Performance of a new hybrid membrane in high temperature pervaporation

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Paper presented at the International Congress on Membranes and Membrane Processes (ICOM), Honolulu, Hawaii, USA, 12-18 July 2008

ECN-M--08-089 DECEMBER 2008

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

Part of this work was supported with a grant from the Dutch Ministry of Economic Affairs via the EOS-LT (Long term energy research subsidy) programme, managed by SenterNovem.

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Energy research Centre of the Netherlands

Performance of a new hybrid membrane in high temperature pervaporation

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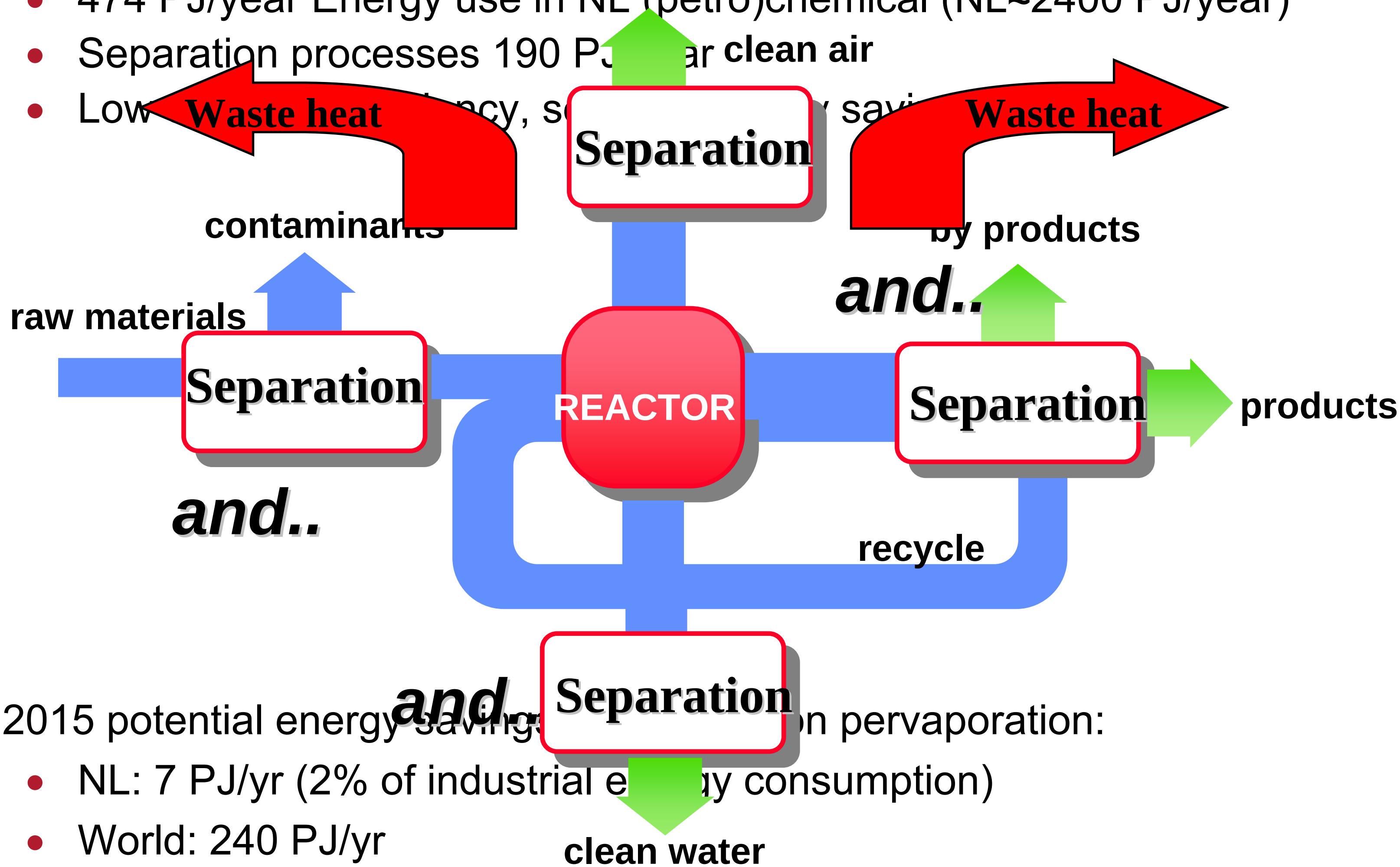
Introduction

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



By 2015 potential energy savings ... ...on 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 1-10.
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

⬇

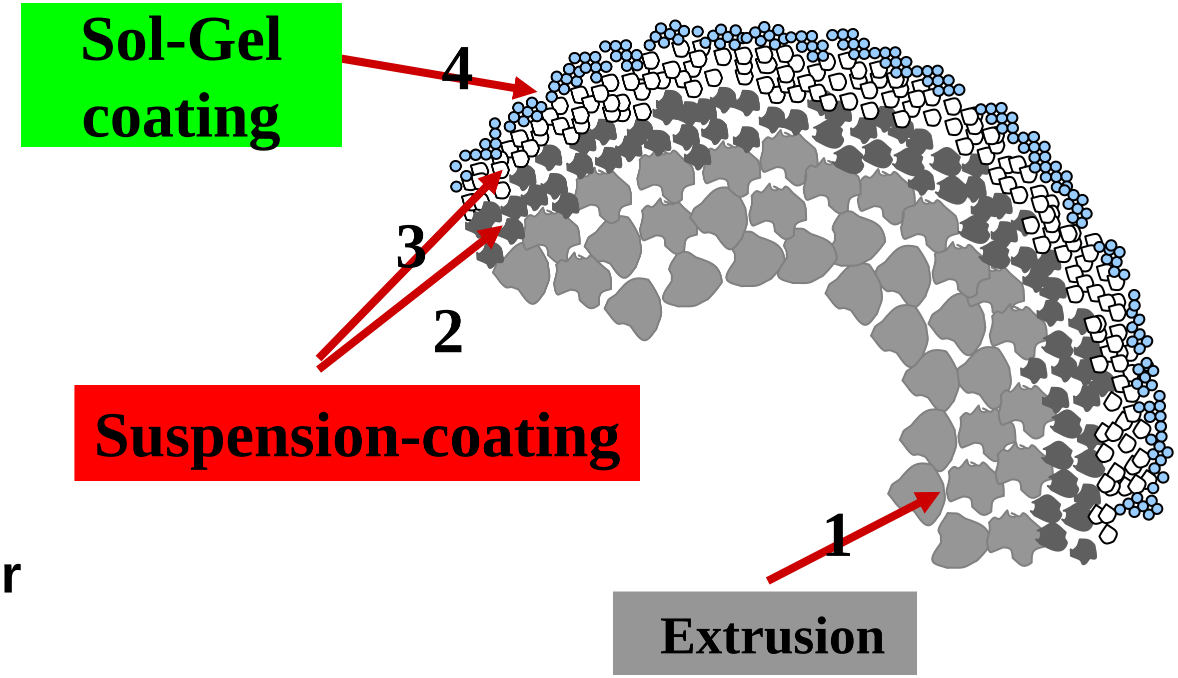
Firing

⬇

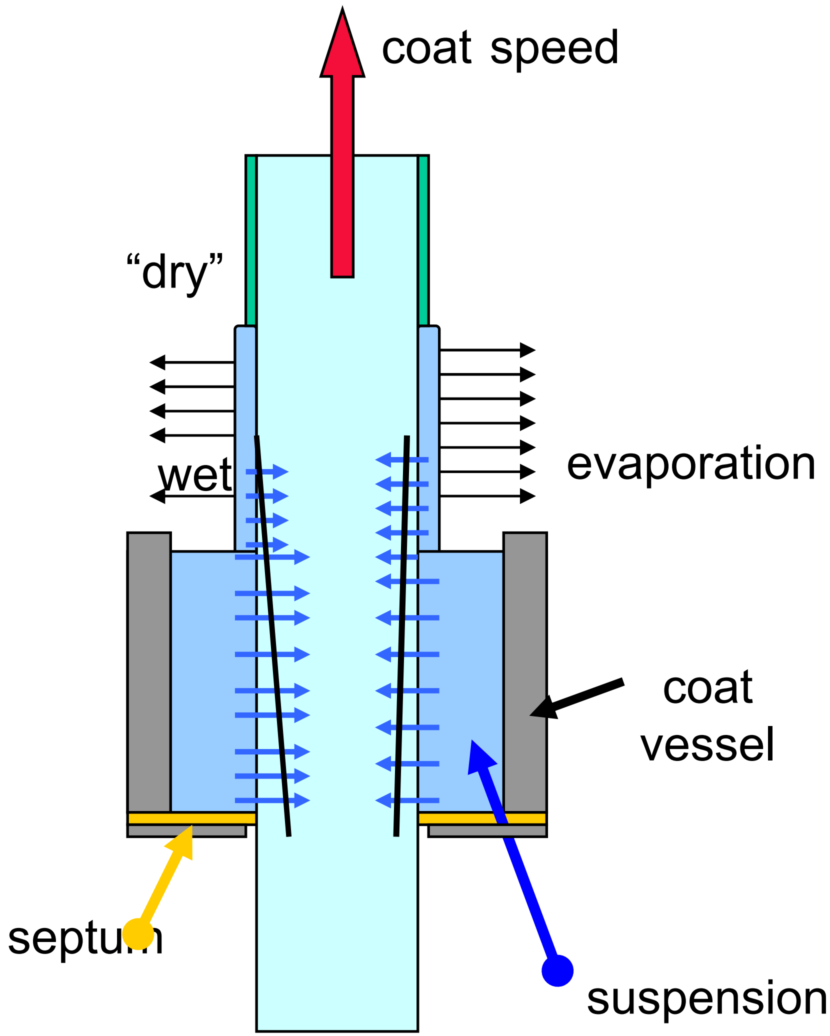
Ceramic membrane layer

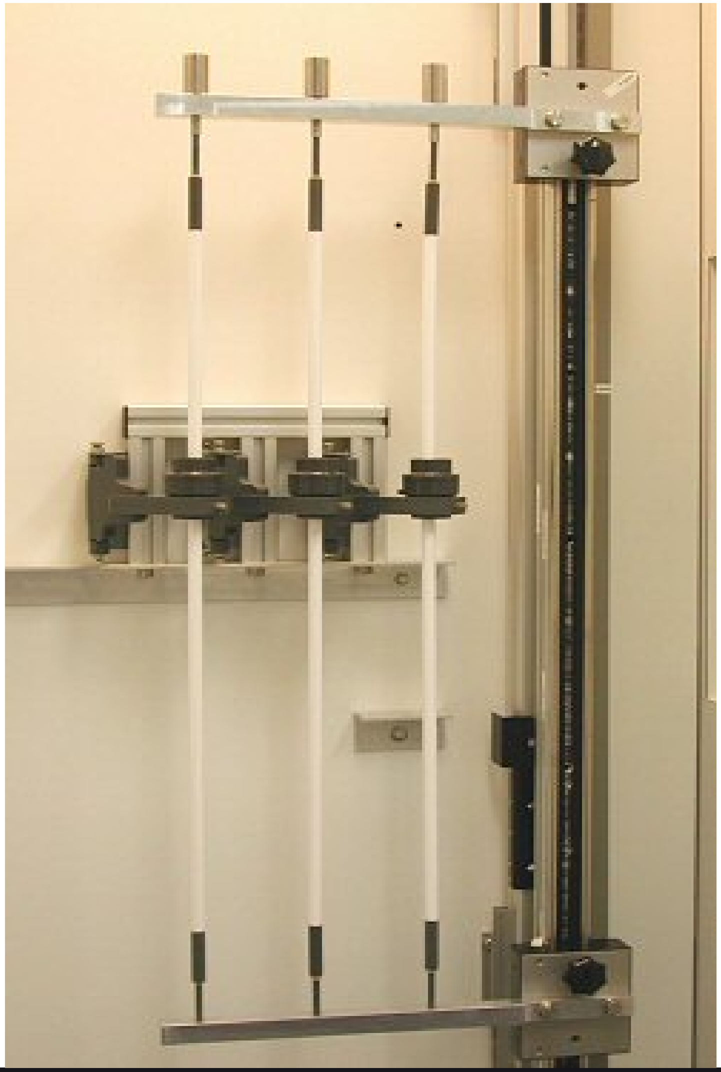
⬇

Membrane characterisation

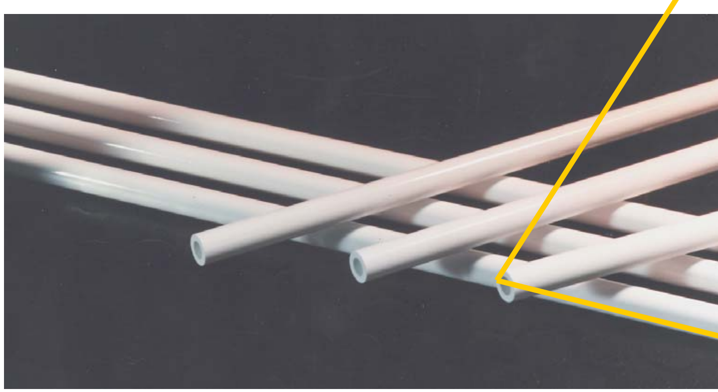


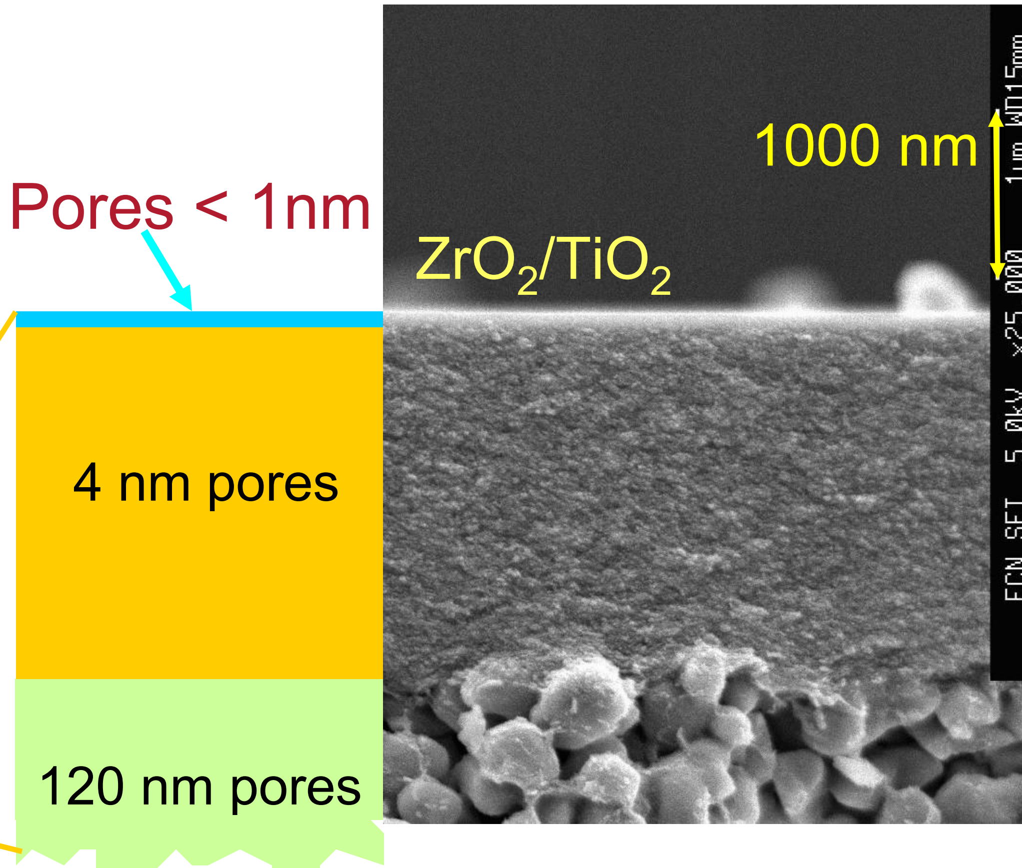
Preparation of the membranes





Tubular microporous membranes





Materials covered

Previous developments:

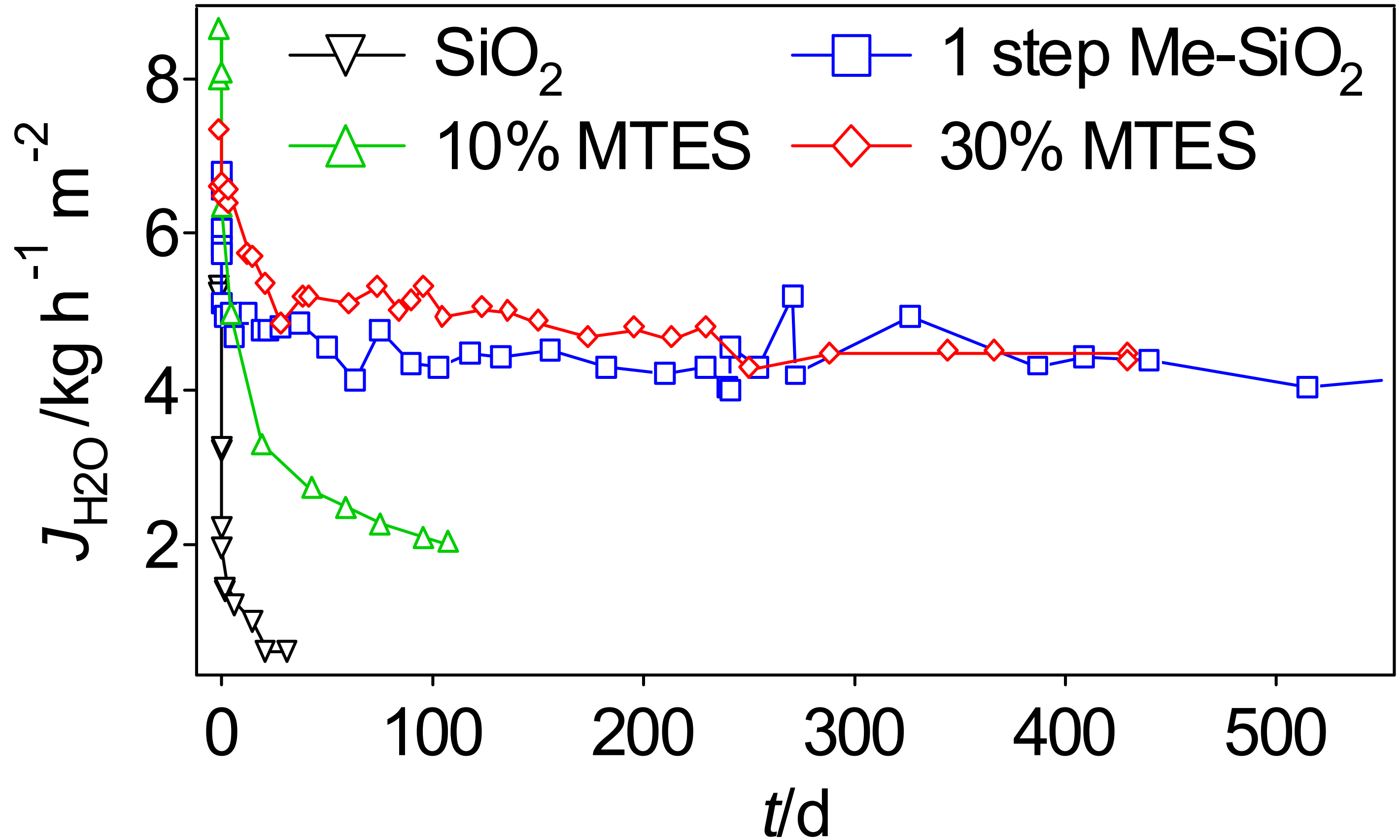
- SiO_2
- Methylated SiO_2

New leads:

- Hybrid silica, organic bridges
- (Ceramic supported polymers, titania, zirconia: see poster sessions)

Silica and Me-Silica long term pervaporation at 95ºC

Feed = 5 wt.% water in nBuOH

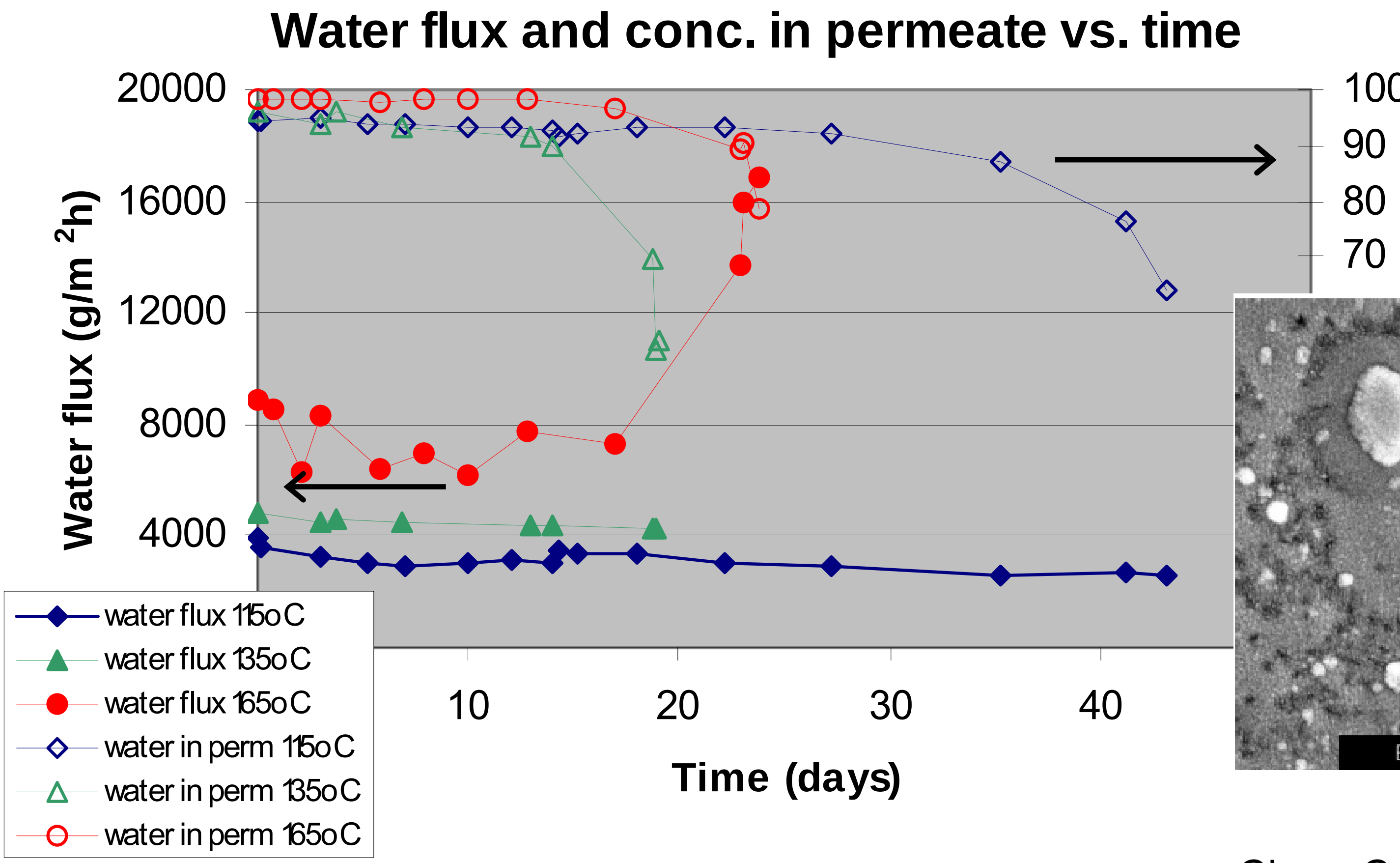


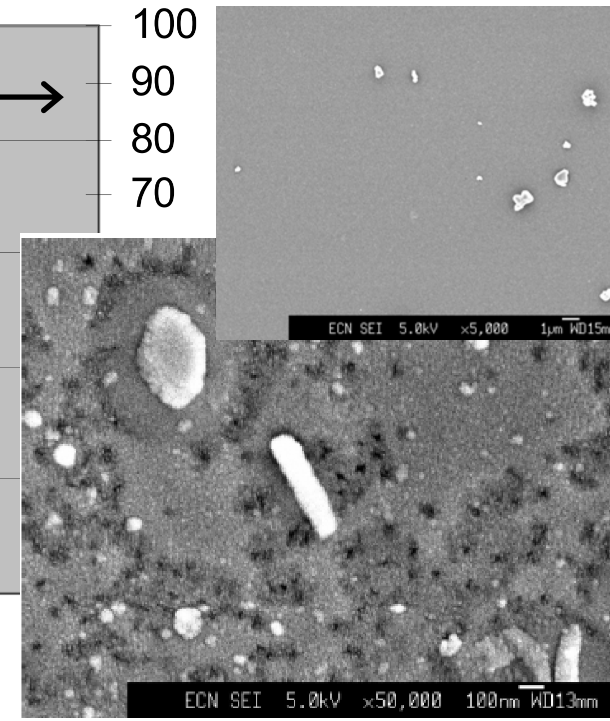
Methylated silica solves problem of the flux decline, selectivity meets demands

Silica and Me-Silica long term pervaporation up to 165ºC

Feed = 2.5 wt.% water in nBuOH

Membrane failure within weeks





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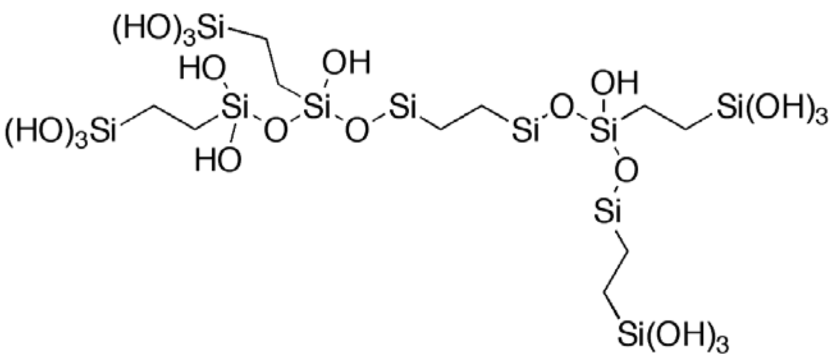
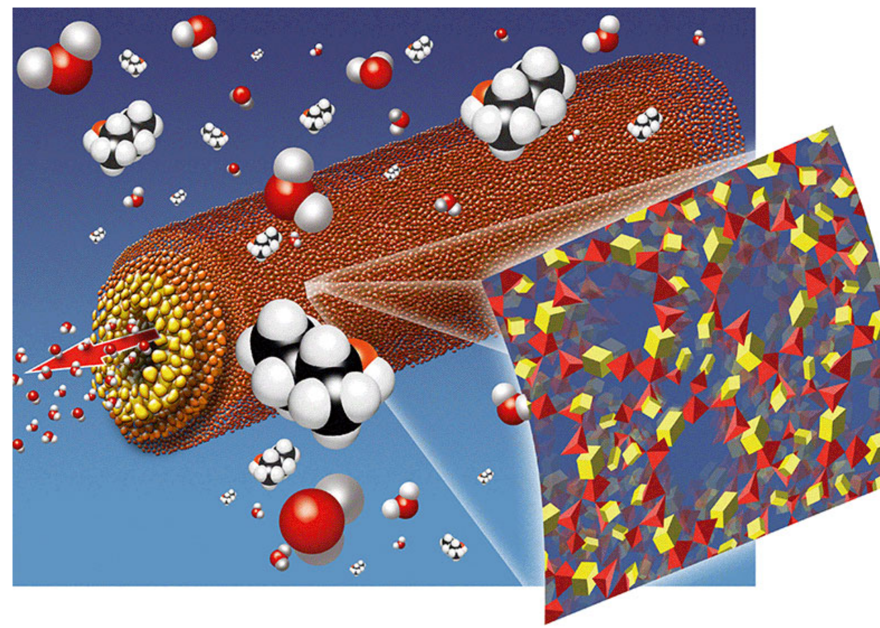
Hybrid membranes from bisfunctional silica precursors

replacing 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)

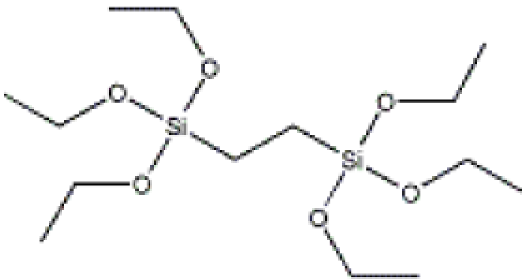




Patented in collaboration with Univ. of Twente and Univ. of Amsterdam (Ashima Sah, Andre ten Elshof, Hessel Castricum, Marjo Mittelmeijer)

Hybrid membranes

BTESE



Water, HNO_3 , EtOH

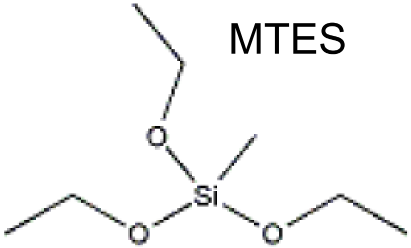
Reflux at 60ºC, 3 hrs

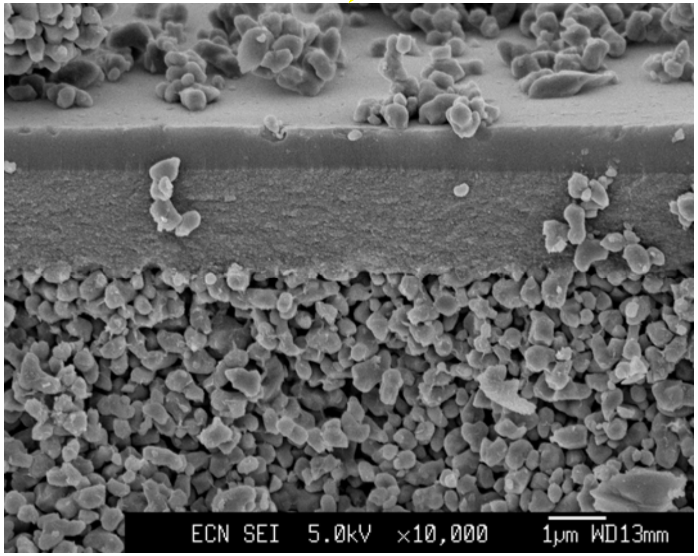
Mix

Coating and calcination

Mix in EtOH

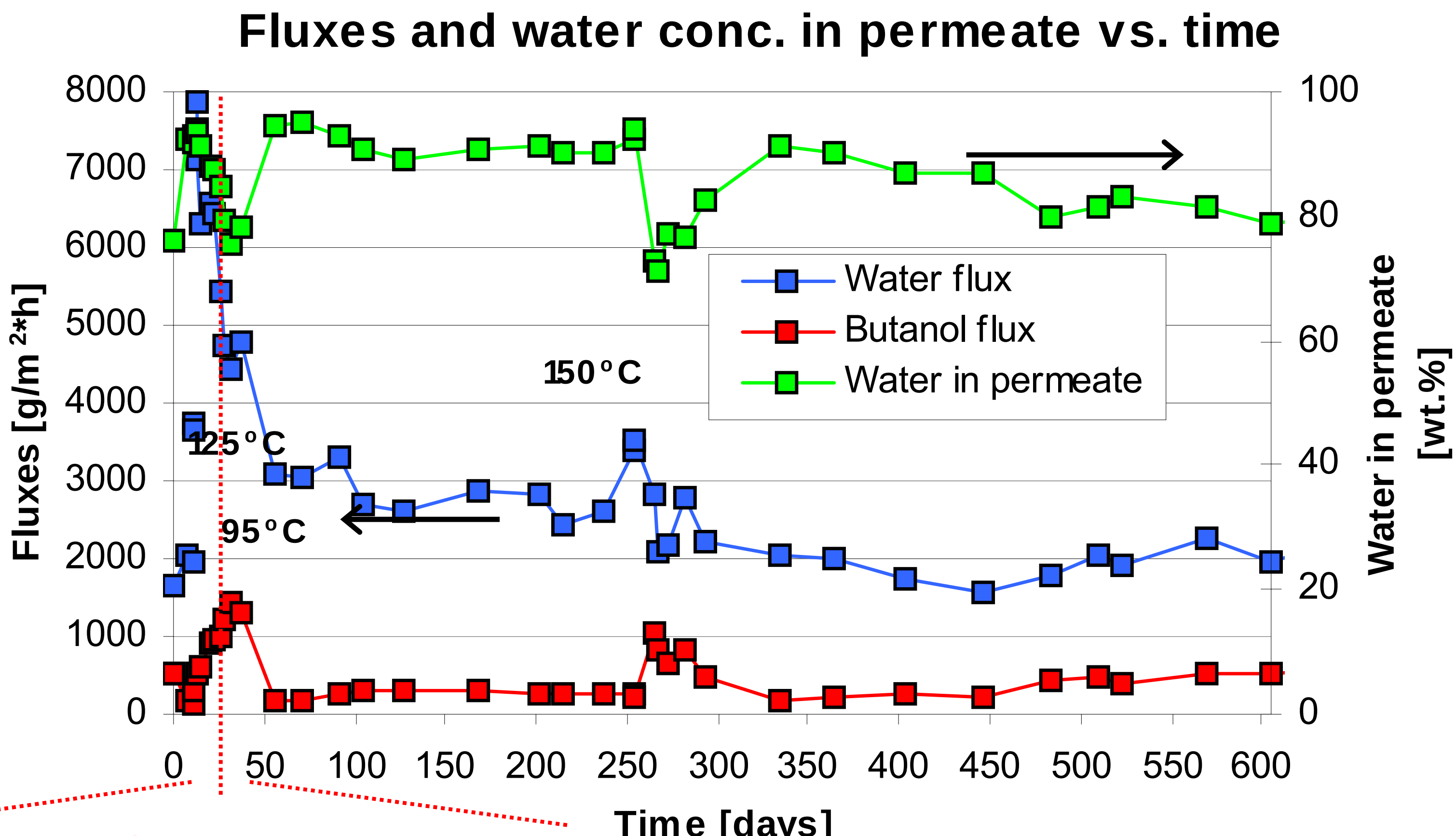
MTES





Performance hybrid membranes, 150ºC

First membrane made
Recipe 1
Feed = 5 wt.% water in nBuOH



Life time state of the art methylated silica

Hybrid membranes:
different precursors for improved performance

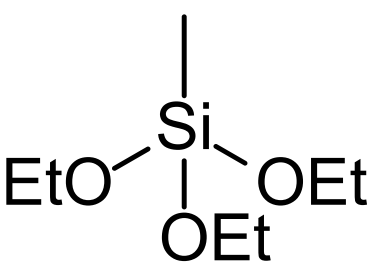
Precursors:

Recipe 1 BTESE + MTES

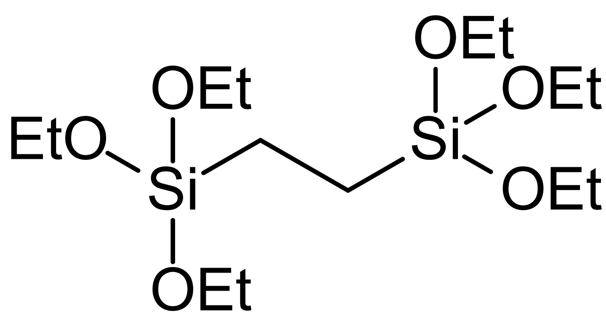
Recipe 2 BTESE

Recipe 3 BTESM

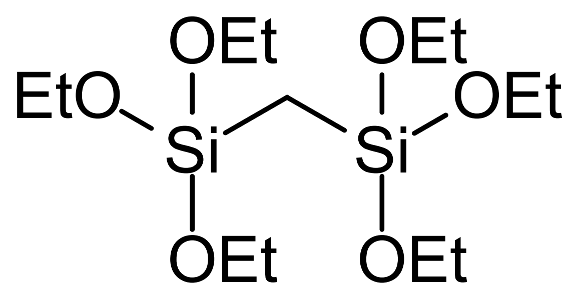
MTES



BTESE

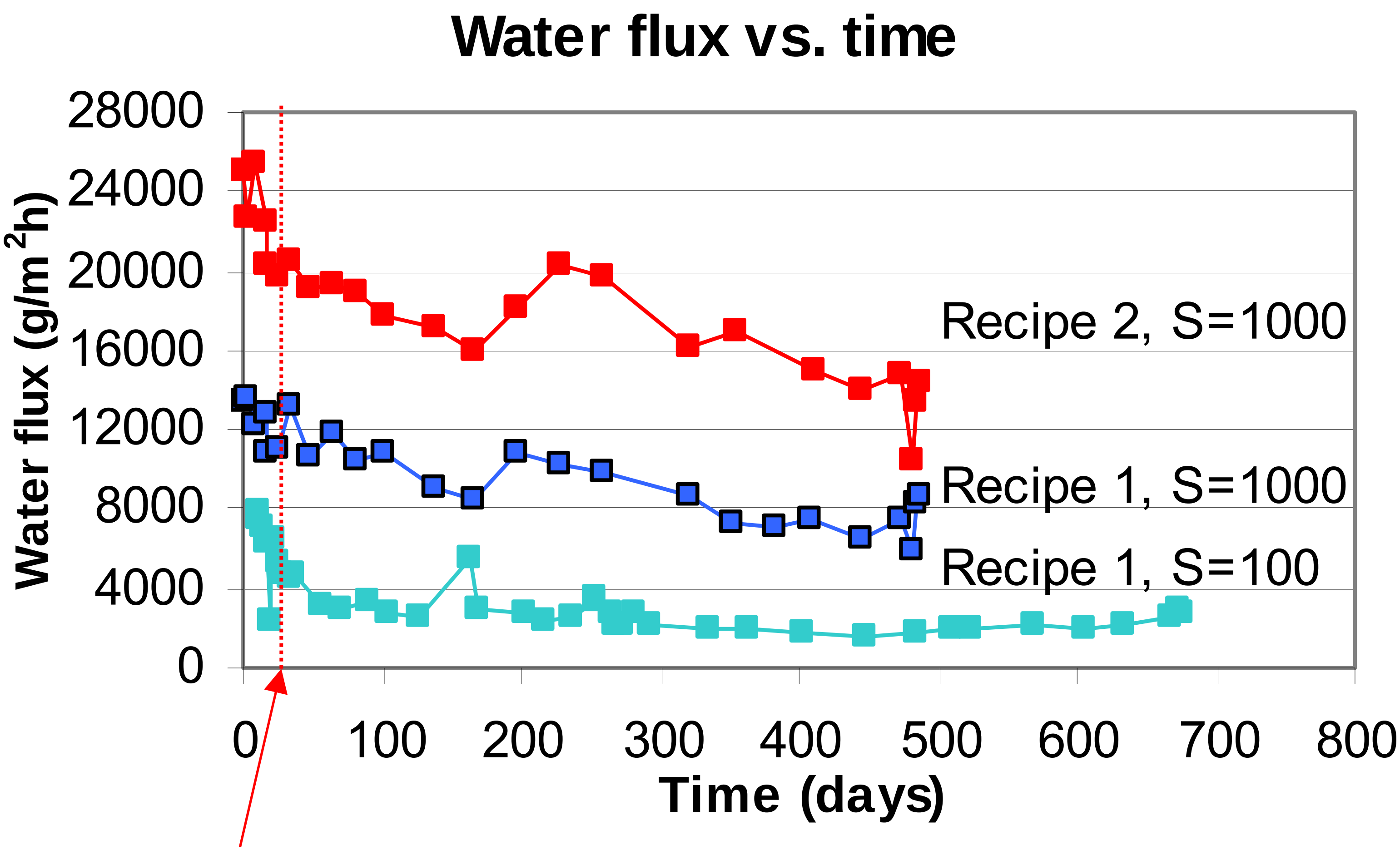


BTESM



Feed = 5 wt.% water in nBuOH

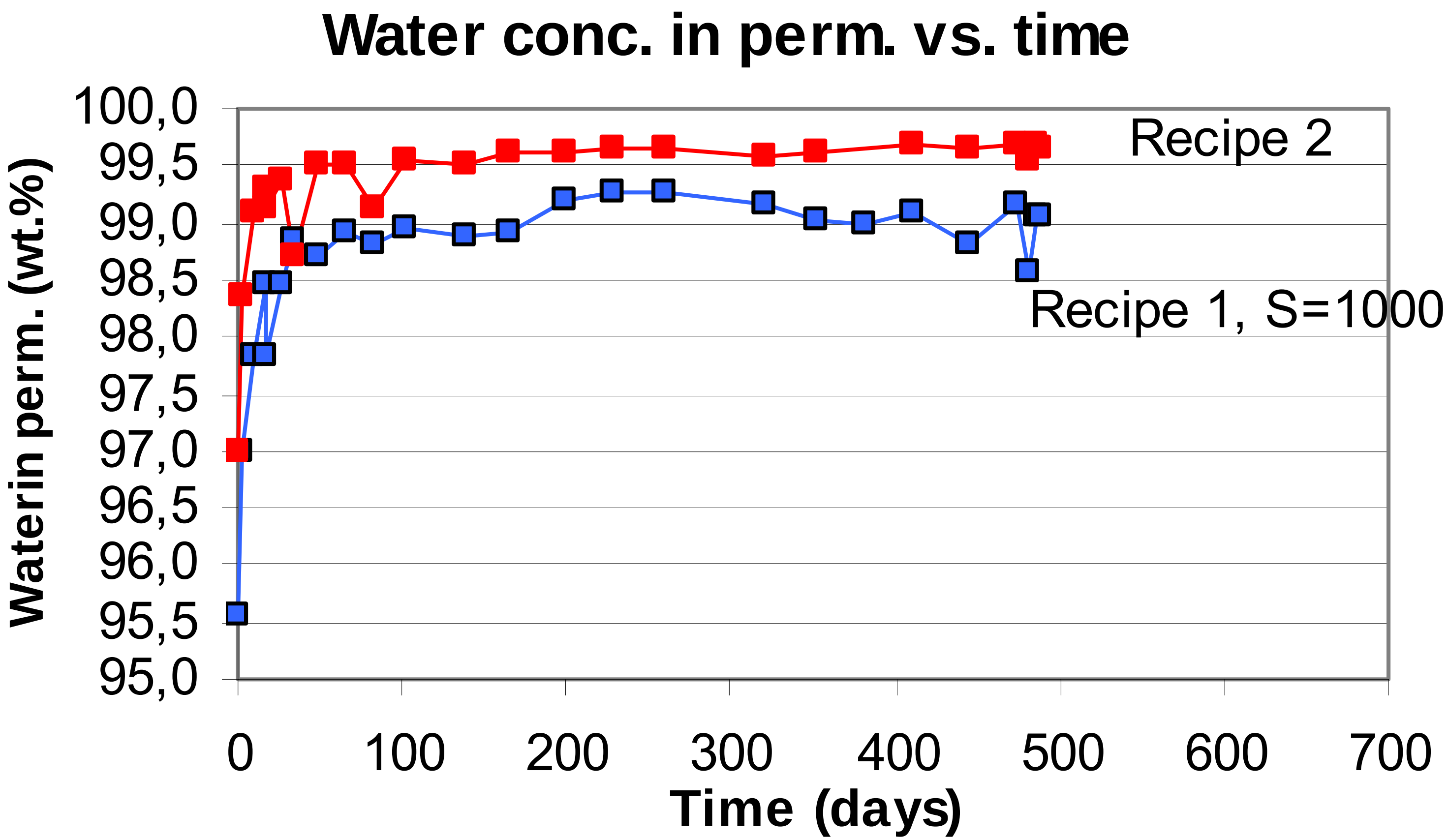
Performance hybrid membranes, 150ºC



Life time state-of-the-art MeSi

Feed = 5 wt.% water in nBuOH

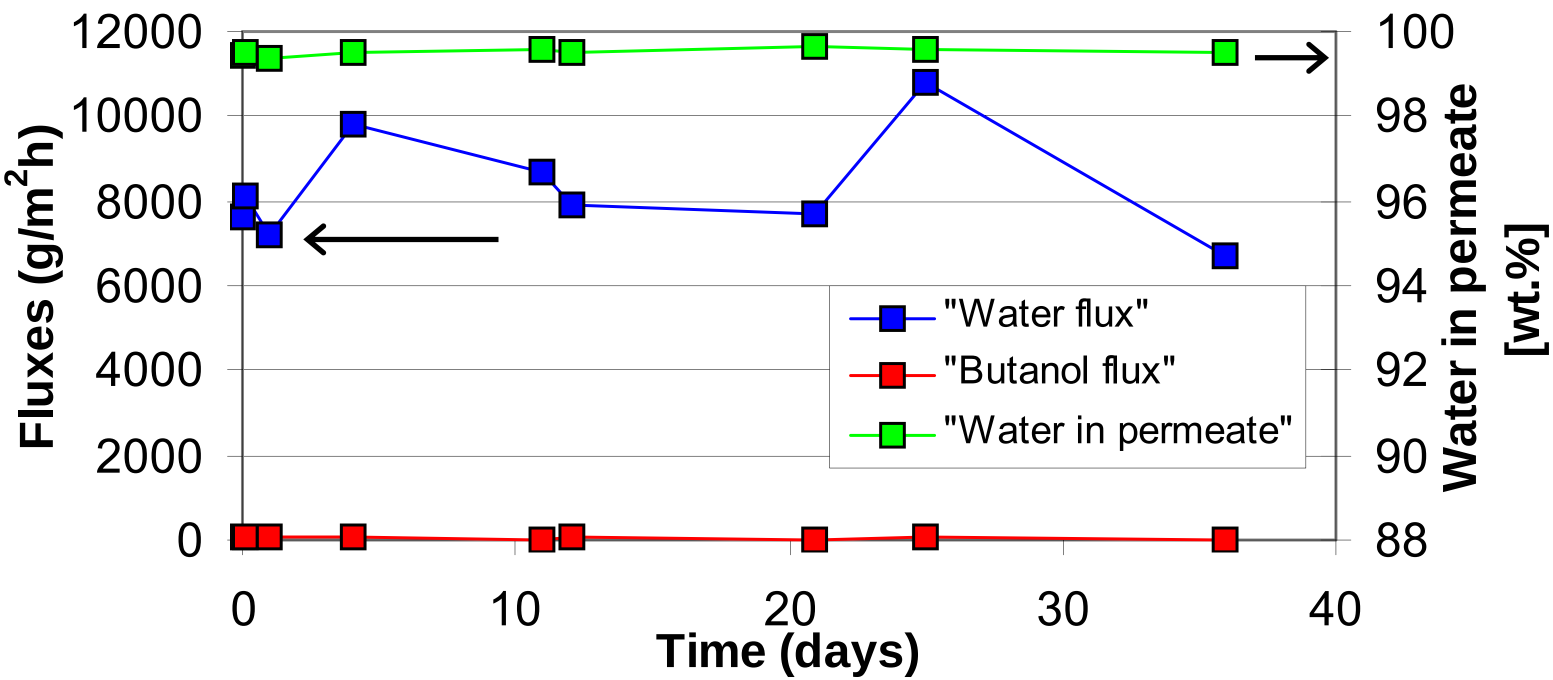
Performance hybrid membranes, 150ºC



Performance hybrid membranes, 190ºC

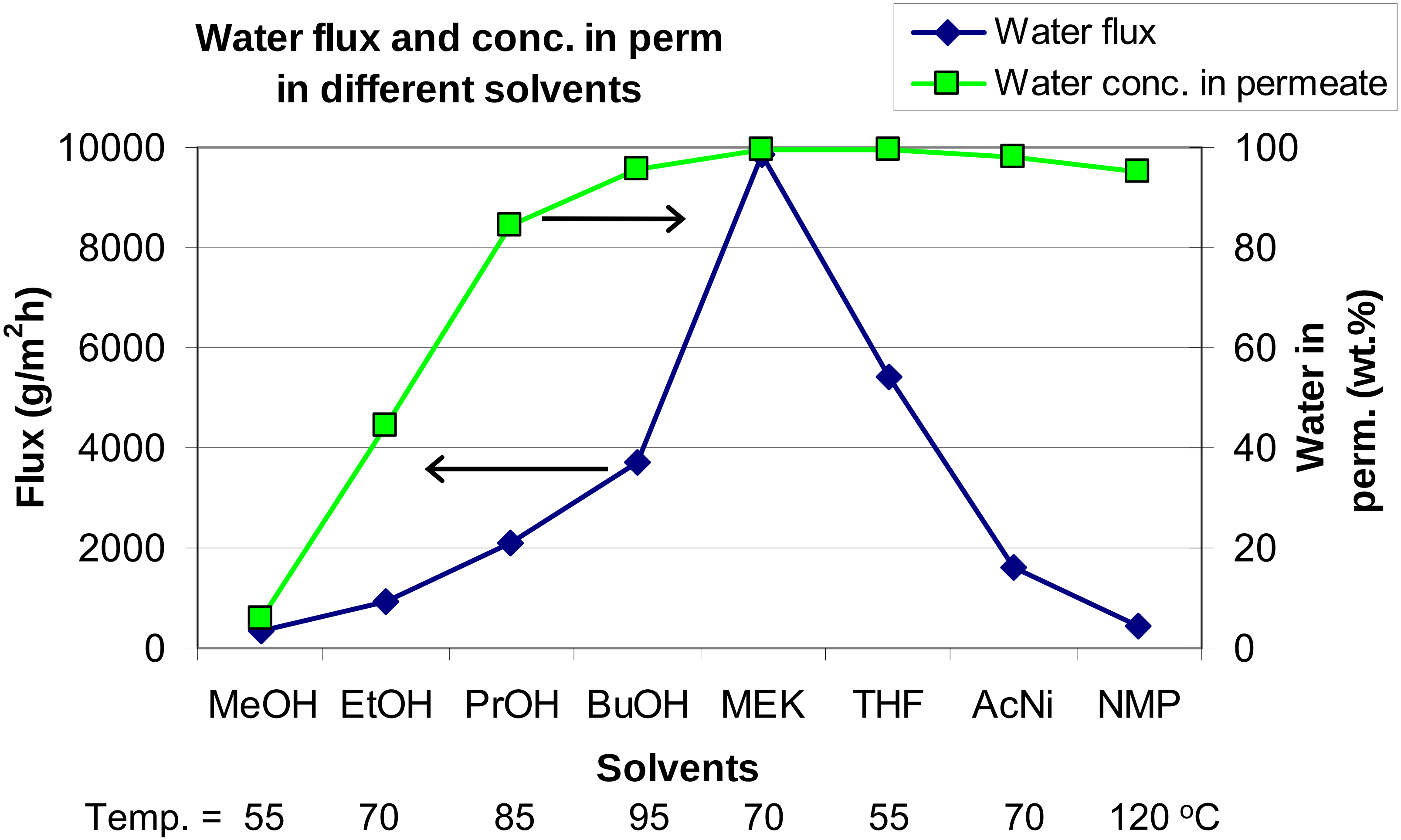
Feed = 5 wt.% water in nBuOH
Recipe 2

Fluxes and water conc. in permeate vs. time



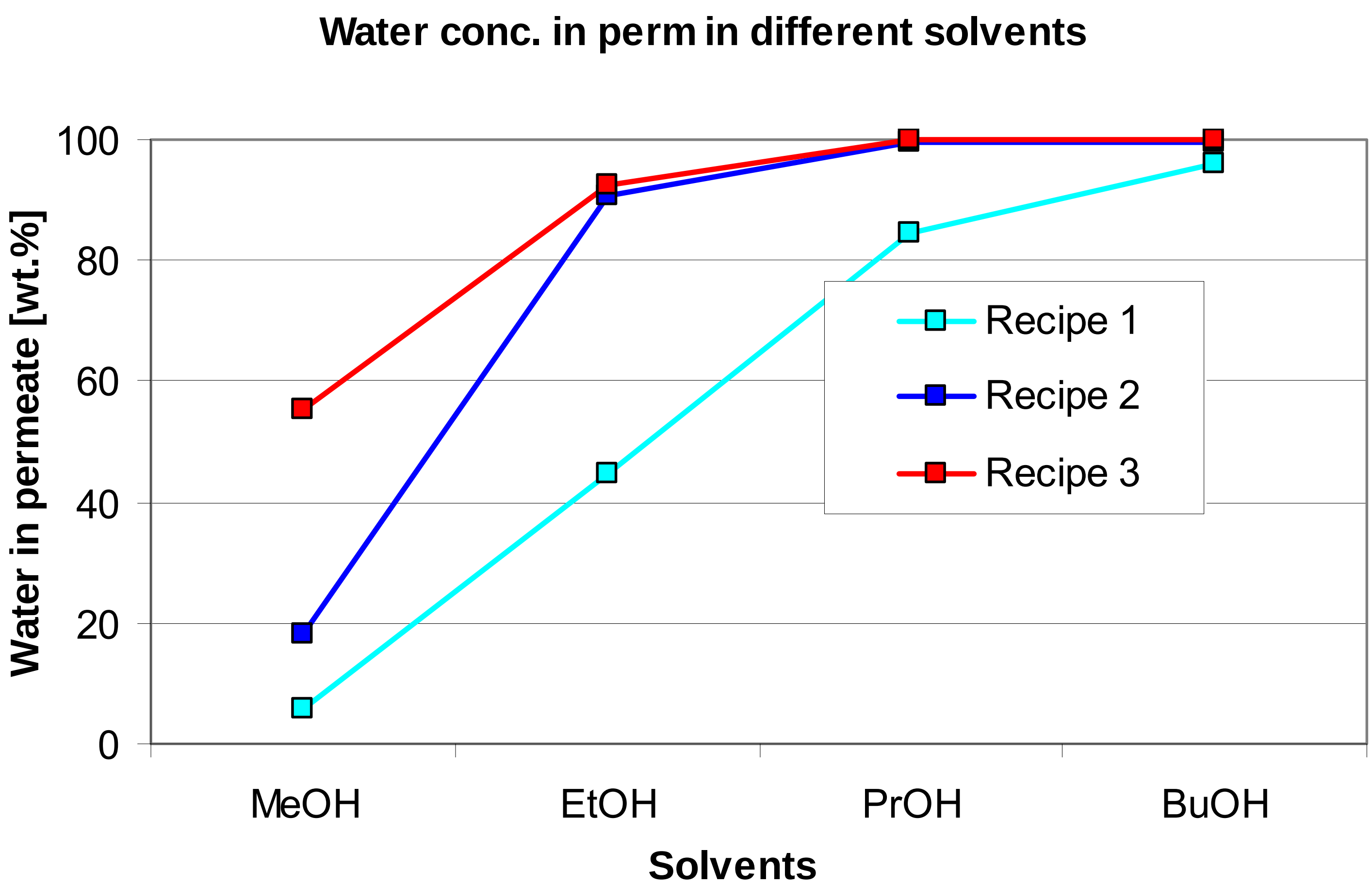
Hybrid membranes application testing

Feed = 5 wt.% water in solvent
Recipe 1



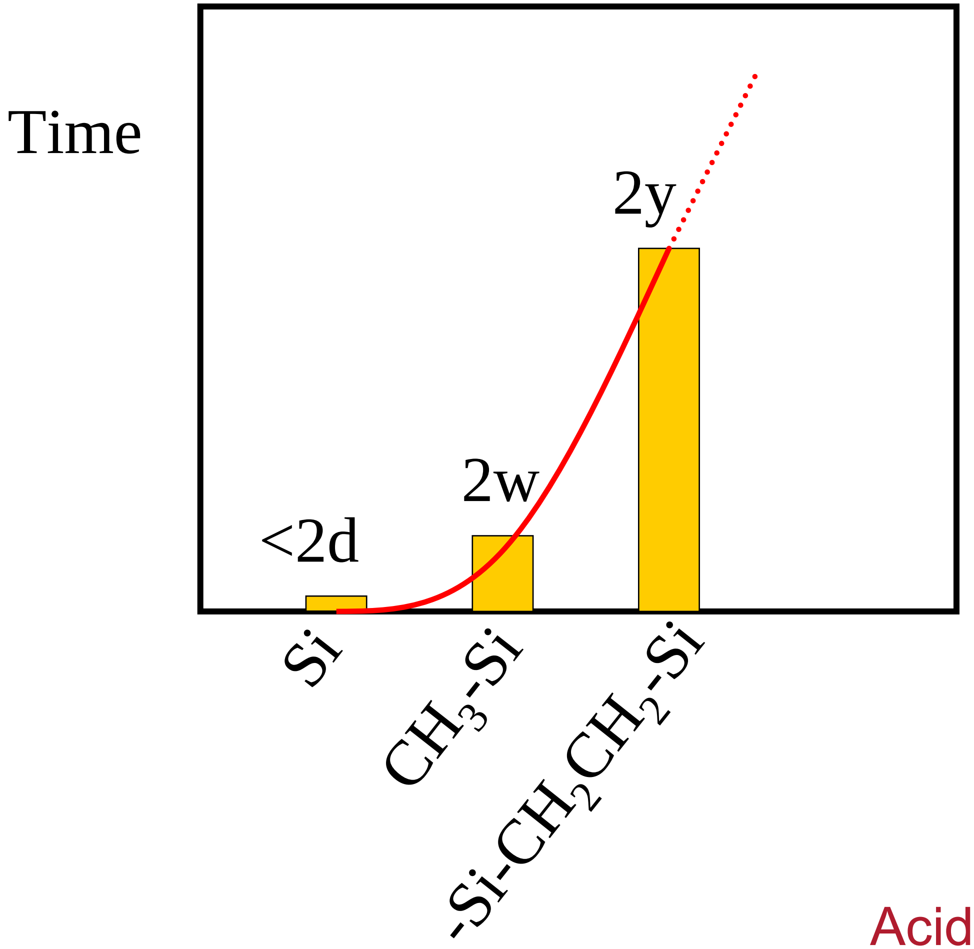
Hybrid membranes application testing

Feed = 5 wt.% water in solvent



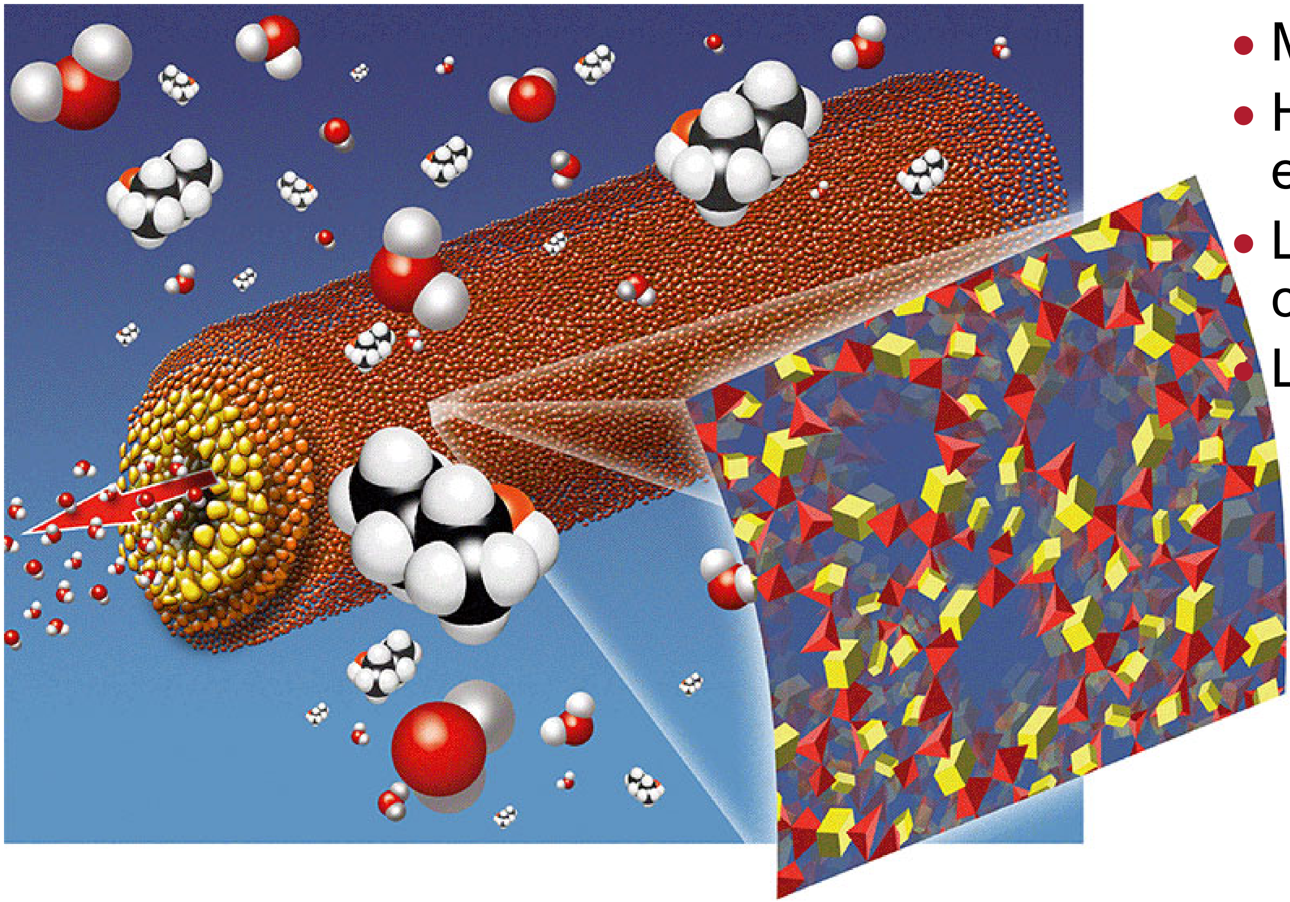
Temp. = 55 70 85 95 °C

Conclusions: hydrothermal stability at 150°C



Acid stability very promising!

Origins of stability of hybrid silica



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

Next steps

- FOCUS: IMPLEMENTATION
  VIA PILOT DEMONSTRATION

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

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

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

ECN

Questions?

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