HybSi® membranes:materials, processes, outlook

J.F. Vente

Presented at the 14th Nordic Filtration Symposium in Aalborg, Denmark, August 30 - 31 2012

ECN-L--12-048 August 2012

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Your energy. Our passion.

HybSi® membranes: materials, processes, outlook

Jaap Vente

Aalborg, Denmark
30th of August 2012

The agenda

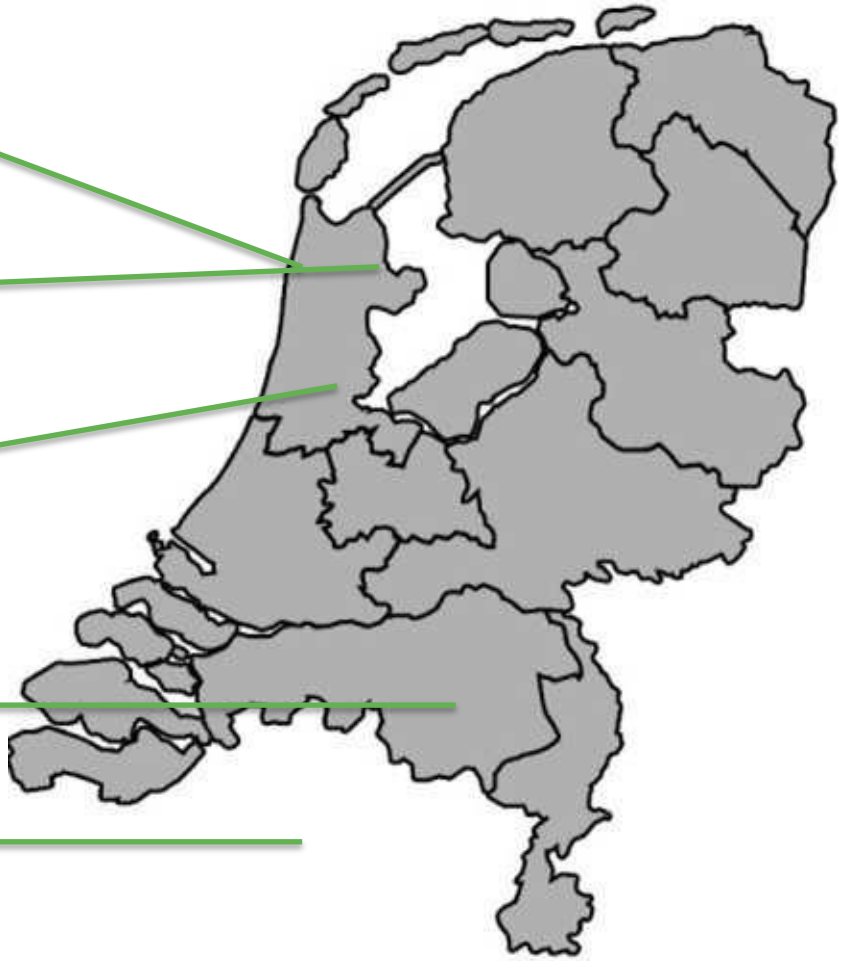
- Commercially ready and available product
- Process design
- Tailoring properties towards new applications

Take home messages

Separate unit operations do have advantages over process integrated options

Organic – Inorganic hybrid silica based membranes can be tailored into various applications

Locations



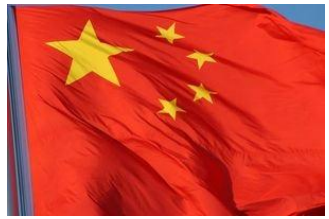
ECN
Petten

ECN
Wieringerwerf

ECN
Amsterdam

ECN
Eindhoven

ECN
Brussels



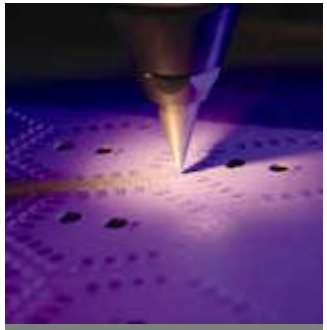
ECN
Beijing

Mission:

With and for the market, we develop knowledge and technology that enable a transition to a sustainable energy system.

R&D fields

Policy Studies



Energy Engineering

Environment

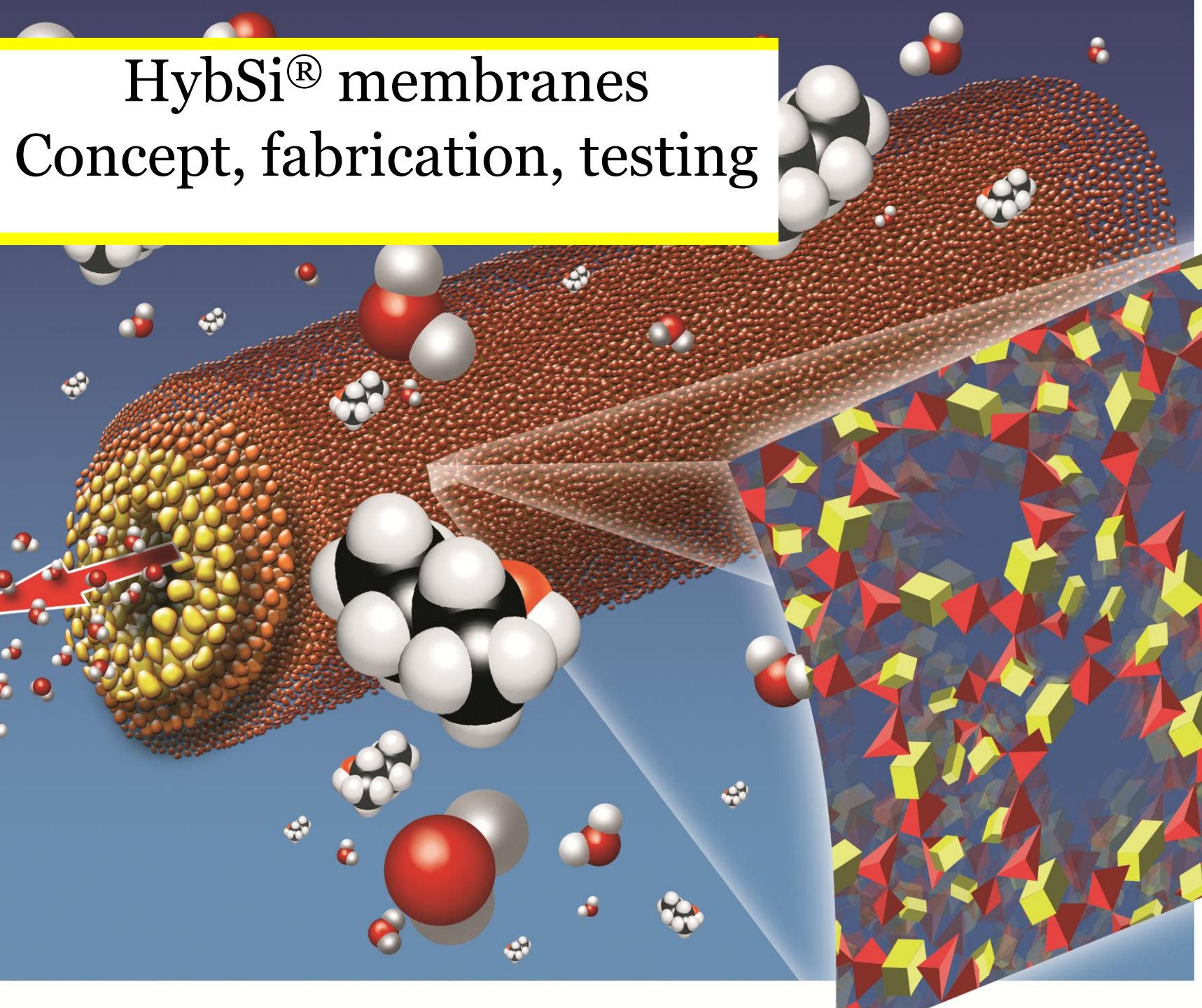
Wind Energy

Solar Energy

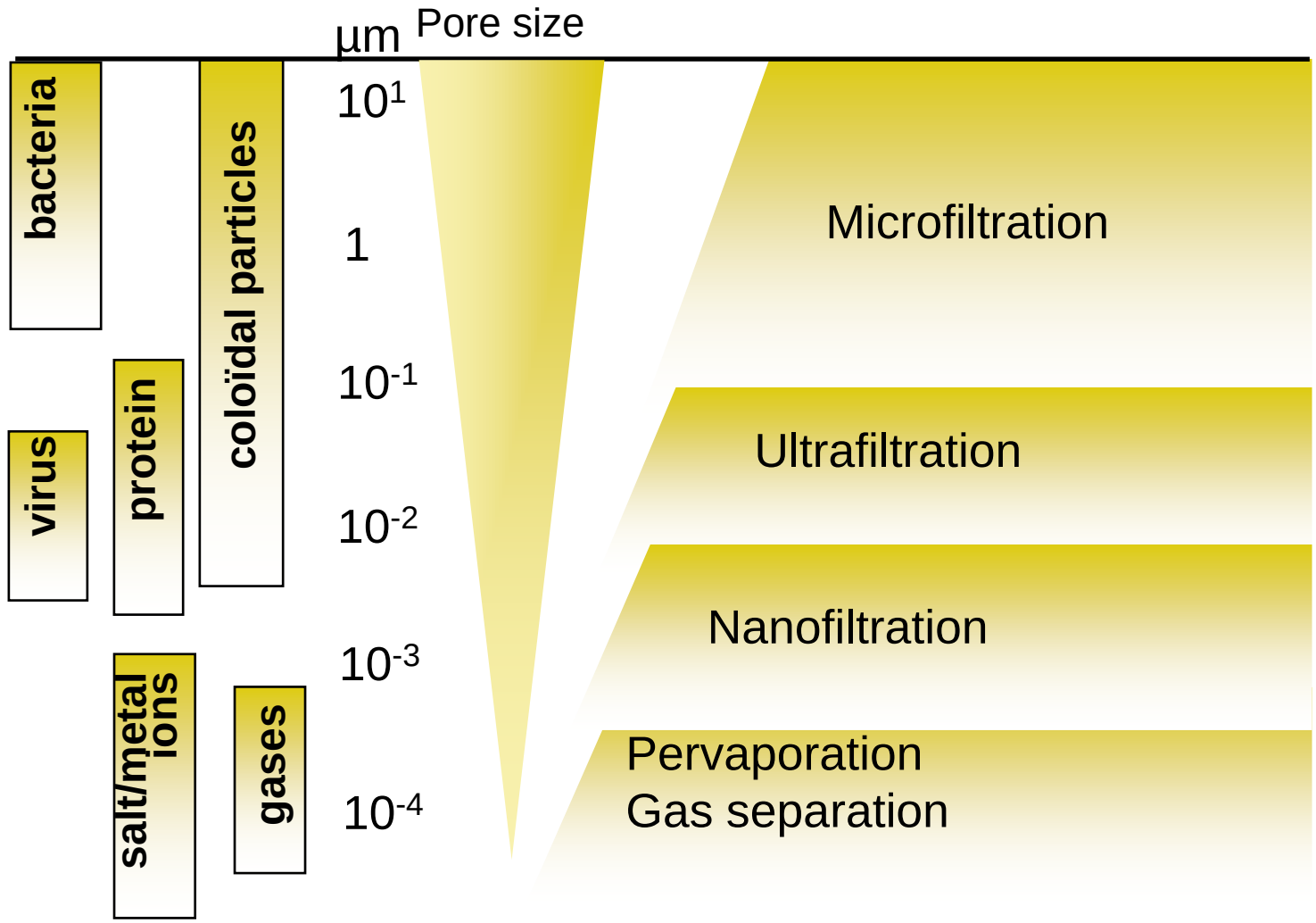
Biomass

Energy Efficiency & CCS

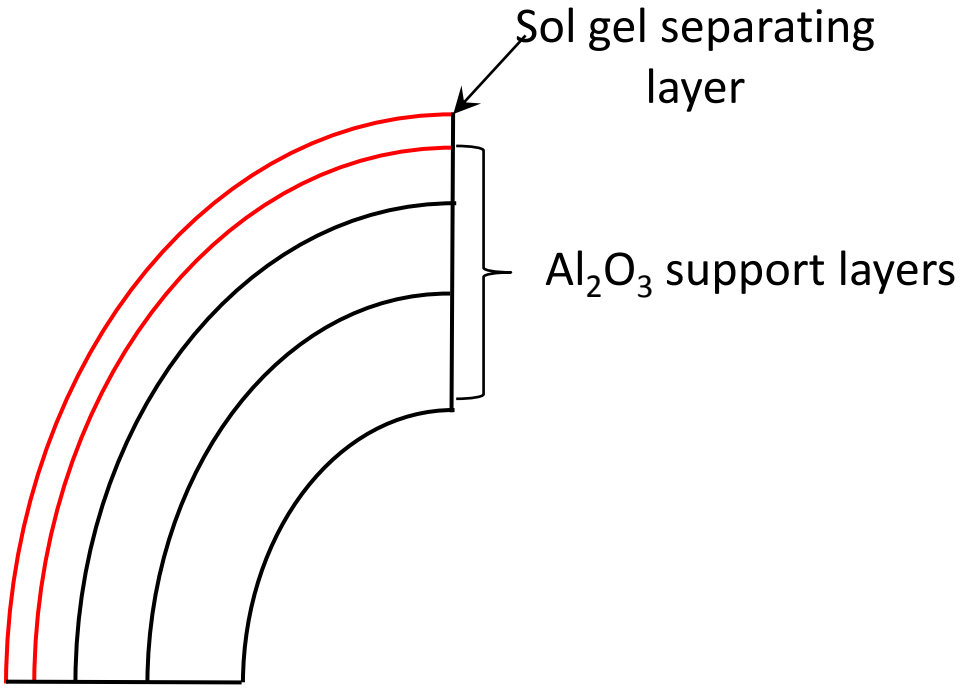
HybSi® membranes
Concept, fabrication, testing



Porous membranes

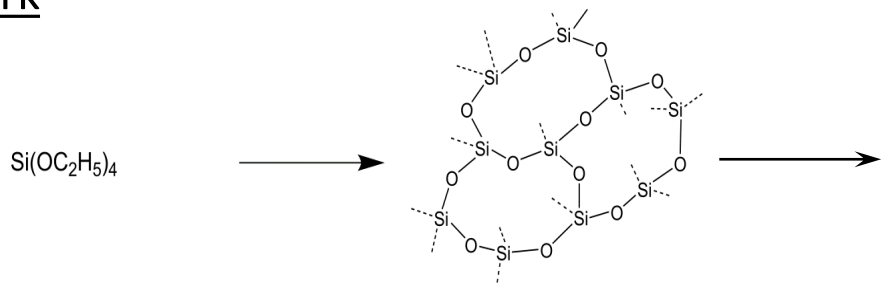


Asymmetric hybrid silica membranes



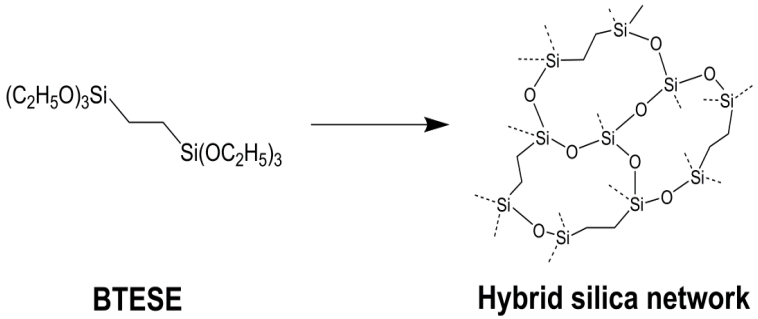
Concept of hybrid silica membranes

Silica network



Hydrothermally unstable

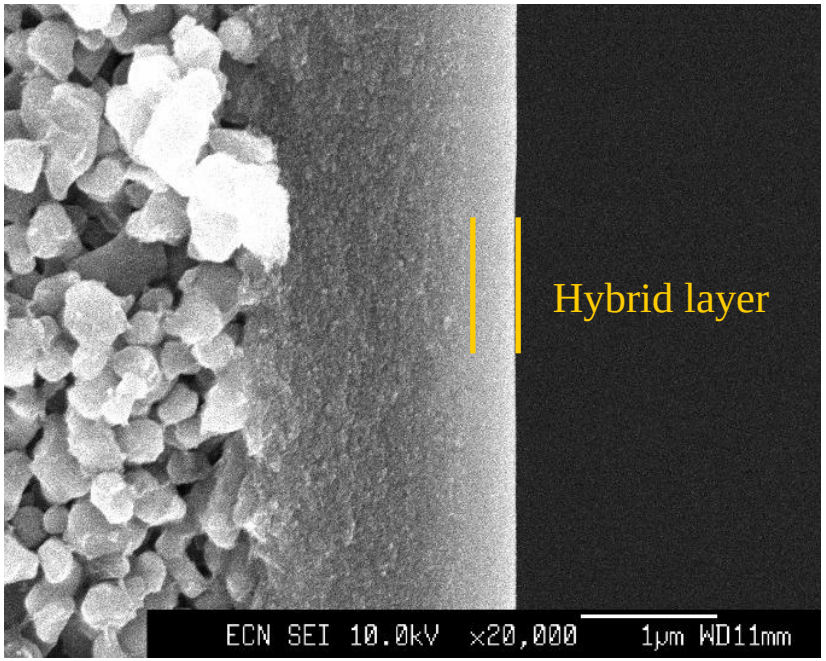
Hybrid silica network



Hydrothermally stable

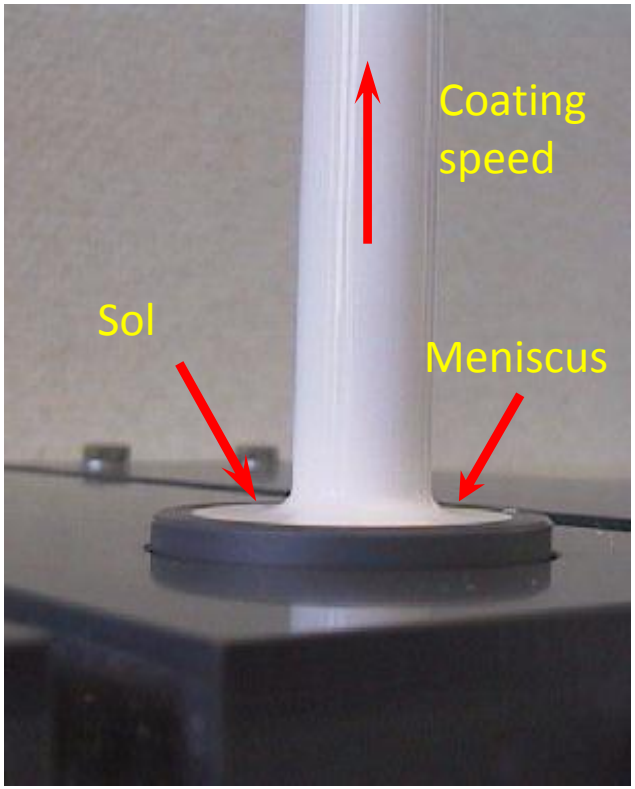
Preparation of the membrane

Sol-gel technology



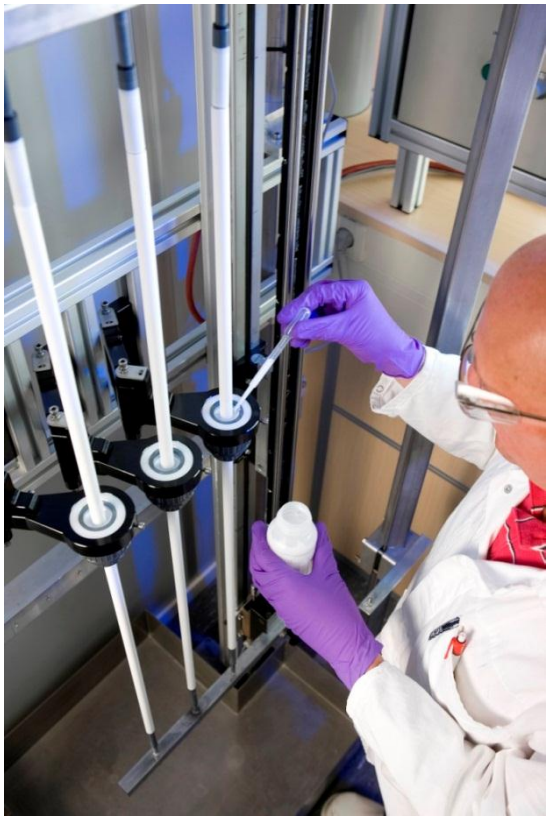
Essential issue:
“particle size” distribution

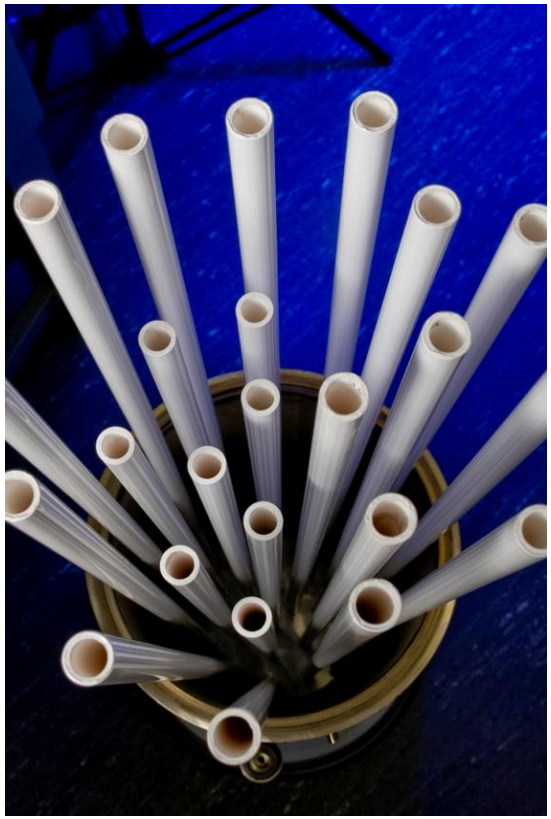
Coating procedure



HybSi® Pervaporation Membranes

ECN

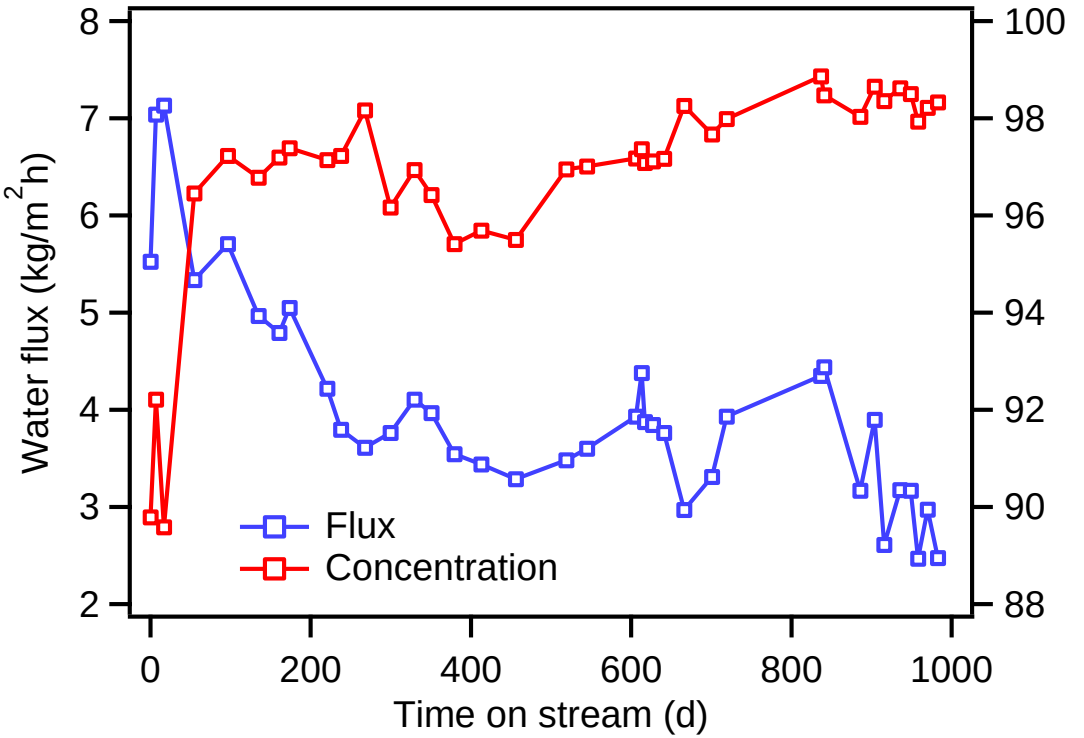




HybSi®
Pervaporation Membranes

Performance in Pervaporation

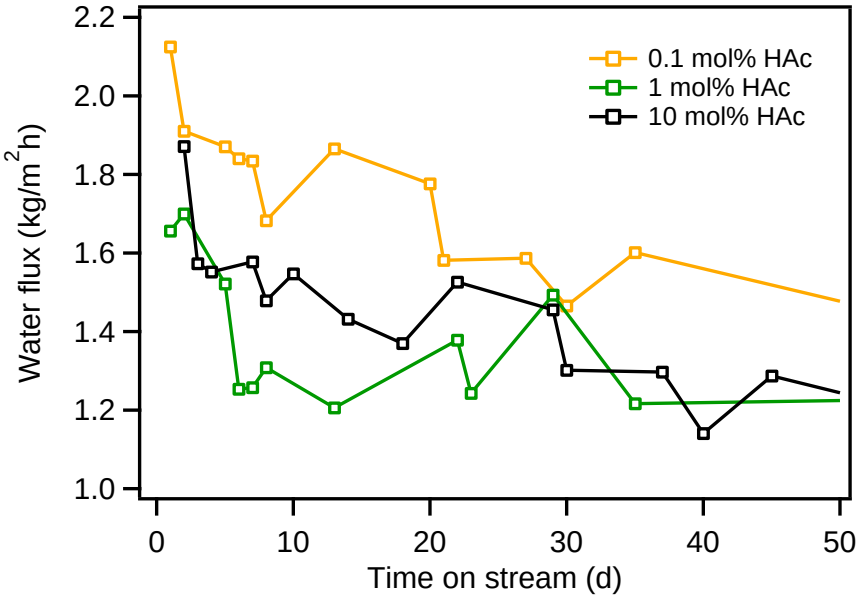
- 150 °C
- 3% H_2O in BuOH
- Measurement stopped after 1000 days



Van Veen *J. Mem. Sci.* 2011, 380, 124-31

Acid stability

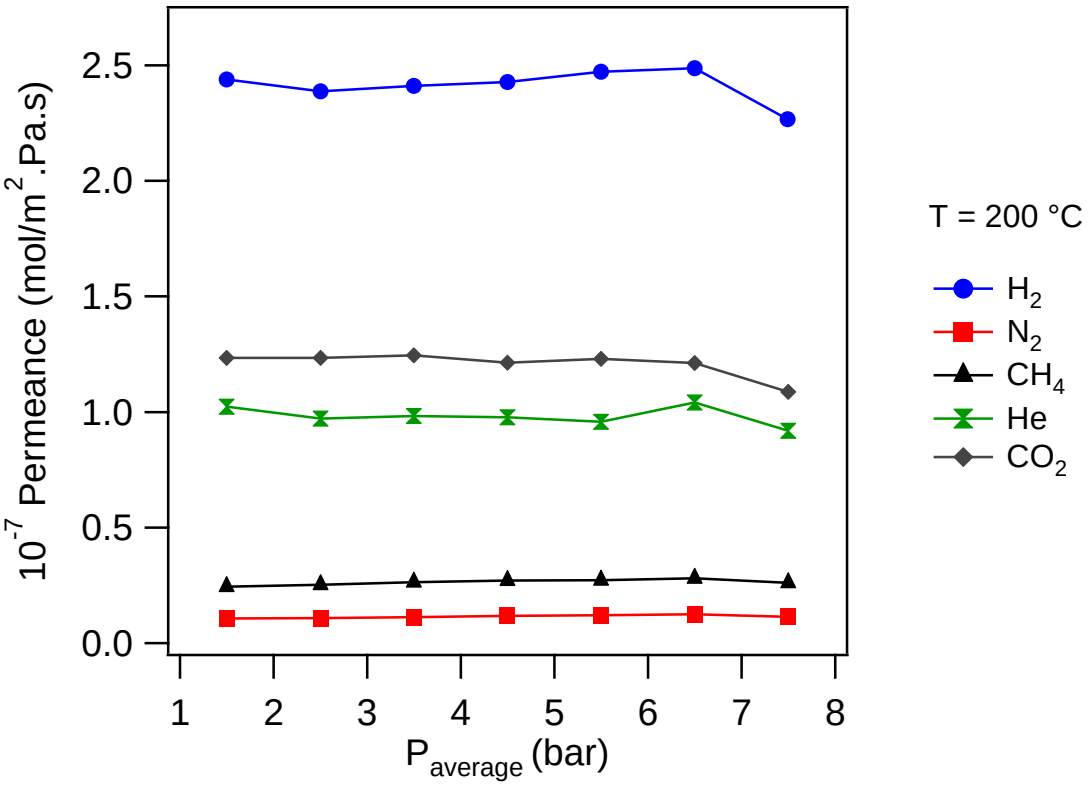
- 70 °C
- 5% H_2O in EtOH
- Water content in permeate: > 85%



Kreiter, *ChemSusChem*, 2009, 2, 158

Gas separation

- H_2/N_2 selectivity 20 – 30
- Later externally confirmed
- Improvements possible by adding metal oxides



Kreiter, ICIM, Tokyo, 2008

Tsuru, *J. Am. Chem. Soc,* 2009, 131, 414
Bouwmeester, *ChemSusChem*, 2010, 3, 1375

HybSi® Pervaporation Membranes

Stability(1): PMO

- MCM-like materials

  Low hydrothermal stability

- Alternative:

  Periodic Mesoporous Organosilicas

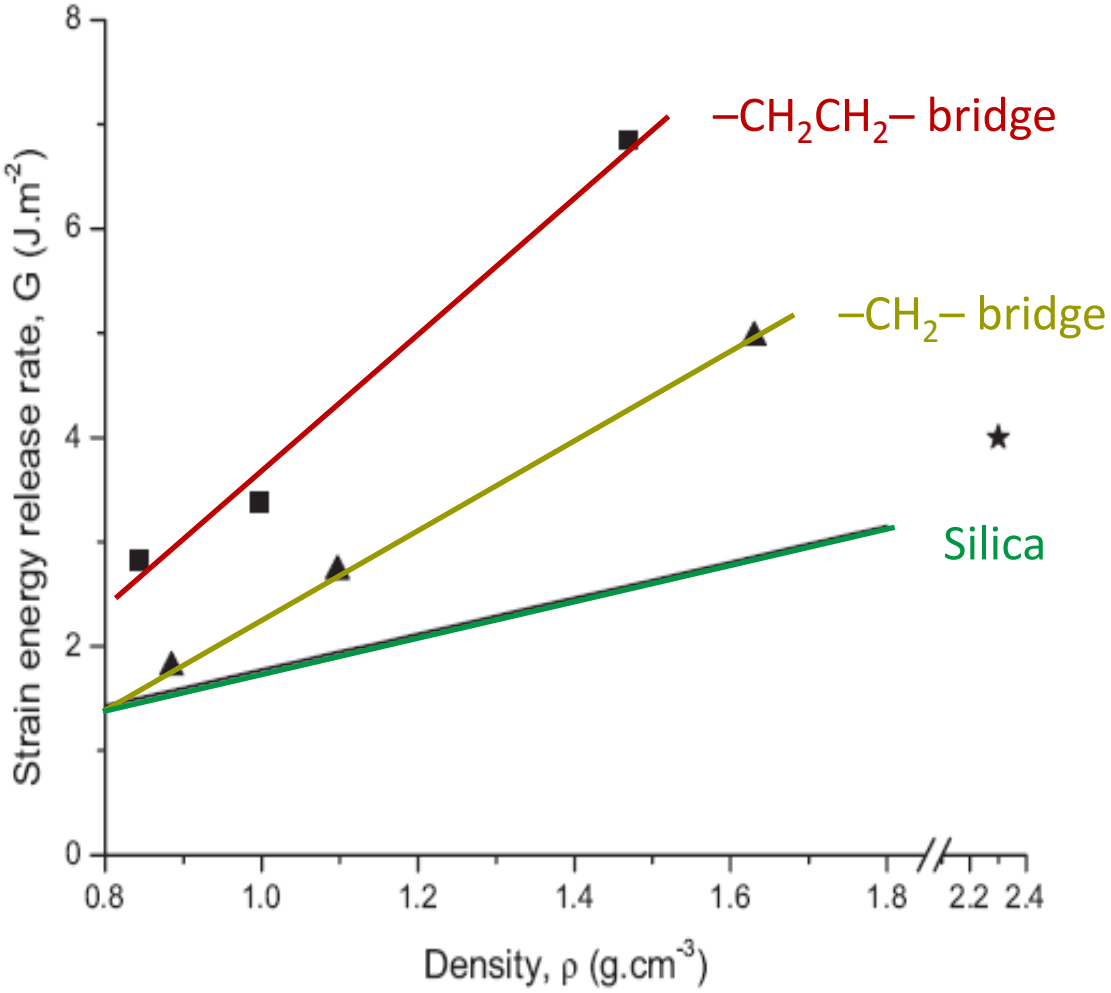
- Conclusions

  "stable materials should possess hydrophobic, organic, parts homogeneously divided and strongly anchored throughout the material. **Only materials which completely exist out of precursor molecules with an organic bridging group, are stable …..** "

Smeulders, *Mater Chem & Phys*, 2012, 132, 1077

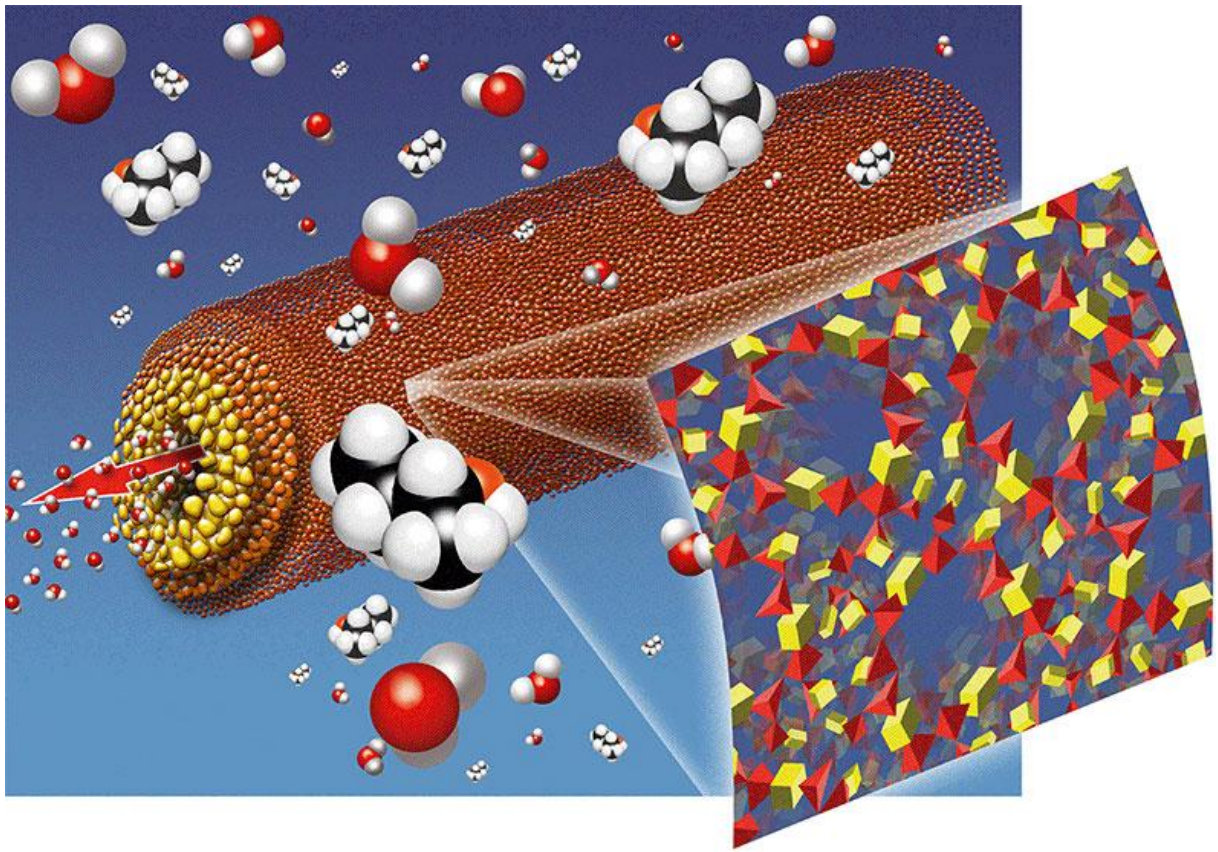
HybSi® Pervaporation Membranes

Stability(2)
Mechanical Properties



Dubois, *Adv. Mater.*, 2007, 19, 3989

Origins of increased stability



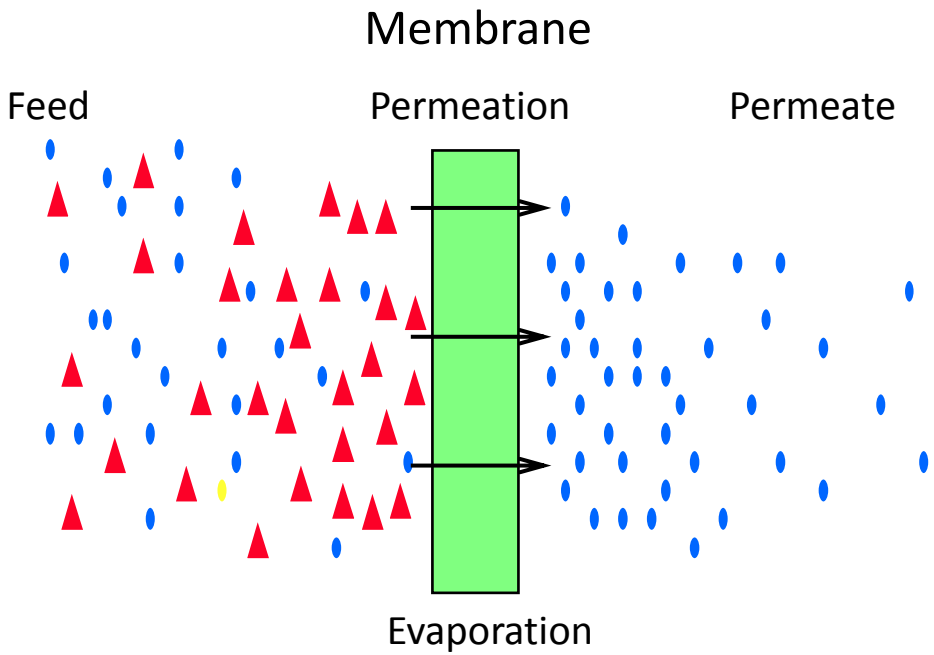
- More stable bonds
- Higher crack propagation energy
- Lower surface diffusion coefficient
- Lower solubility

Energy Efficiency:

Reduce energy consumption,
increase competitive power

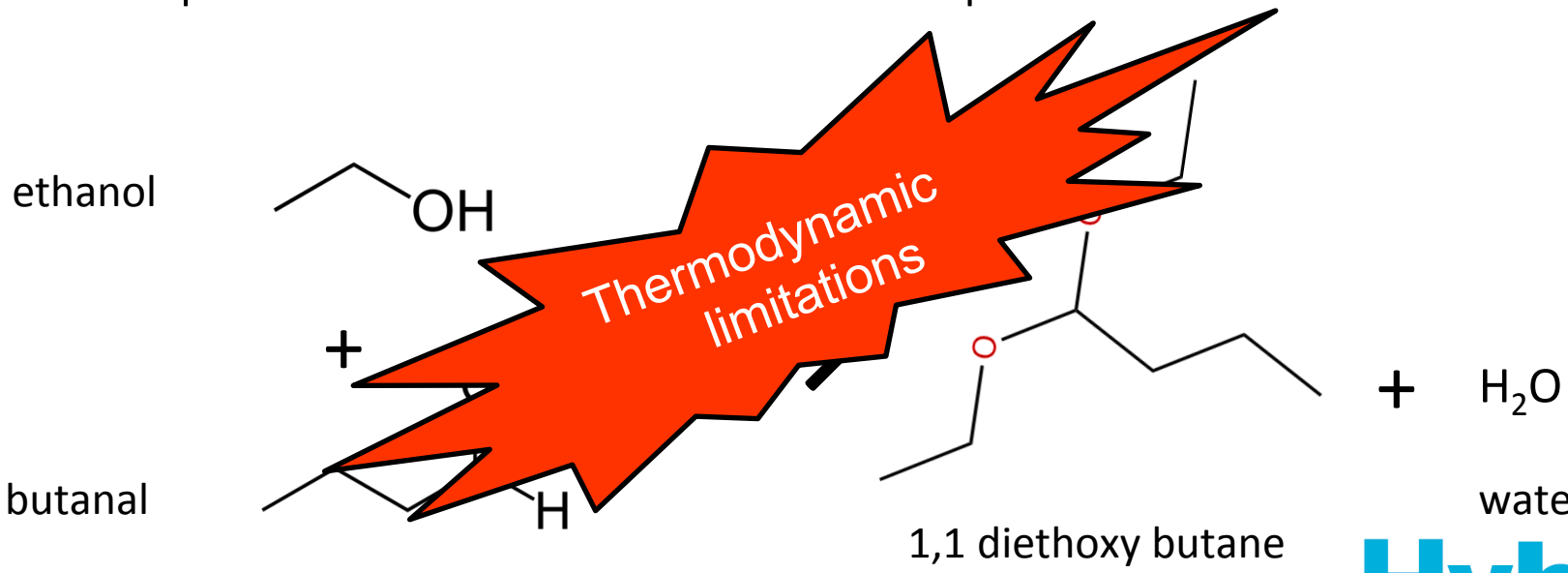
Pervaporation

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



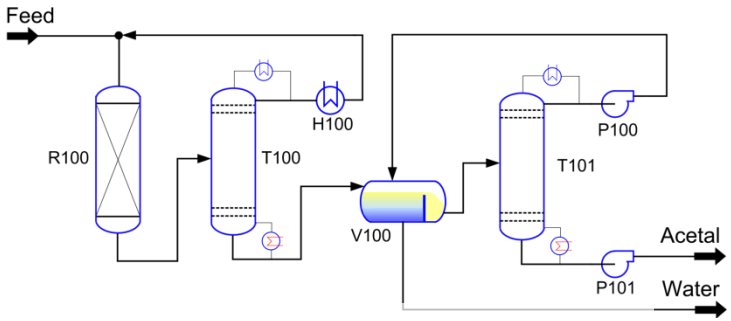
Acetal Production

- Bio-additive to diesel → Completely miscible
  Low NO_x, low particles
- Alcohol + aldehyde ↔ acetal + water
- Separation issues because of **FIVE** azeotropes



Agirre, *J. Chem. Technol. Biotechnol.*, 2012, 87, 943

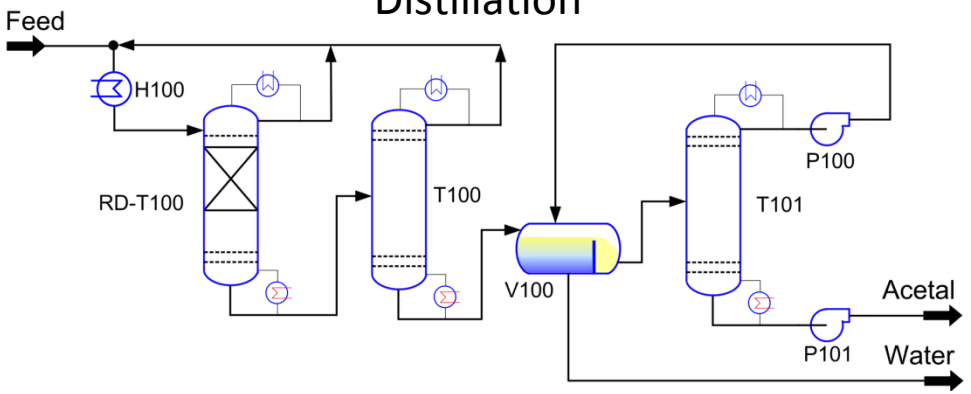
Options



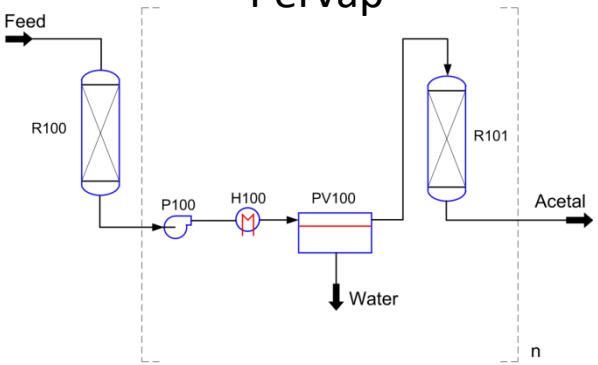
1. Base case

Reactor + Distillation

2. Reactive distillation + Distillation

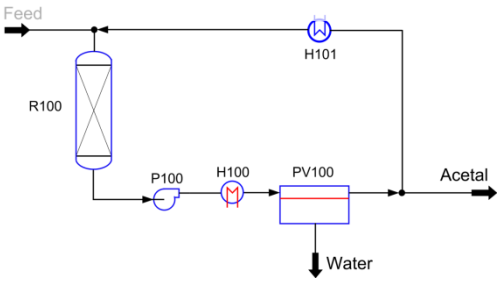


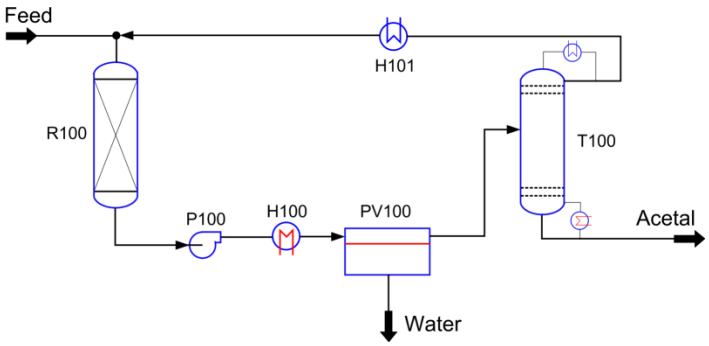
3. Repetitive Reactor + Pervap



4. Membrane Reactor

5. Reactor + Pervap + recycle

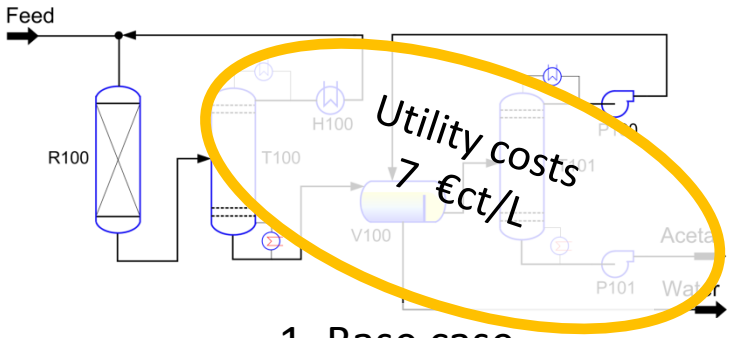




6. Reactor + Pervap + Distillation + recycle

Agirre, *J. Chem. Technol. Biotechnol.*, 2012, 87, 943

Options



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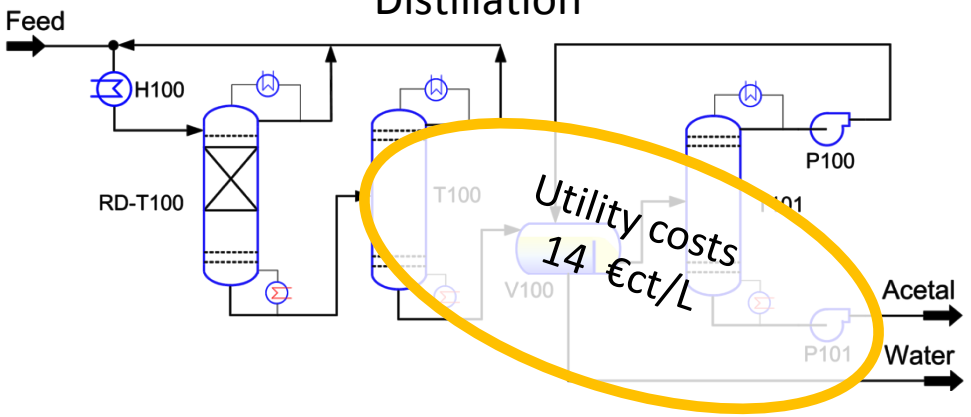
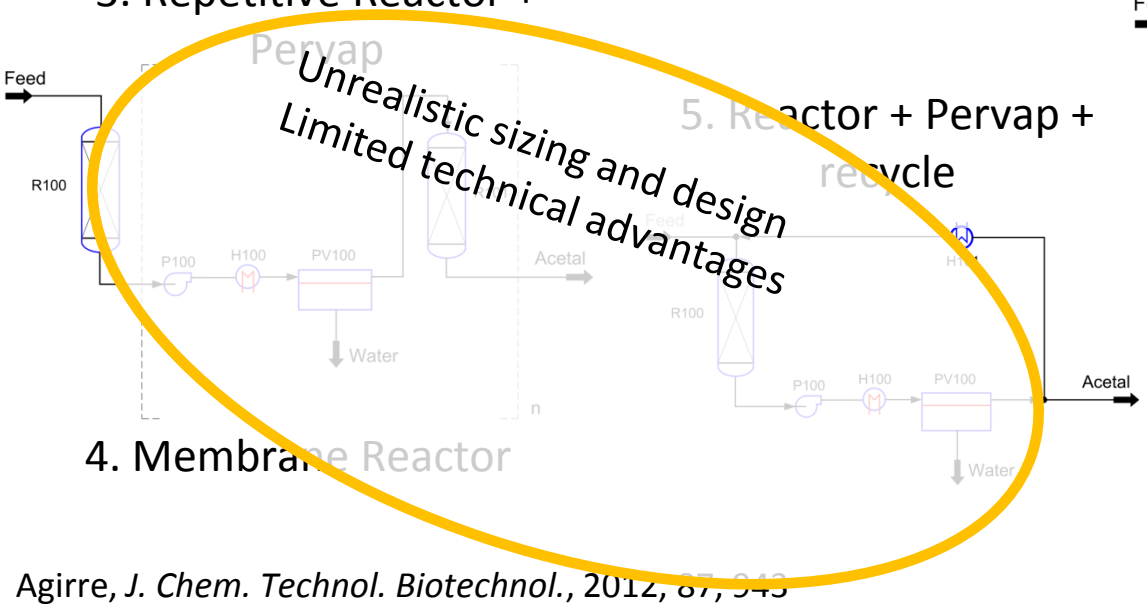
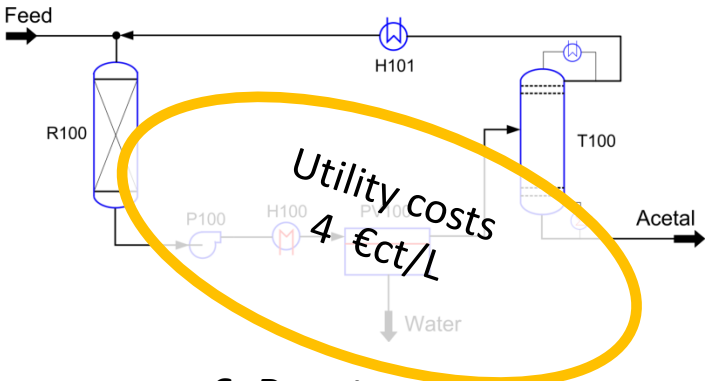


3. Repetitive Reactor + Pervap

4. Membrane Reactor



5. Reactor + Pervap + recycle



6. Reactor + Pervap + Distillation + recycle

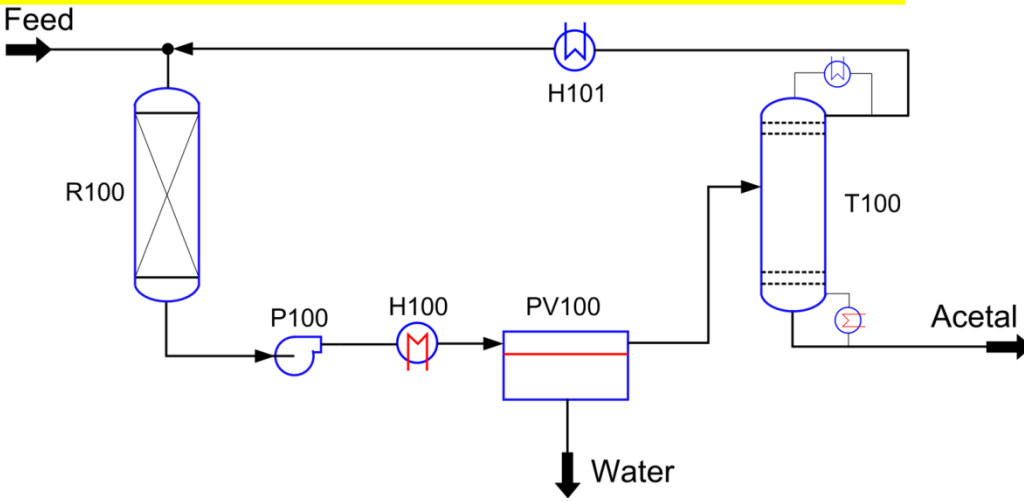
Agirre, *J. Chem. Technol. Biotechnol.*, 2012, 87, 943

HybSi® Pervaporation Membranes

Conclusion Acetal

- Most profitable case:

reactor →
membrane unit →
distillation →



- Avoid azeotropic distillation
- Small unit sizes, optimization for each step
- High conversion: only the reactants are recycled
- Low energy consumption

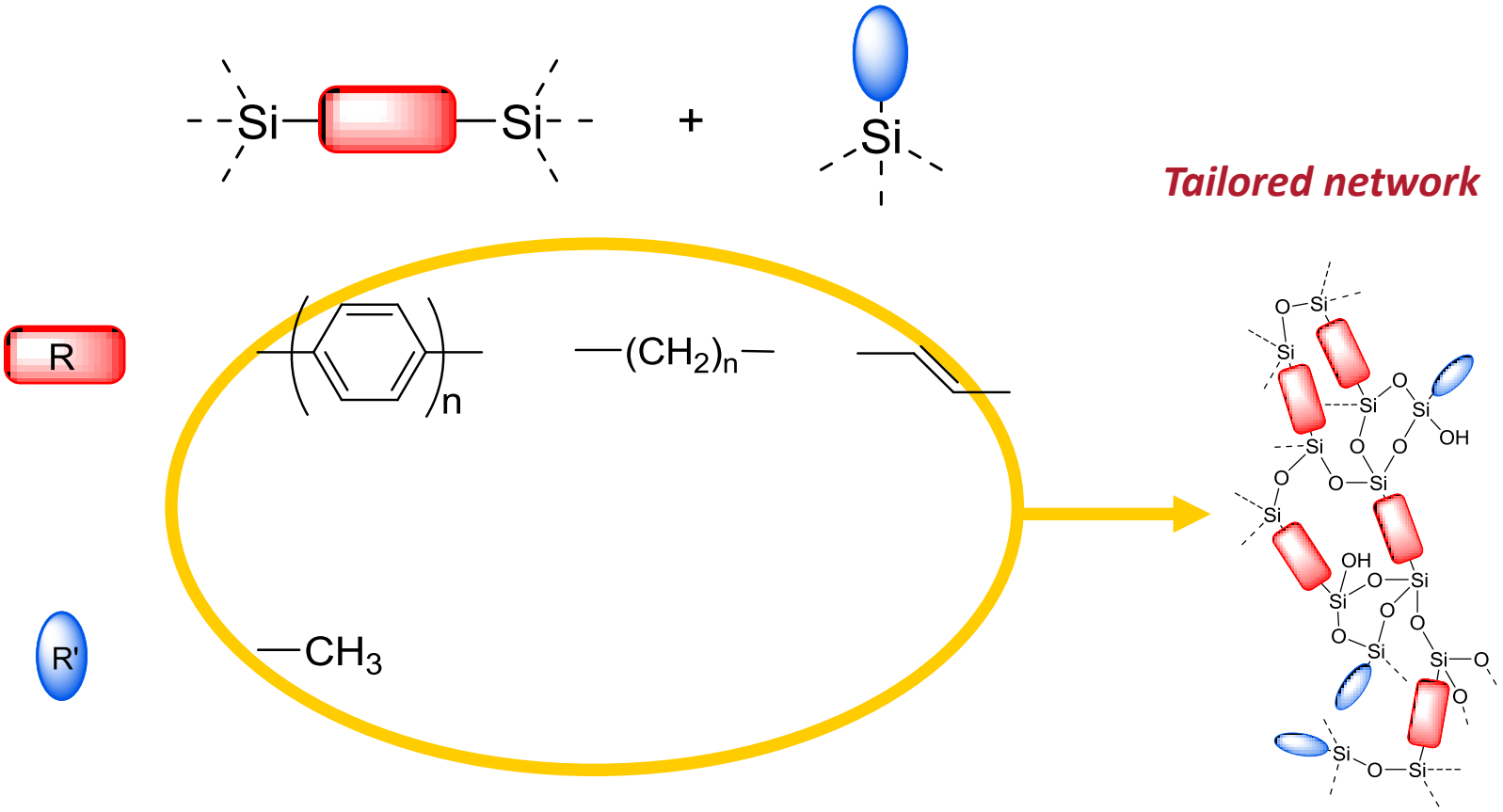
- High investment
- Costs of reactants is much higher than the production costs (~70€ct/L)

Agirre, *J. Chem. Technol. Biotechnol.*, 2012, 87, 943

HybSi® Pervaporation Membranes

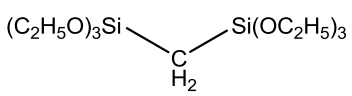
New directions and latest developments

Toolbox approach

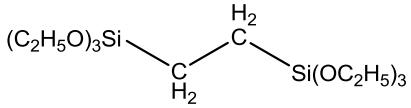


The influence of the bridges

M



E



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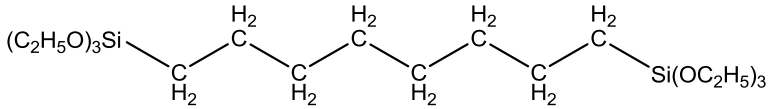

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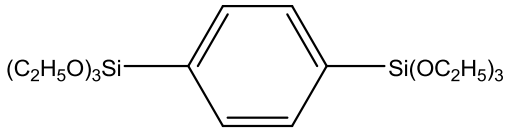
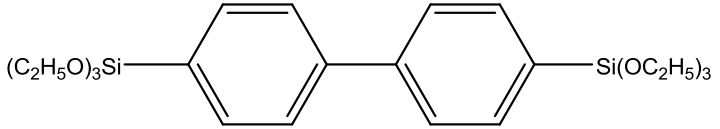
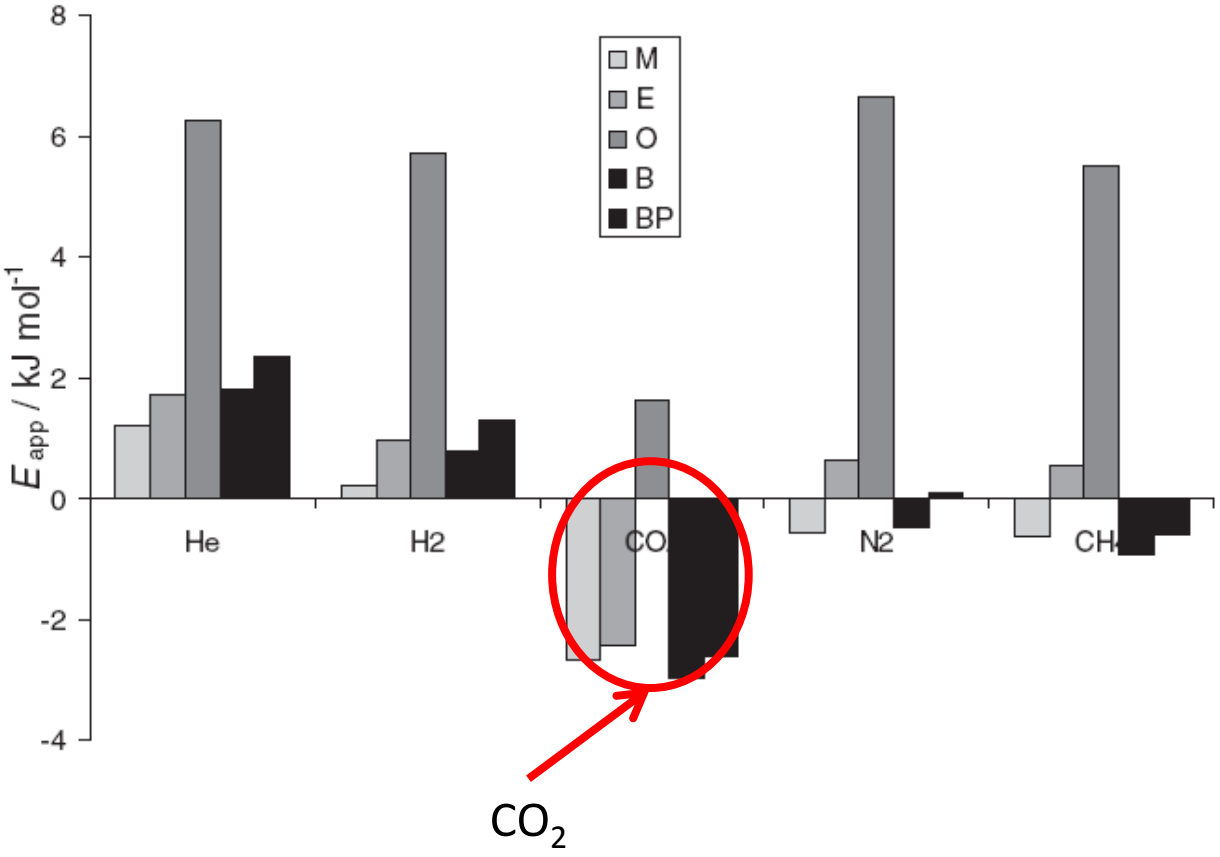


BP



Castricum, *Adv. Func Mater*, 2011, 21, 2319

The influence of the bridges

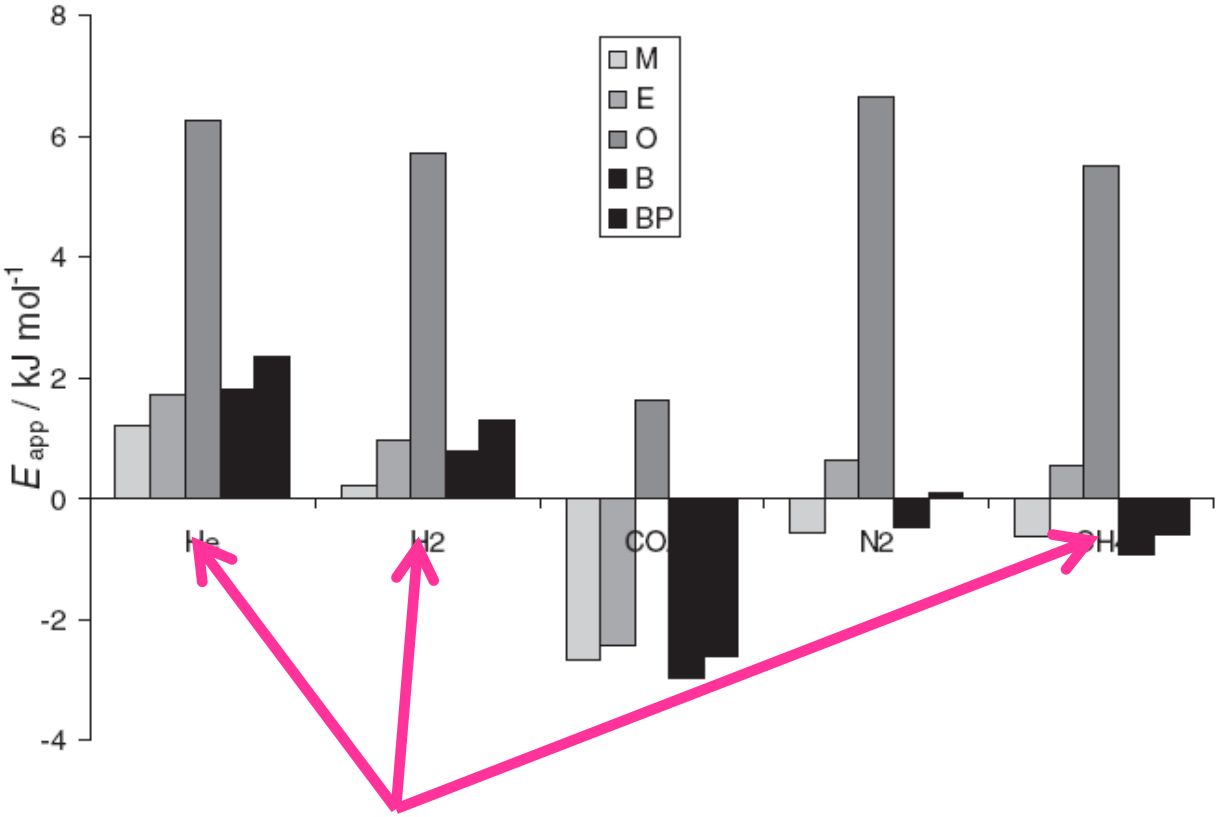


CO_2

Negative E_{app} strong interactions

Castricum, *Adv. Func Mater*, 2011, 21, 2319

The influence of the bridges

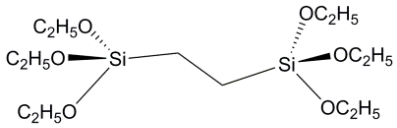


Octane bridge

High E_{app}, high chain mobility

Castricum, *Adv. Func Mater*, 2011, 21, 2319

Alkyl terminating groups



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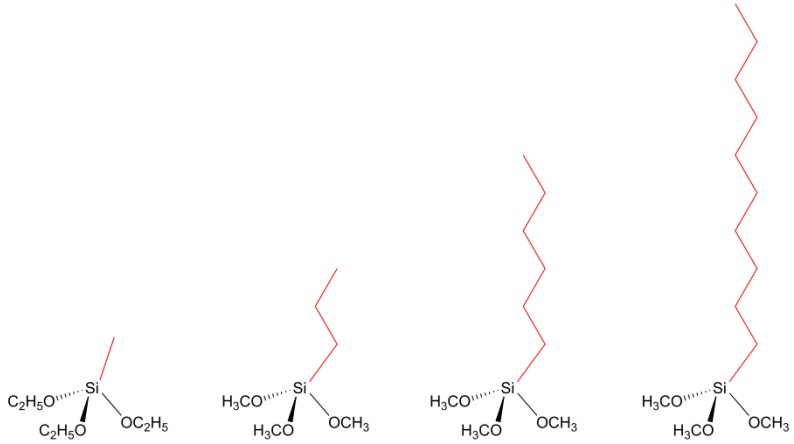

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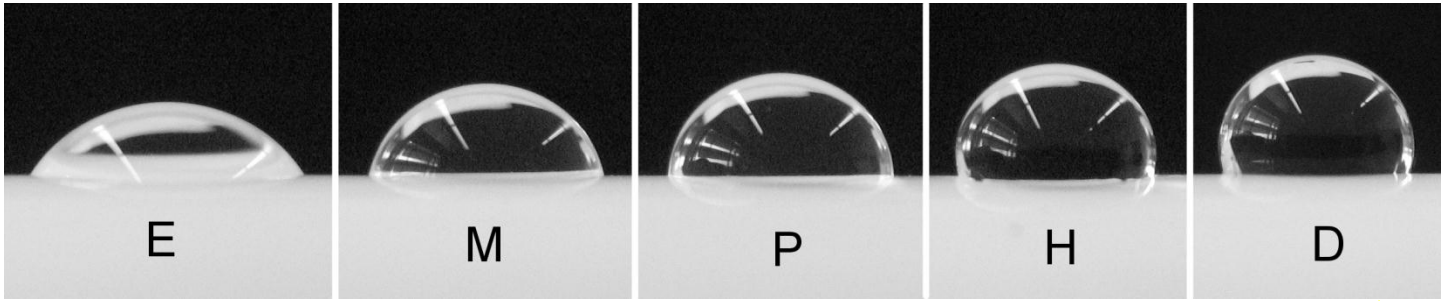
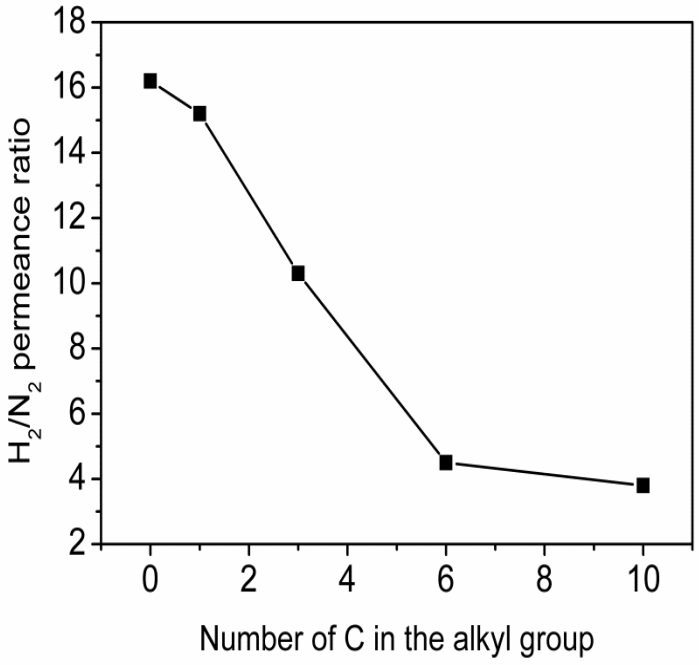


Increasing hydrophobicity

Gas permeance measurements

At 250 °C

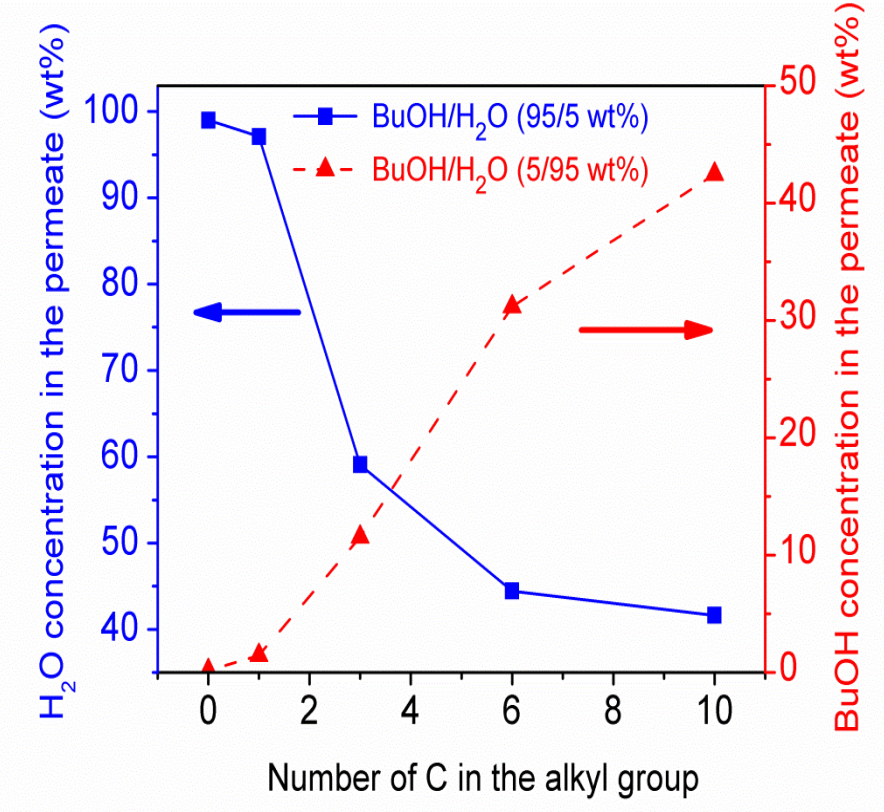


Decrease of the H_2/N_2 permeance ratio with increase of the length of the alkyl groups

Reduced molecular sieving properties

Paradis, *J. Membr. Sci*, 2012, accepted

Pervaporation measurements



Increase of the length of the alkyl group

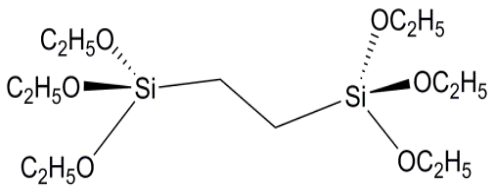
→ Lower water separation factor

→ Increased separation factor towards *n*-BuOH

Organophilic hybrid silica membrane with a separation based on affinity

Paradis, *J. Membr. Sci*, 2012, accepted

Amino terminating groups



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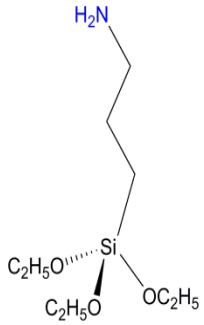
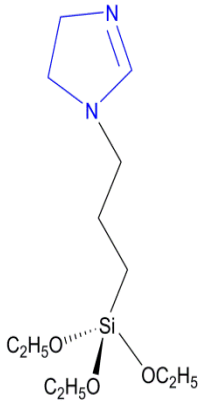
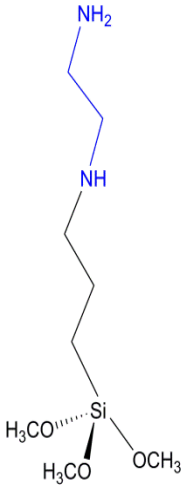
Hydrophilic amino-groups



PA



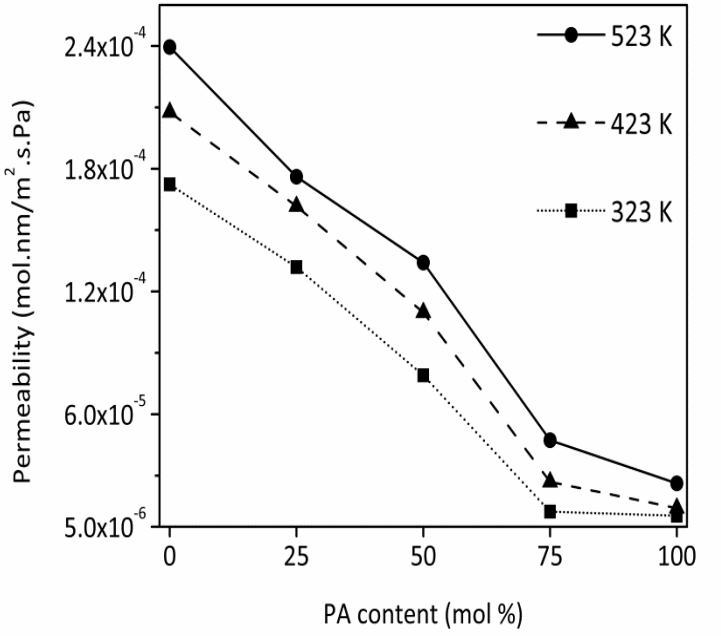
IM

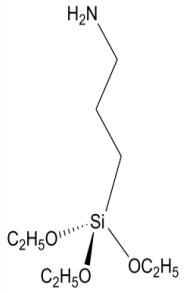


LDA

Paradis, *J. Mater. Chem.*, 2012, 22, 7258

H_2 permeabilities





PA

Decreasing permeabilities with increase of PA concentration

Pervaporation properties largely unchanged

Experimental indication of presence of water in the porous structure

"Super" hydrophilic functionalized hybrid silica membranes !

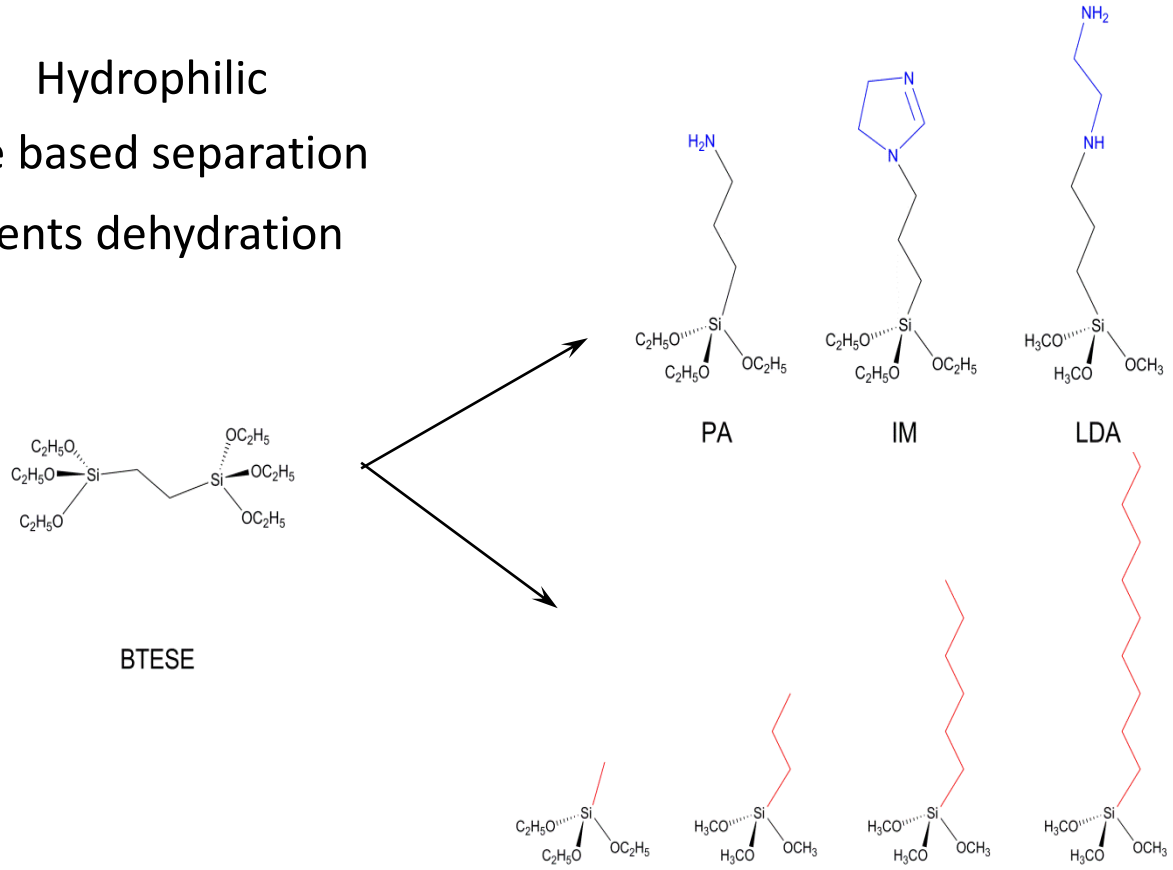
Paradis, *J. Mater. Chem.*, 2012, 22, 7258

Terminating groups

Hydrophilic

Size based separation

Solvents dehydration



"Super" hydrophilic

Affinity based separation

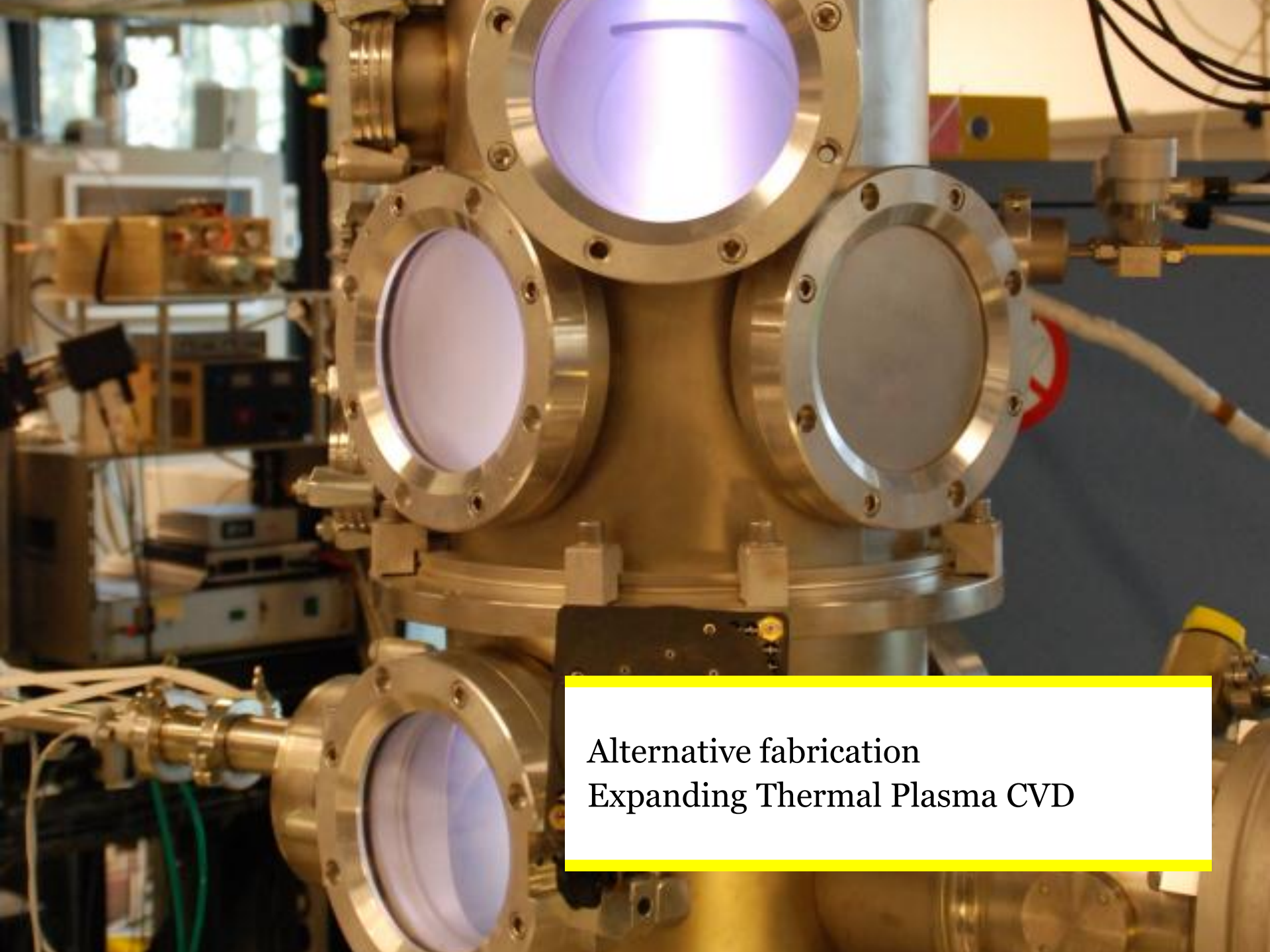
Solvents dehydration

Hydrophobic/organophilic

Affinity based separation

Solvents enrichment

Paradis, *Novel Concepts for Microporous Hybrid Silica membrane,* Ph.D,. Thesis, 2012



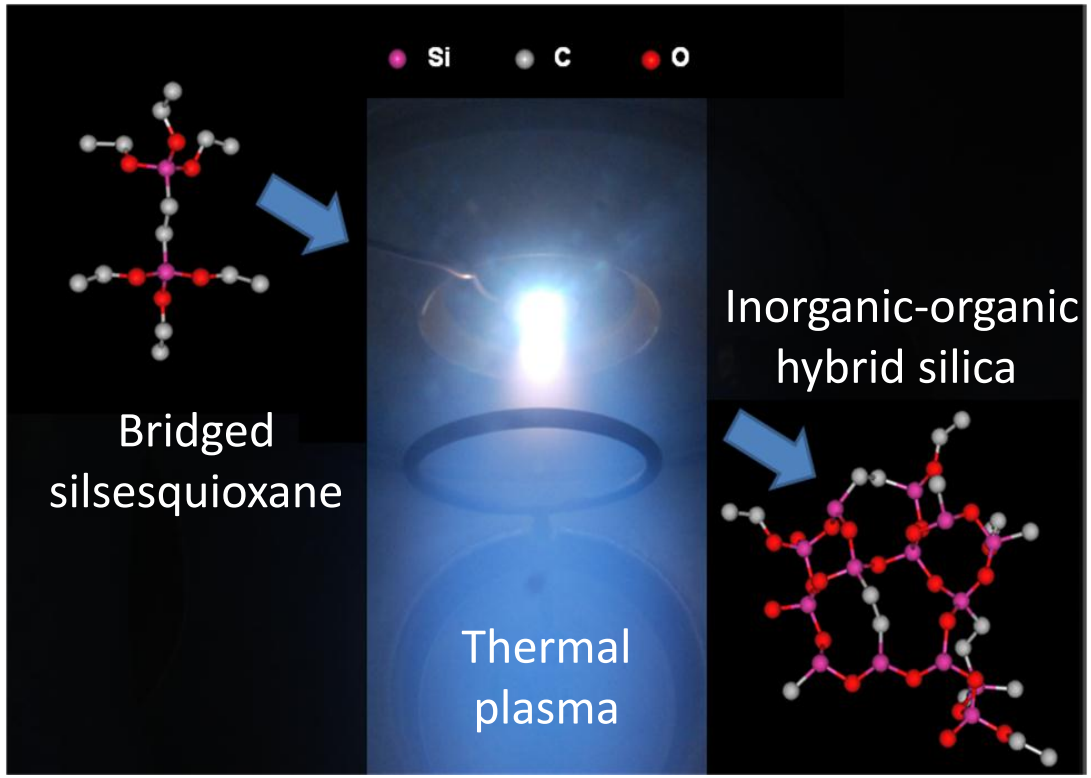
Alternative fabrication
Expanding Thermal Plasma CVD

Solvent Resistant Nanofiltration

- Market dominated by polymers
- Limitations due to swelling
- Low temperature applications allow for non-swelling, non-selective polymer supports
- Sol-gel technology less suitable because of high curing temperature

Expanded Thermal Plasma

- Mild conditions that can be tailored
- Scalable technology (role-to-role)
- One step process



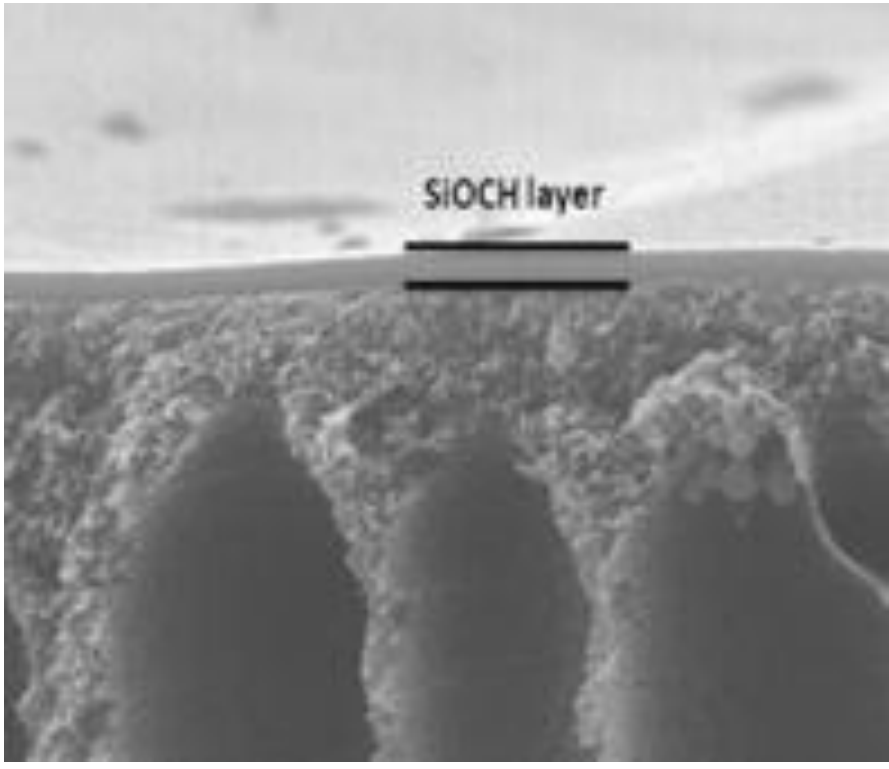
Ngamou, in preparation

First results

- Proof of concept:
  membrane performance of polymer supported hybrid silica

  equals that of

  ceramic supported hybrid silica



(Pervaporation at 95 C BuOH/H_2O)

Ngamou, in preparation

Moving into the market

Scope HybSi® directions

- Existing & proven concept
  - Licenses to manufacturers
  - Formation of value chains with end users, OEM, & licensees
  - Technology transfer

- Facilitated by application driven research
  - System approach
  - Process design
  - Prediction tools Aspen+
  - Creating references
  - Industrial tests
  - Detailing application window
  - Anti-fouling strategies and CIP's

PERVATECH
selective ceramic membranes
process design

CTI

HybSi®
Pervaporation Membranes

The launching client

- Who will be brave enough?

© Auke van der Weide

HybSi® Pervaporation Membranes

Acknowledgements

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  - AgentschapNL
  - ISPT

- Knowledge network
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  - Amsterdam
  - Bilbao
  - Eindhoven
  - Twente

- The ECN Membrane team!

Public available information

- Website: www.HybSi.com
- Follow us on Twitter: @HybSi_membranes
- Sign up: HybSi news letter

- Scientific Papers
  - *J. Mater. Chem.*, **2012**, 22, 7258
  - *J Chem Technol Biotechnol.*, **2012**, 87, 943
  - *AIChE J.* **2012.**, 58, 1862
  - *J. Mem. Sci.*, **2011**, 380, 124-31
  - *Advan. Func. Mater.*, **2011**, 21, 2319
  - *J .Mem. Sci.*, **2011**, 371, 179
  - *J. Sol-Gel Sci Techn.*, **2011**, 57, 245-52
  - *ChemSusChem.*, **2009**, 2, 158-60
  - *J. Mem. Sci.*, **2008**, 319, 126-32
  - *J. Sol-Gel Sci Techn.*, **2008**, 48, 203-11
  - *J. Mater. Chem.*, **2008**, 18, 2150
  - *Chem. Commun.*, **2008**, 1103

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HybSi® Pervaporation Membranes