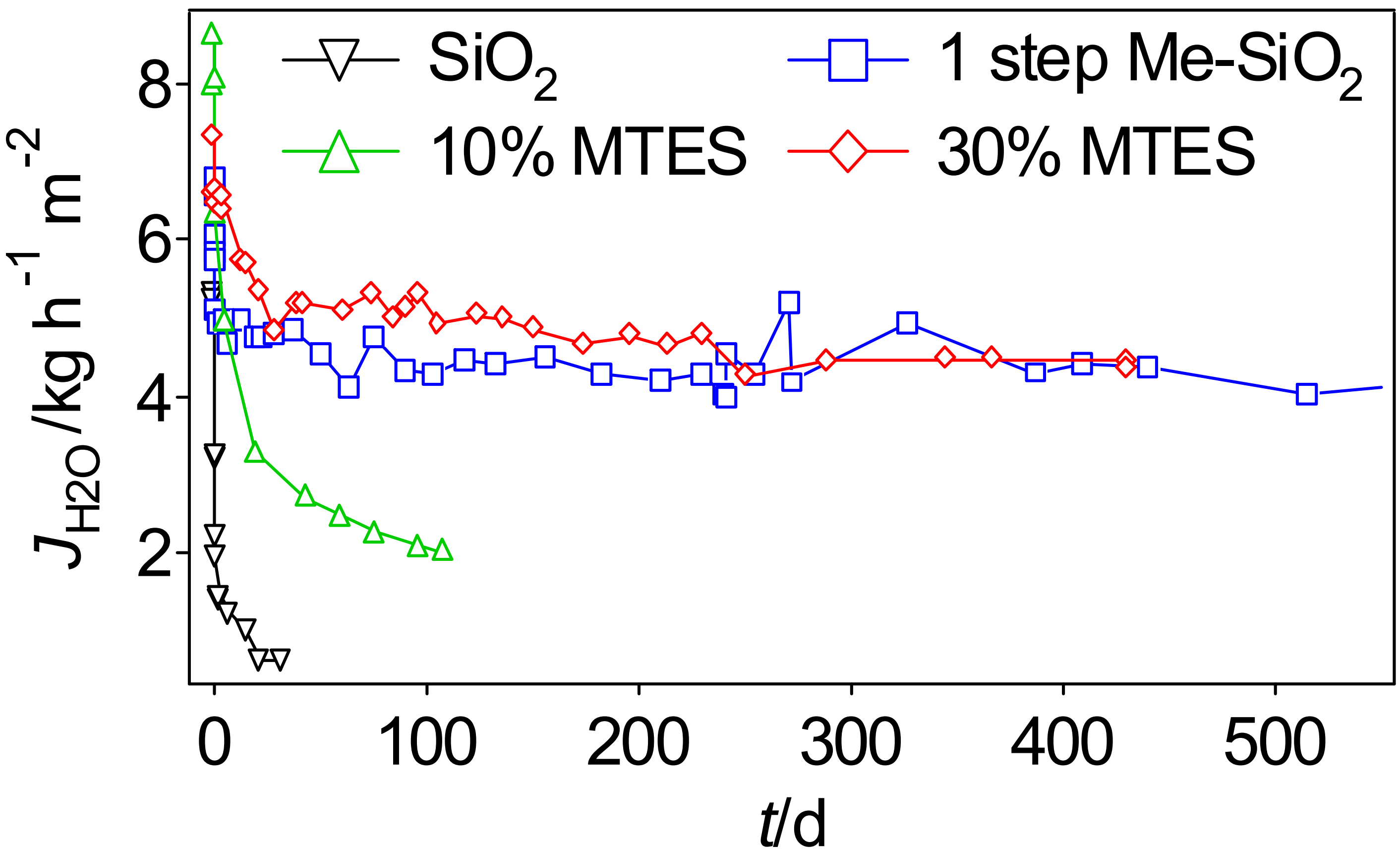
- SiO_2
- Methylated SiO_2

New leads:

- Ceramic supported polymers (J.Membr.Sci., (2008) 319, 126-132)
- TiO_2 }
- ZrO_2 } (J.Sol-gel Sci.Technol. (2008) 48, 203-211)
- Hybrid silica (HybSi®), organic bridges

Silica and Me-Silica long term pervaporation at 95ºC

Feed = 5 wt.% water in nBuOH

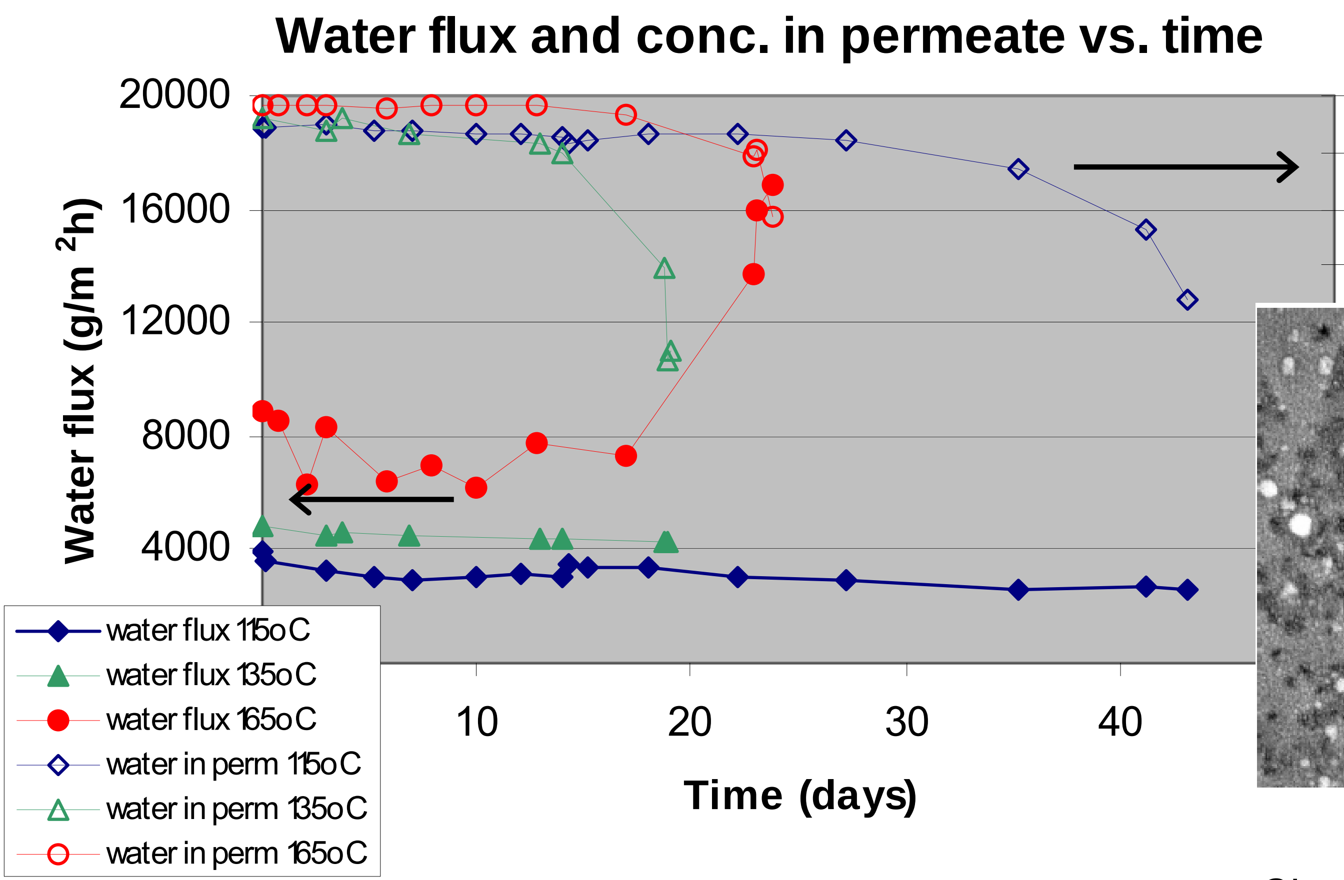


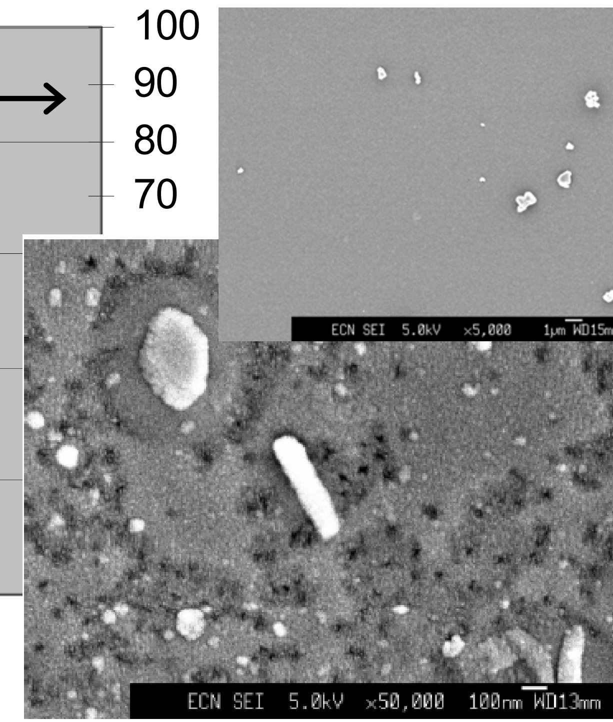
Methylated silica solves problem of the flux decline, selectivity meets demands

Me-Silica long term pervaporation up to 165ºC

Feed = 2.5 wt.% water in nBuOH

Membrane failure within weeks





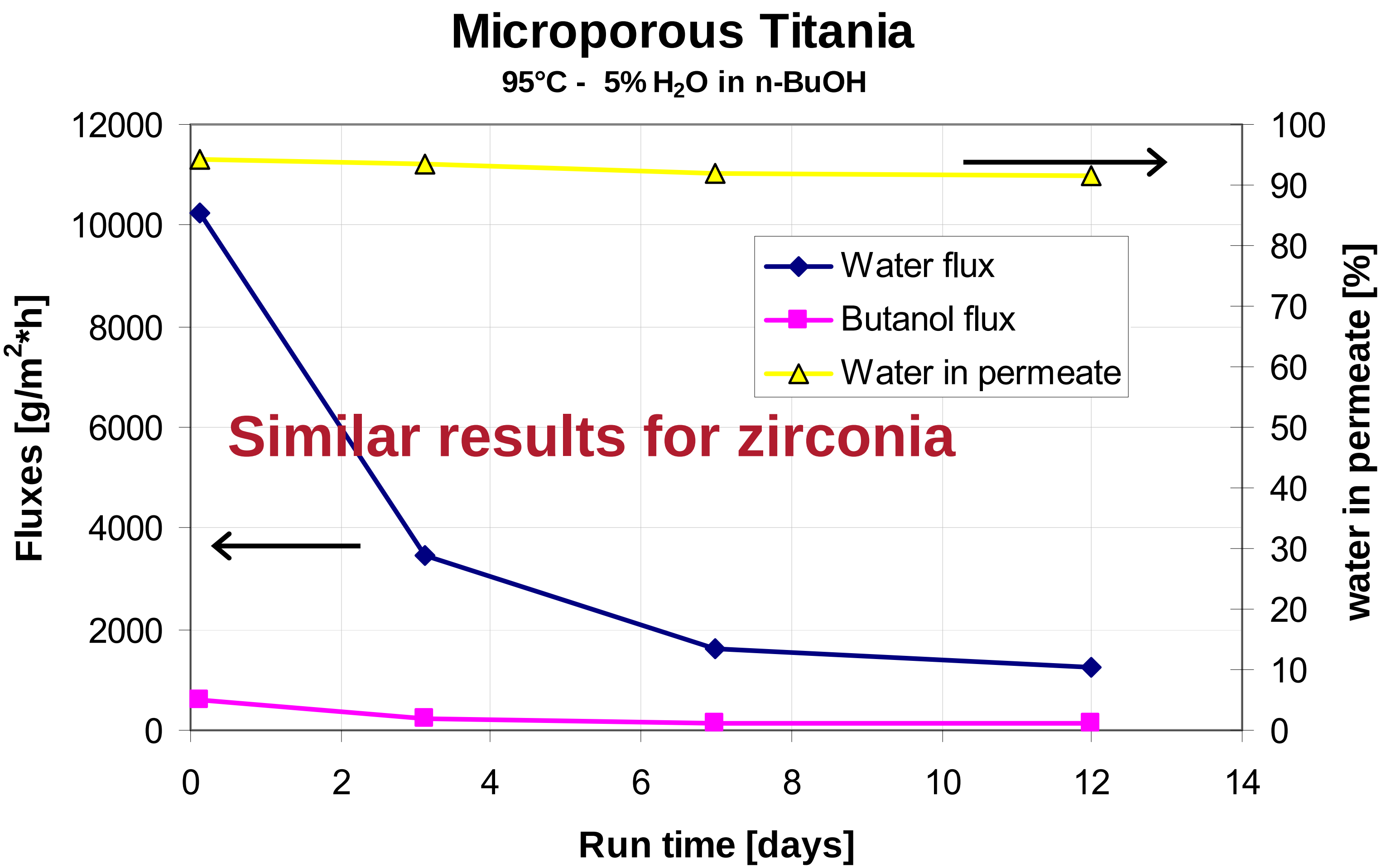
Chem.Comm.2004, 834-835

ECN

Pervaporation with titania membrane

Feed = 5 wt.% water in nBuOH

Strong flux decline in time

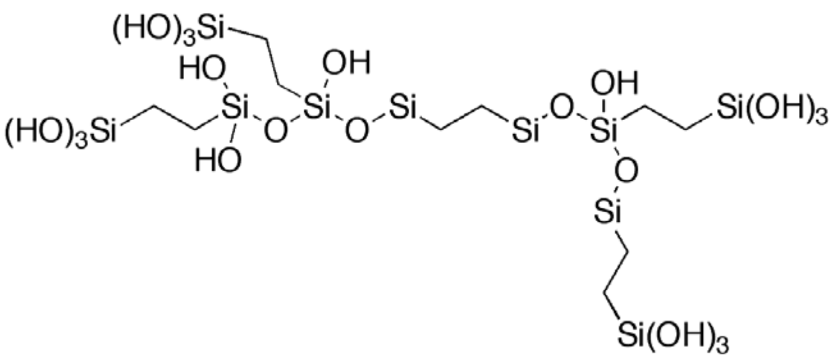


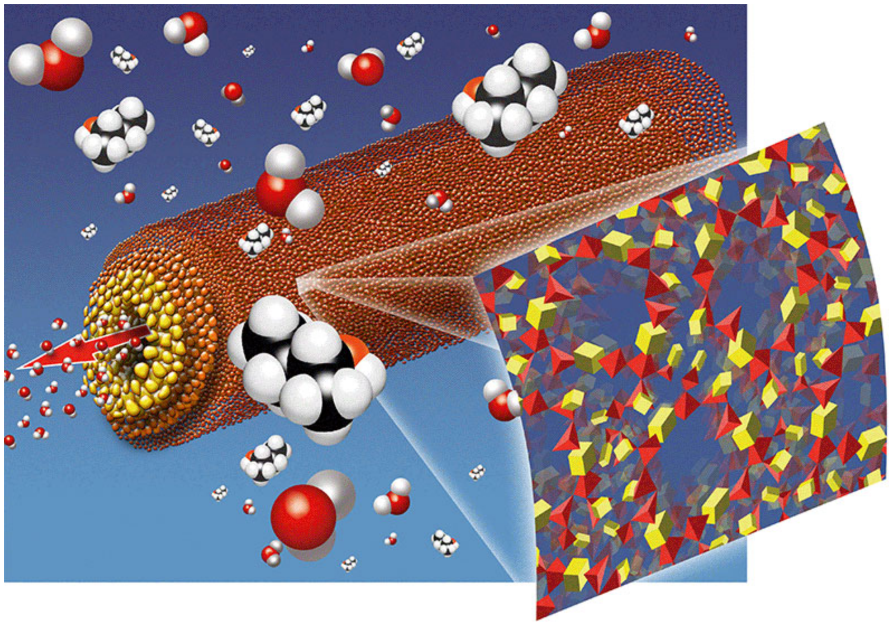
Hybrid membranes from bisfunctional silica precursors HybSi®

Strategy: replace Si—O—Si bonds by Si—C—C—Si bonds

$(OC_2H_5)_3 - Si - CH_2 - CH_2 - Si - (OC_2H_5)_3$

(bis(triethoxysilyl)ethane, BTESE)



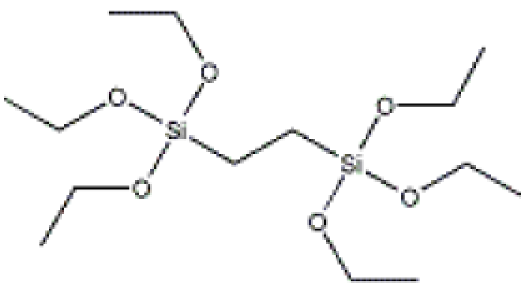


Patented in collaboration with Univ. of Twente and Univ. of Amsterdam (Ashima Sah, Andre ten Elshof, Hessel Castricum, Marjo Mittelmeijer)

WO2007081212, 2006; *Chem. Commun.* 2008, 1103-1105

Hybrid membranes

BTESE



Water, HNO_3 , EtOH

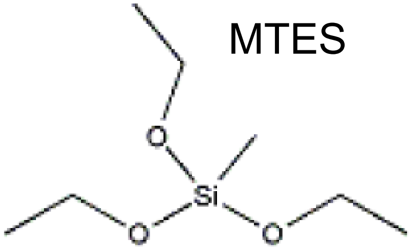
Reflux at 60ºC, 3 hrs

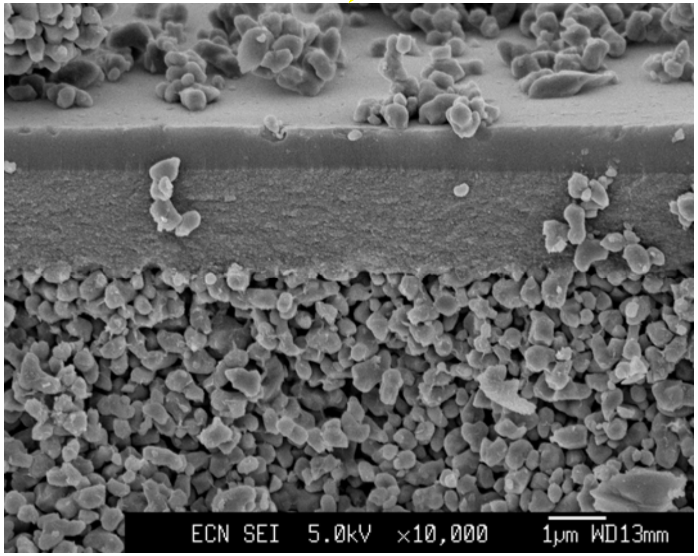
Mix

Coating and calcination

Mix in EtOH

MTES





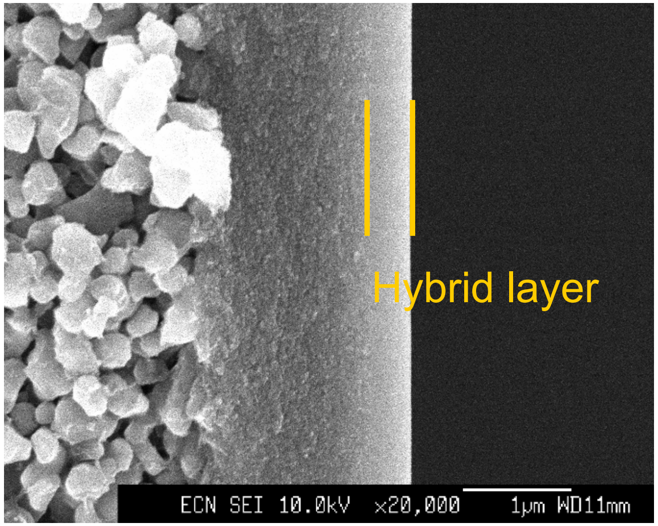
Hybrid membranes:
different precursors for improved performance

Precursors:

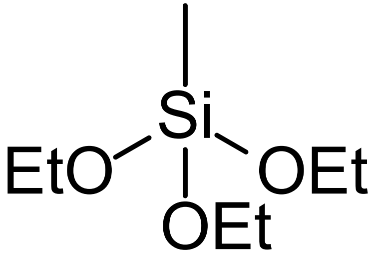
Recipe 1 BTESE + MTES

Recipe 2 BTESE

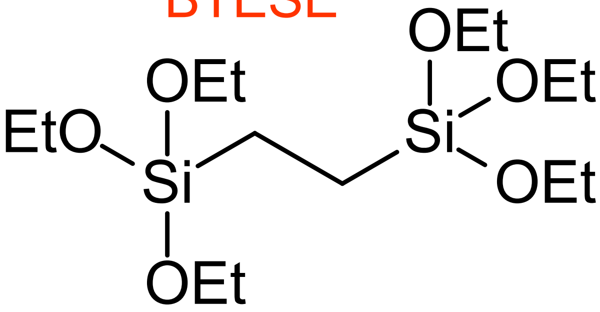
Recipe 3 BTESM



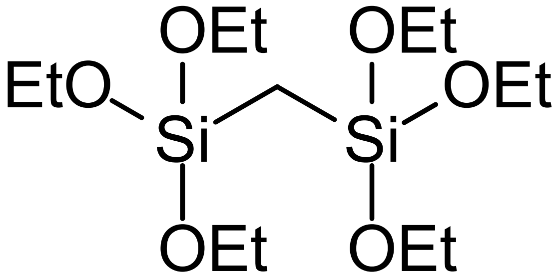
MTES



BTESE

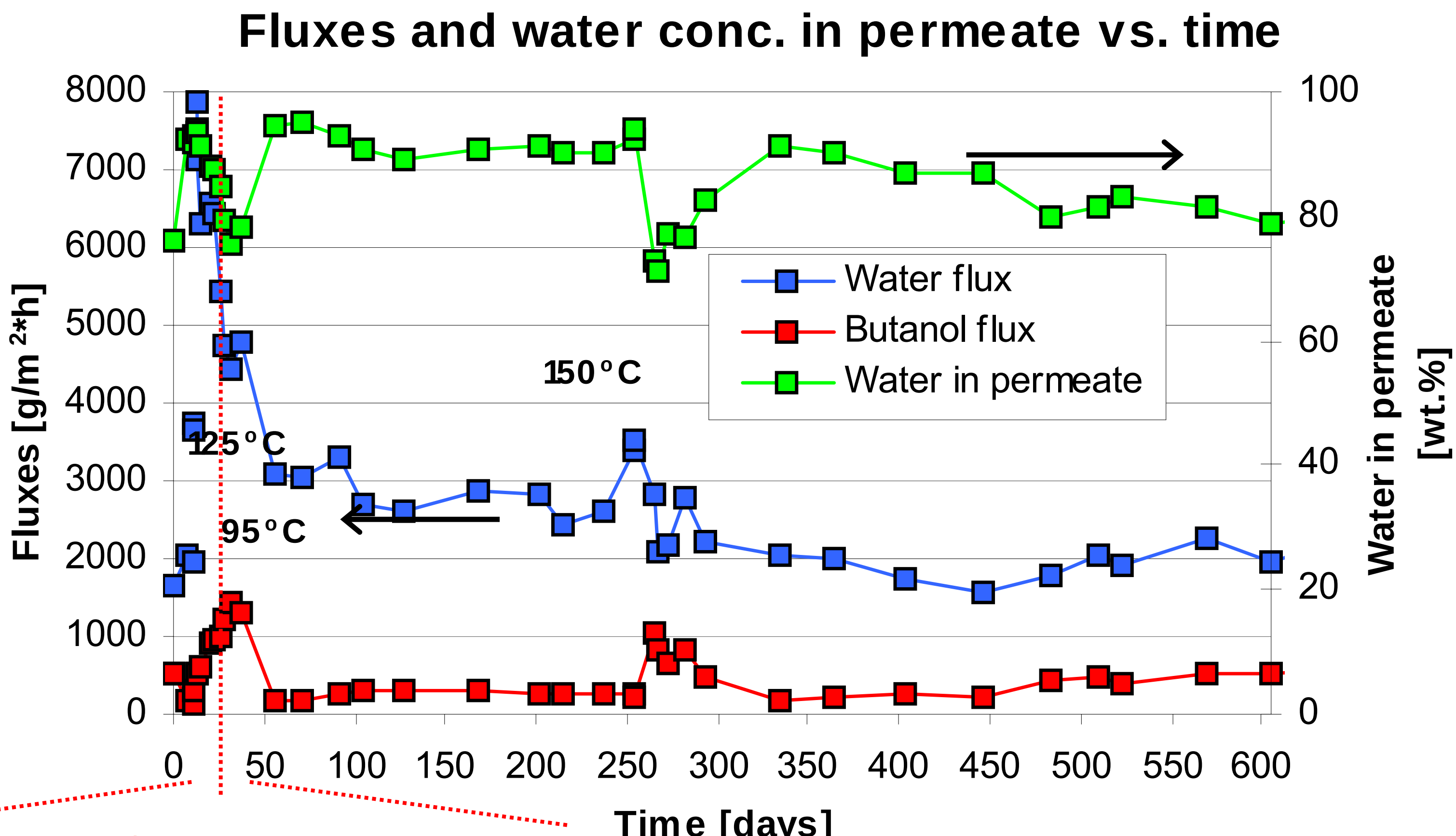


BTESM



Performance hybrid membranes, 150ºC

First membrane made
Recipe 1
Feed = 5 wt.% water in nBuOH
Lifetime > 650 days

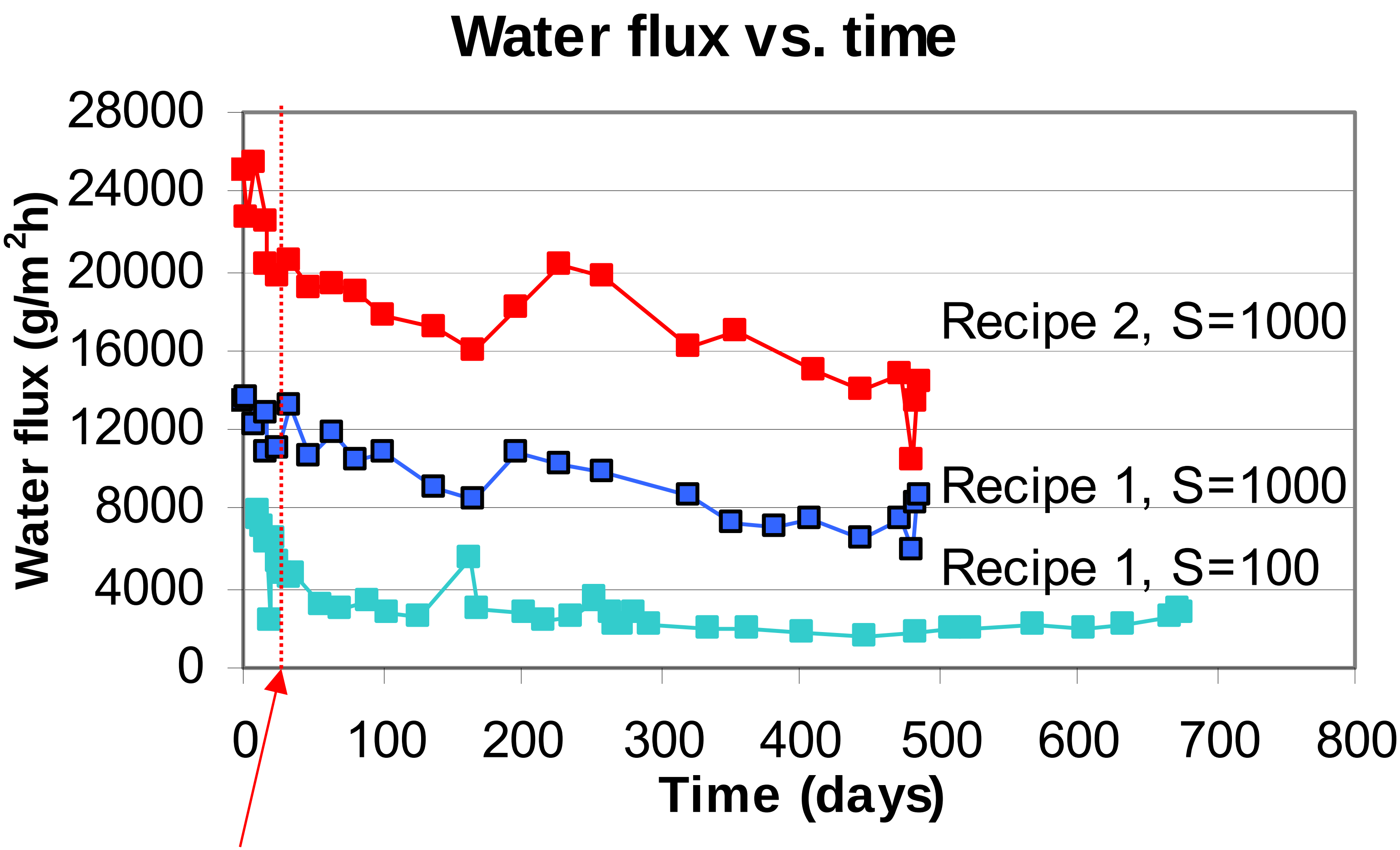


Life time state of the art methylated silica

J. Mater. Chem. 2008, 18, 2150-2158

Feed = 5 wt.% water in nBuOH

Performance hybrid membranes, 150ºC



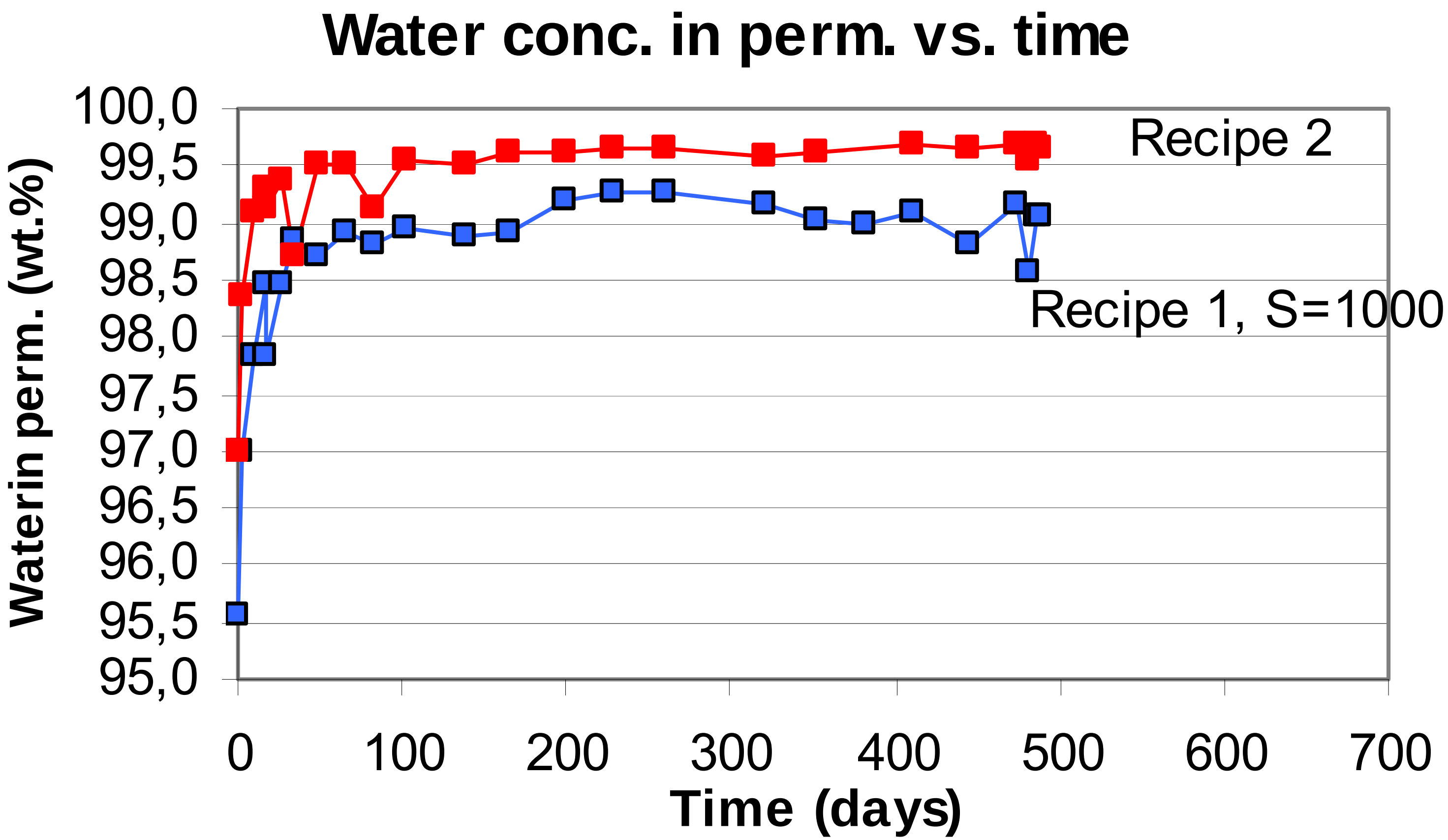
Life time state-of-the-art MeSi

J. Membr. Sci. 2008, in press

ECN

Feed = 5 wt.% water in nBuOH

Performance hybrid membranes, 150ºC

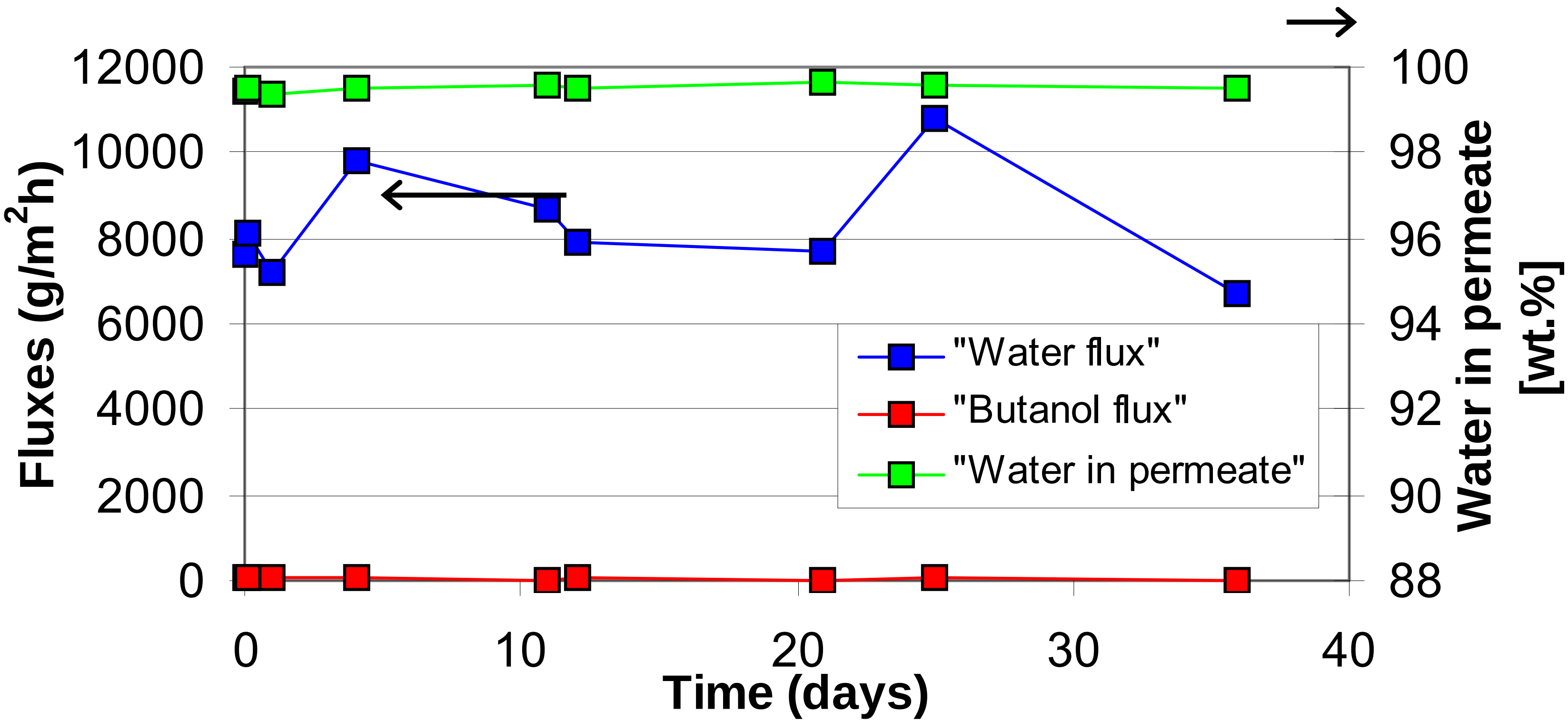


J. Membr. Sci. 2008, in press

Performance hybrid membranes, 190ºC

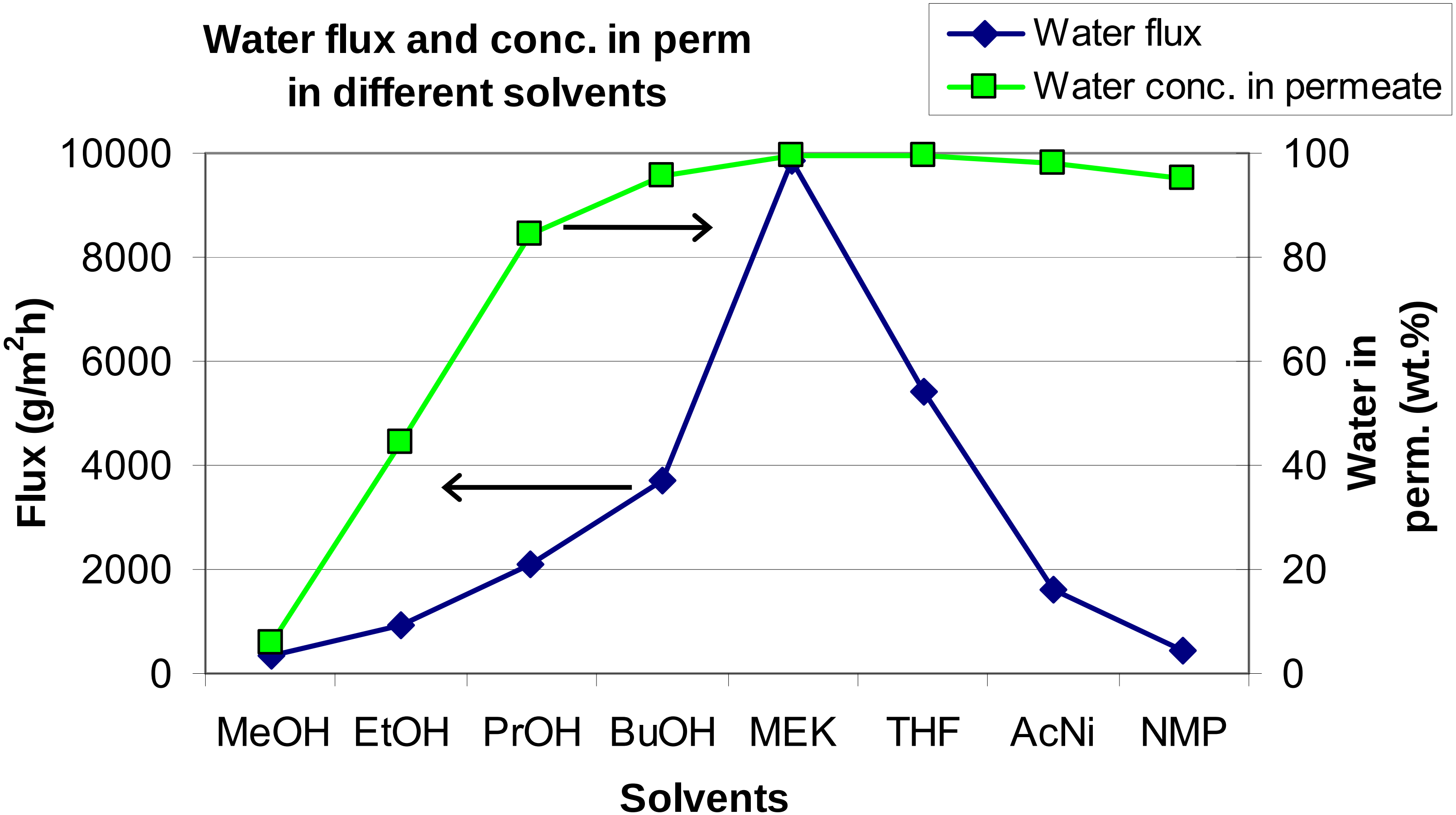
Feed = 5 wt.% water in nBuOH
Recipe 2
On stream > 1 month, selectivity stable

Fluxes and water conc. in permeate vs. time



Hybrid membranes application testing

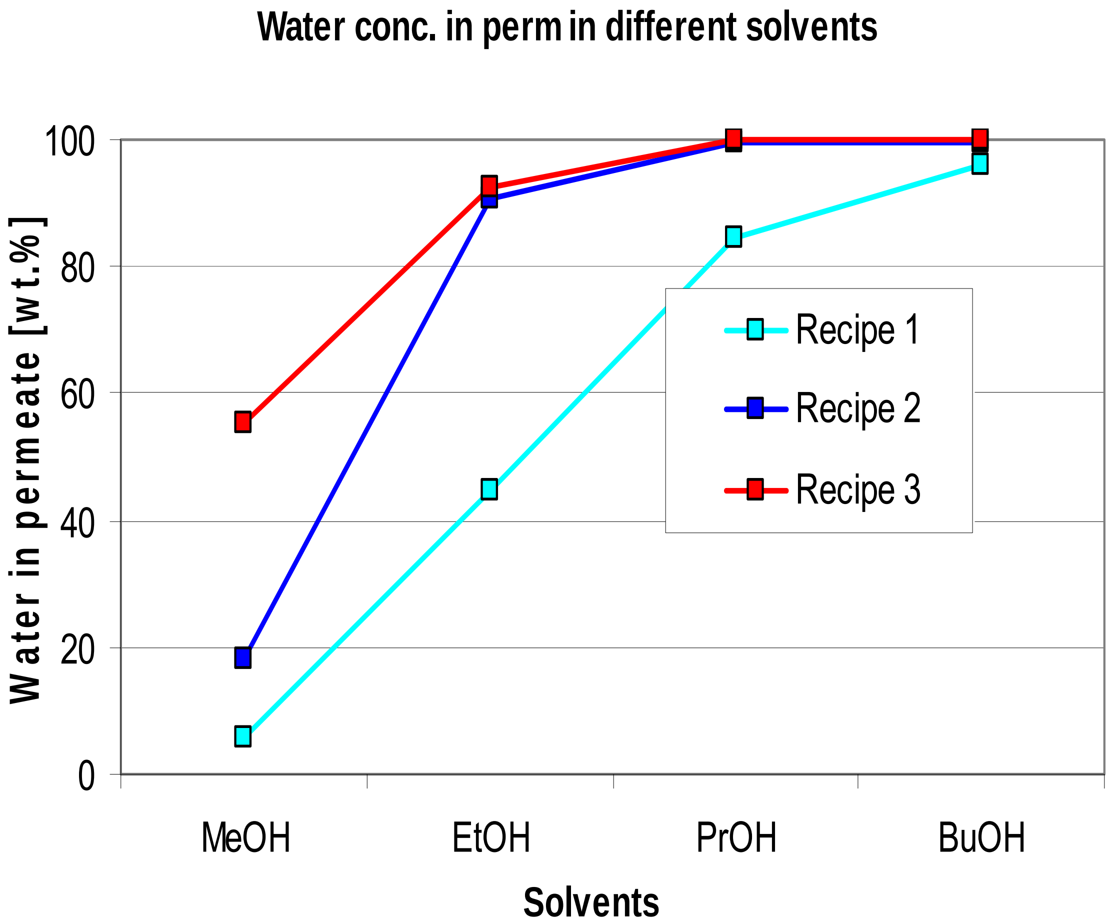
Feed = 5 wt.% water in solvent
Recipe 1



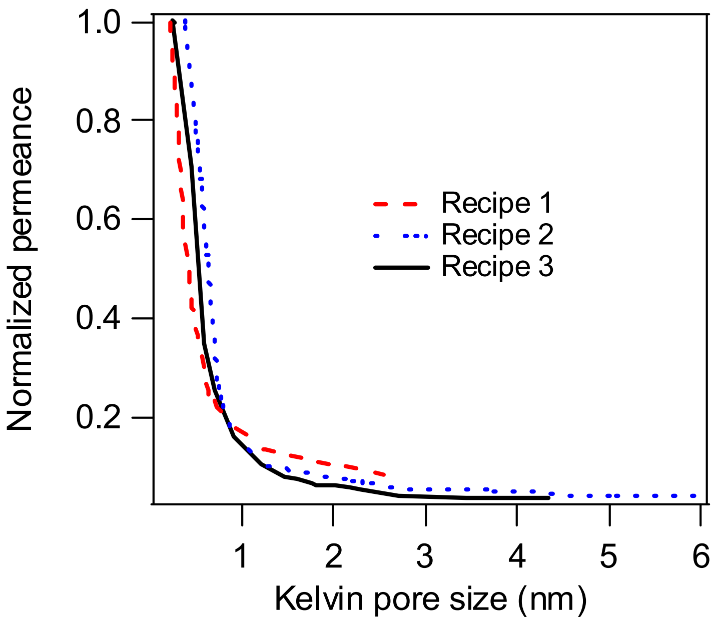
Temperature = 55 70 85 95 70 55 70 120 °C

Hybrid membranes application testing

Feed = 5 wt.% water in solvent

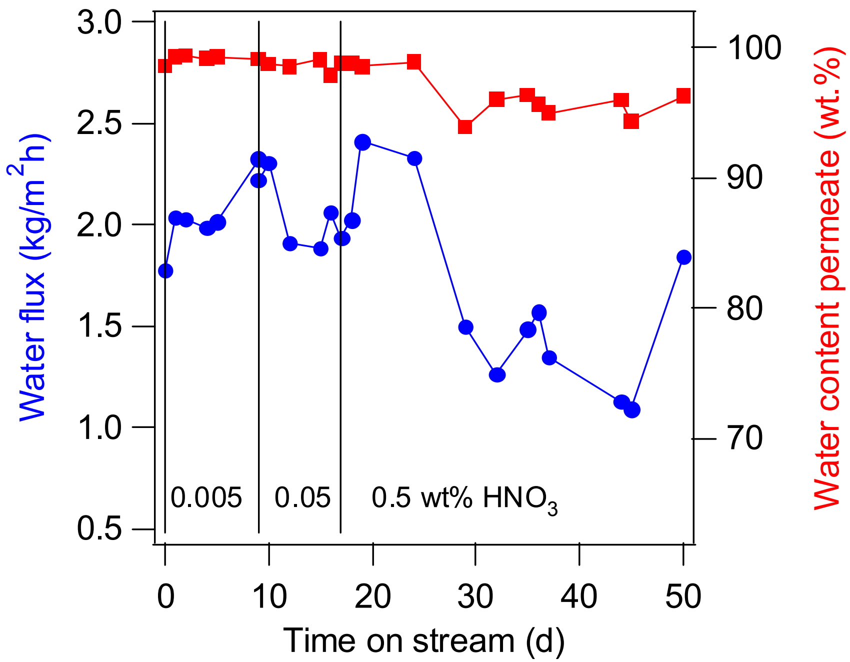


Temp. = 55 70 85 95 °C

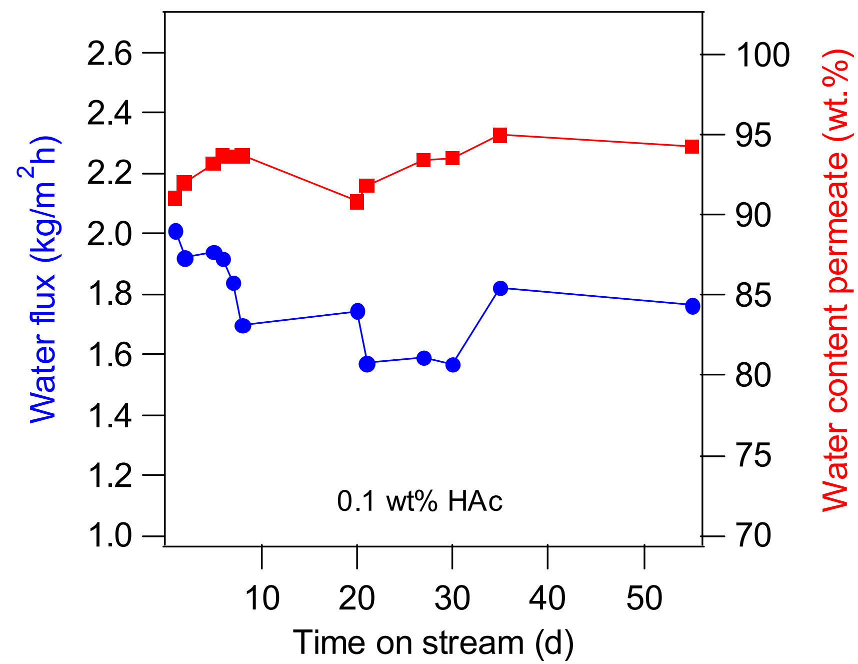


Acid stability

Feed : 5 wt.% water in *n*-BuOH
0.005 – 0.5 wt.% HNO_3
Recipe 2

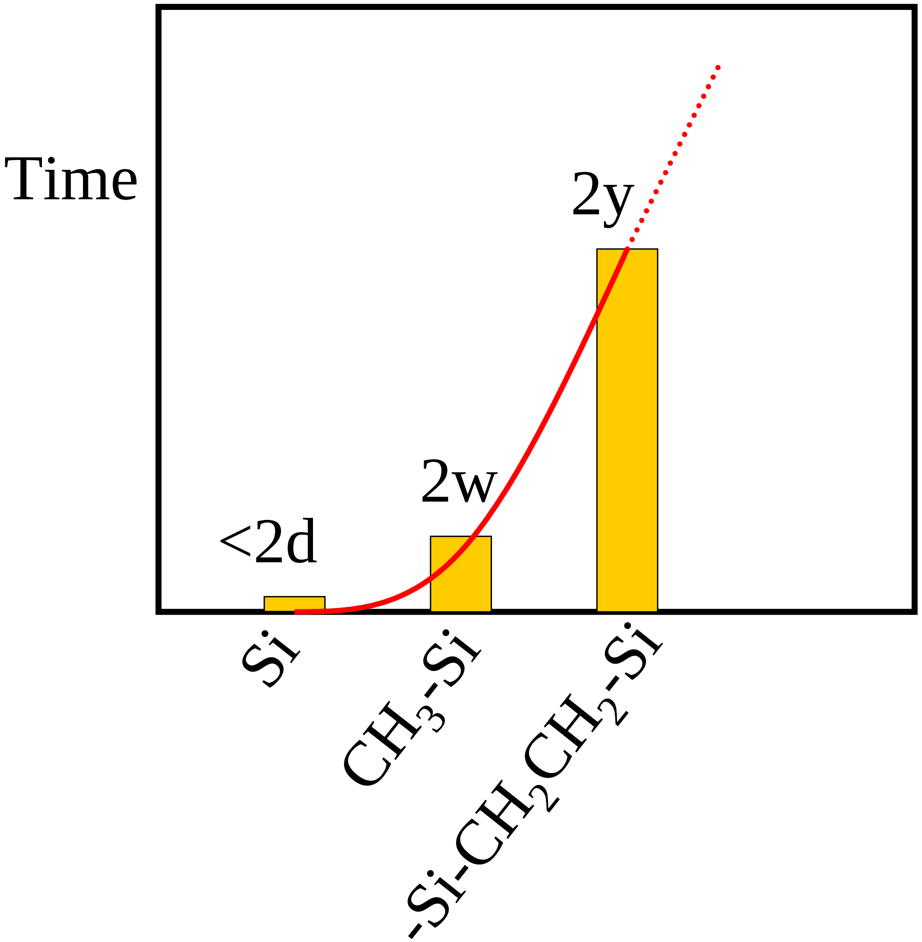


Feed : 5 wt.% water in EtOH
0.1 wt% HAc
Recipe 3



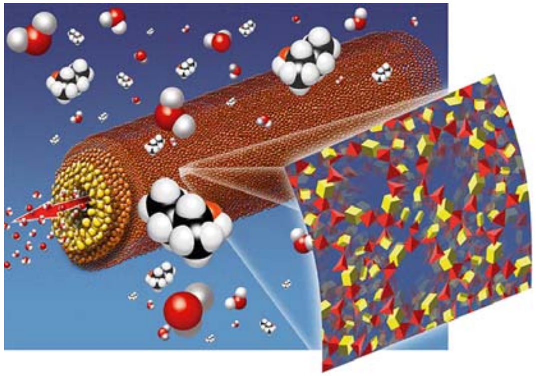
Acid stability very promising

Origins of hydrothermal stability hybrid silica - HybSi®



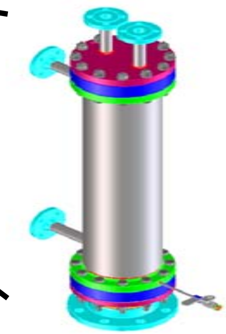
- Non-hydrolysable bonds
- Crack propagation limited
- Lower surface diffusion coefficient
- Lower solubility

Conclusions



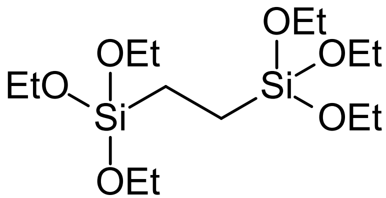
- High hydrothermal stability
- Wide range of organics possible
- Excellent performance in aggressive solvents
- Good acid stability
- Straightforward preparation, good reproducibility

Next steps



Pilot plant PV/VP installation, 1000 litre liquid
A_{mem}= 1 m^2 (24 tubes of 1 meter length)
T_{max} = 150ºC, P_{max} = 10 bar

- FOCUS: IMPLEMENTATION VIA PILOT DEMONSTRATION



- State of the art membrane
  - Further define application window pH, H_2O content, solvents
  - Create consortium for commercialisation of HybSi®: end user(s), membrane producer(s), system integrator(s), supplier(s) enabling parts.
  - Launching application(s).

- Further developments:
  - Reduce pore size: H_2O-EtOH, and hydrogen separation
  - Increase pore size: nanofiltration, MeOH from organics
  - Module geometry optimisation

Questions?

Chem. Commun., 2008, 1103-1105

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J. Mem. Sci, 2008, 324, 111-118

Patent: WO2007081212

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