Organic-inorganic hybrid microporous membranes (HybSi®) for pervaporation applications

J.F. Vente

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ECN-M--09-065 May 2009

ECN

Energy research Centre of the Netherlands

Organic-Inorganic Hybrid Microporous Membranes (HybSi®) for Pervaporation Applications

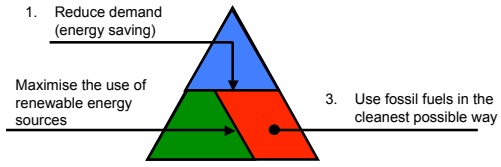
Jaap Vente

ECN's location

ECN's main features

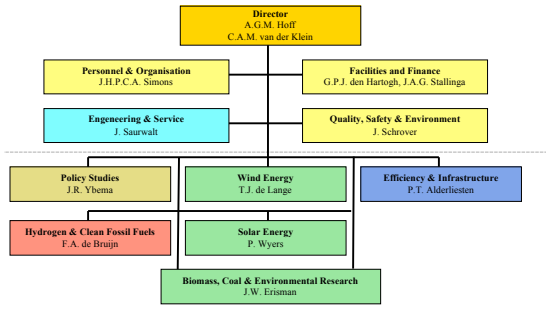
- ECN develops high-level knowledge and technology for a sustainable energy management and transfers it to the market.
- Annual turnover of 70 million euro
- Approx. 5-10 international patents granted each year
- Approx. 600 reports and publications each year
- (Inter)national co-operation with companies, universities and research institutes

Trias Energetica

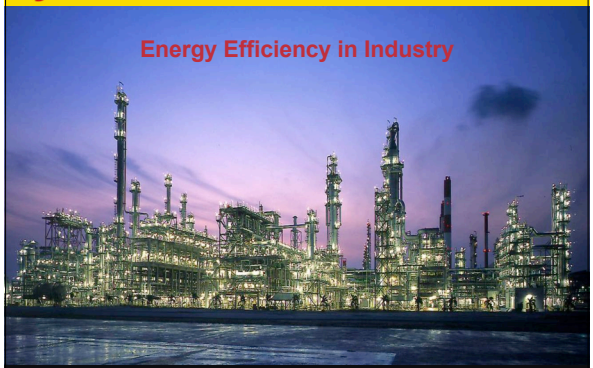


Energy demand

ECN's Structure



Energy Efficiency in Industry



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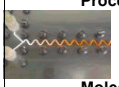
Energy Efficiency in Industry

Industrial Heat Management
(10 fte)

Upgrading industrial waste heat
Thermo-acoustic heat pump
Chemical heat pump

Process Intensification
(7 fte)



Combined unit operations
Structured Membrane reactors
advanced distillation

Molecular Separation Technology
(13 fte)

Molecular separations
Materials, processes
Systems development

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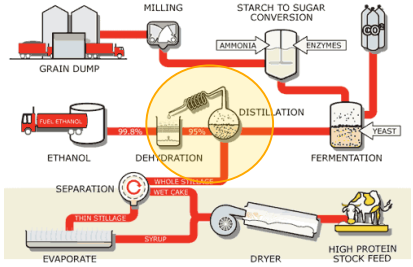
Bio-ethanol



Source: www.miningnews.net

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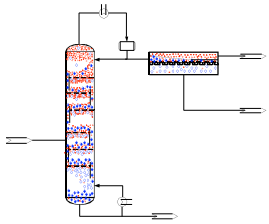
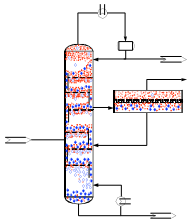
Distillation – Membrane Integration



Azeotrope separation,



Debottlenecking, including recycle stream

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Pervaporation membranes

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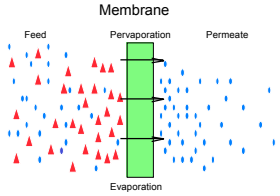
What is pervaporation

Pervaporation is a membrane based separation technique
= permeation + evaporation
= selective evaporation of liquids via a membrane
= much more energy efficient than distillation

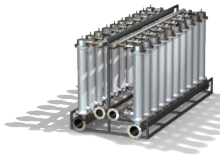


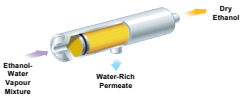
External Developments

- Sulzer:
  PVA based membranes
  - Market leader
  - Well established
- Vaperma:
  Polyimide bases
  - Recently started
  - Large demonstrations
- Mitsui, Mitsubishi, Inocermic, Hyflux, Hitachi
  Zeolite A
  - Various stages of commercialisation
  - Most widely used inorganic PV membrane

Siftek™ Membrane by Vaperma

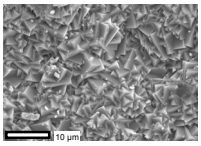
- Hydrophilic polyimide hollow fiber concept
- Vapour permeation from the bore side
- 100m² membrane area per module





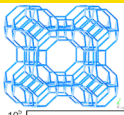
Source vaperma

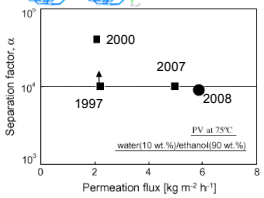
Zeolite A membrane



Top view

Tubular form





Pervaporation 75ºC

Source MITSUBISHI CHEMICAL

Applications

Main benefits expected:

- Azeotrope separations
  - (bio)-ethanol / water
  - acetonitrile / water
  - toluene / methanol
- Difficult distillations / close boilers
  - Acetic acid / water
  - Acetone / water
- Various recycle streams
  - NMP / water
  - DMF / water
- End of pipe (by)-product upgrading

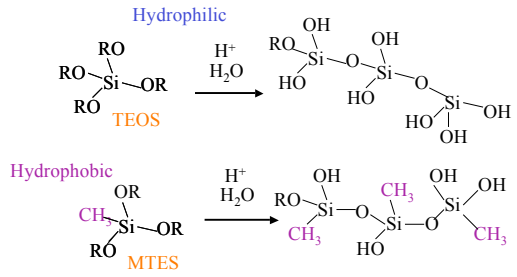
Present challenges

- Higher application temperatures
- Higher acid resistance
- Higher stability in aggressive solvents
- Resistance against contact with liquids (i.e. pervaporation vs vapour permeation)
- Larger application window w.r.t. water content
- Effective methanol removal

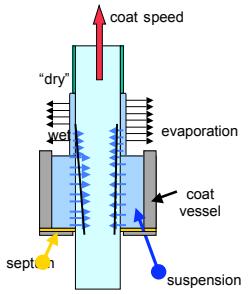
Amorphous inorganic microporous networks

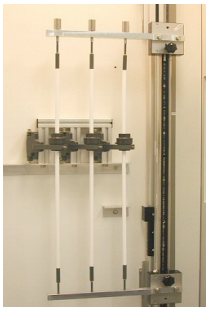
- SiO_2
- Methylated SiO_2
- Ti/ZrO_2
- HybSi®: SiO_2 with organic bridges

Preparation: Sol Gel



Membrane fabrication





Large scale production


Coat robot


Drying Carousel

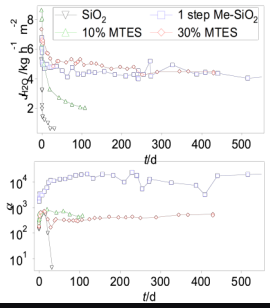

Welding robot


Module


Furnace

Sulzer Chemtech

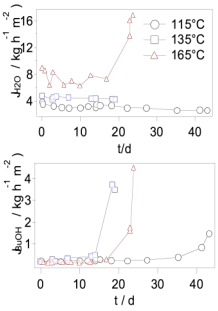
SiO_2 – Me-SiO_2 pervaporation results (95ºC)



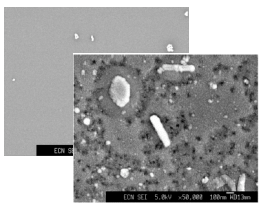
- 5 wt.% H_2O in BuOH, 10 mbar
- Addition of MTES gives better performance with time
- Constant performance possible for over 18 months!

Chem.Comm.2004, 834-835

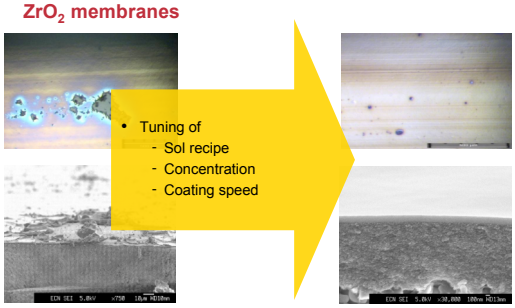
Me-SiO_2 pervaporation up to 165ºC



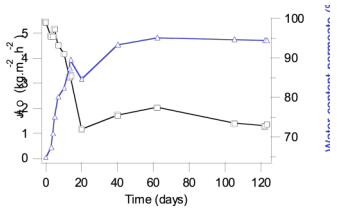
2.5 wt.% H_2O in BuOH, 10 mbar
Failure within weeks
No clear relation with temperature



ZrO_2 membranes



Pervaporation performance ZrO_2

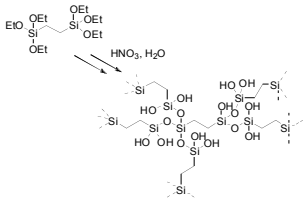


- 95°C, n-butanol/H_2O (95/5%)
- Flux decline, but stable after 20 days
- Operating for at least 120 days

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

HybSi® membranes from bridged precursors

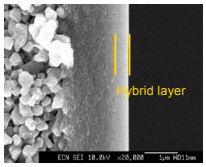
Strategy: replace Si—O—Si bonds by Si—C—C—Si bonds



Collaboration with Universities of Twente and Amsterdam (Ashima Sah, Andre ten Elshof, Hessel Castricum, Marjo Mittelmeijer), started in 2003

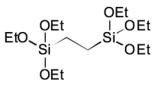
Precursor selection for improved performance

Precursors:
Recipe 1: BTESE + MTES
Recipe 2: BTESE
Recipe 3: BTESM

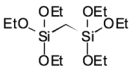


MTES

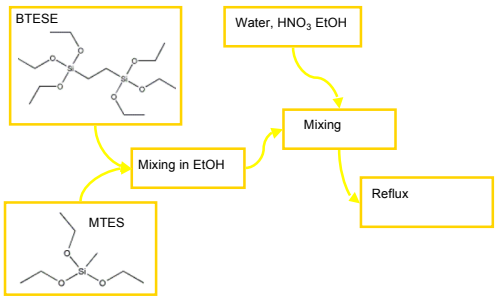
BTESE



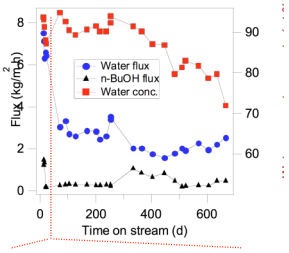
BTESM



Sol-Gel procedure HybSi®



Performance HybSi® membranes, 150°C



Life time state of the art methylated silica

Feed = 5 wt.% water in *n*-BuOH

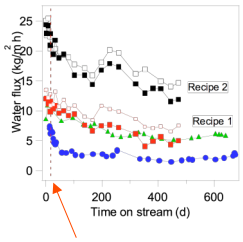
First membrane made
Recipe 1

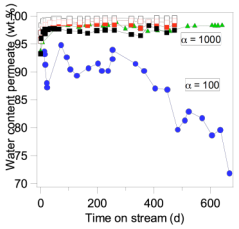
Life time >650 days

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

Performance HybSi® membranes, 150°C

Feed: 5 wt.% water in *n*-BuOH





Life time state-of-the-art Me-SiO_2

J. Membr. Sci., **324**, 111-118 2008

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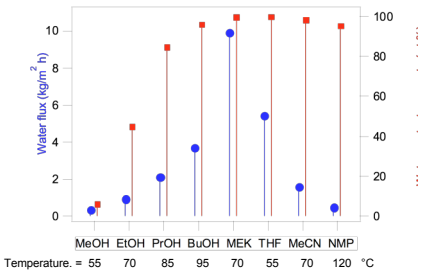
Application testing

Feed = 5 wt.% water in solvent; Recipe 1



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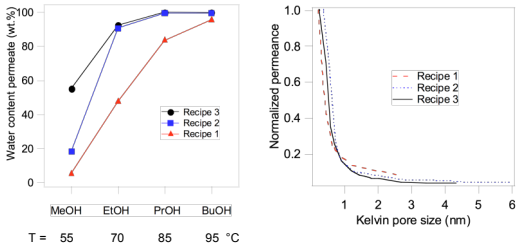
Application testing - alcohols

Feed = 5 wt.% water in alcohol



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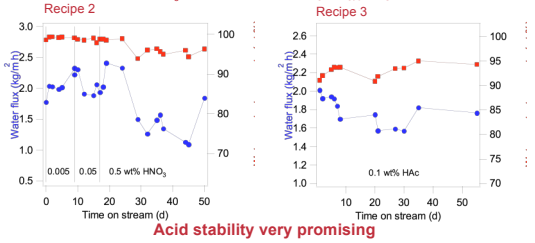
Acid stability

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

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

ChemSusChem., **2**, 2, Feb 2009

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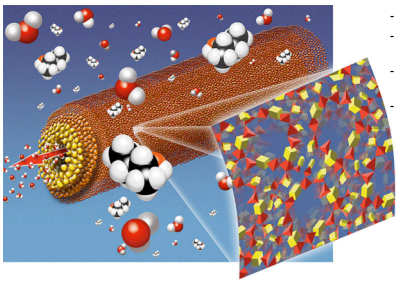
Origins of stability of hybrid silica



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

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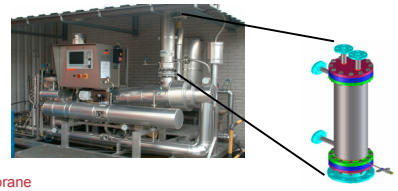
Next steps

- FOCUS: IMPLEMENTATION
  VIA PILOT DEMONSTRATION



- State of the art membrane
  - Further determine application window pH, H_2O content, solvents
  - Create consortium for commercialization.
  - Definition launching application(s).

***Chem. Commun.*, 2008, 1103**
***J. Sol-Gel Sci Techn*, 2008, 48, 203-11**
***ChemSusChem.* 2009, 2, *pp.*.**
***J. Mater. Chem.*, 2008, 18, 2150**
***J. Mem. Sci.*, 2008, 319, 126-32**

Patent: WO2007081212

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