



Energy research Centre of the Netherlands

# **The HybSi® membrane: from research to industrial demonstration**

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# The HybSi<sup>®</sup> membrane: from research to industrial demonstration

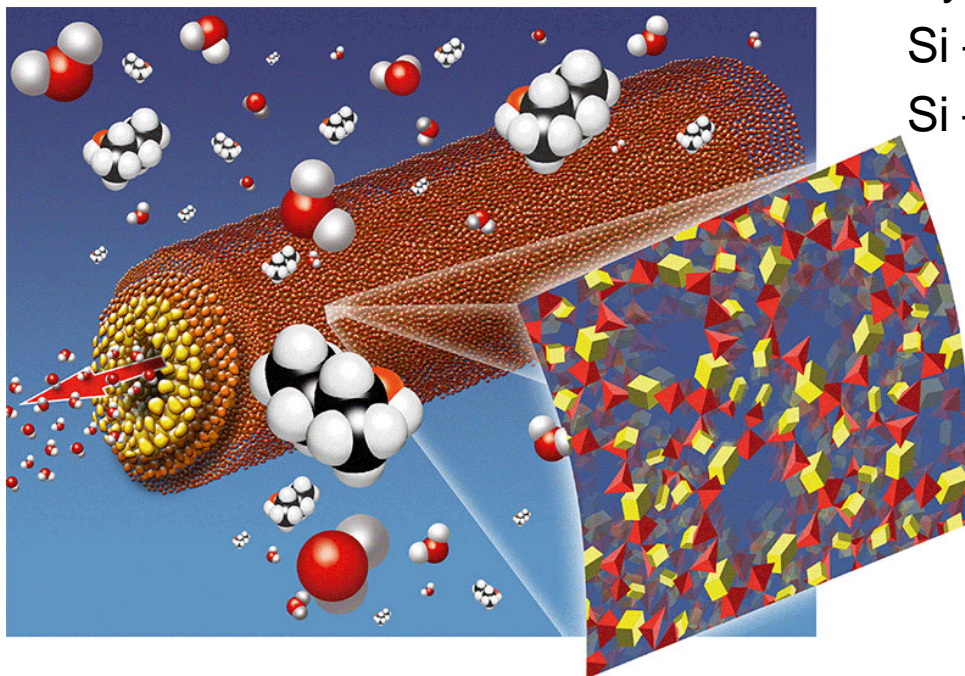
Jaap Vente



## HybSi<sup>®</sup> Characteristics

Pervaporation membrane with unrivalled stability:

- Higher temperatures
- Acid conditions
- Aggressive solvents



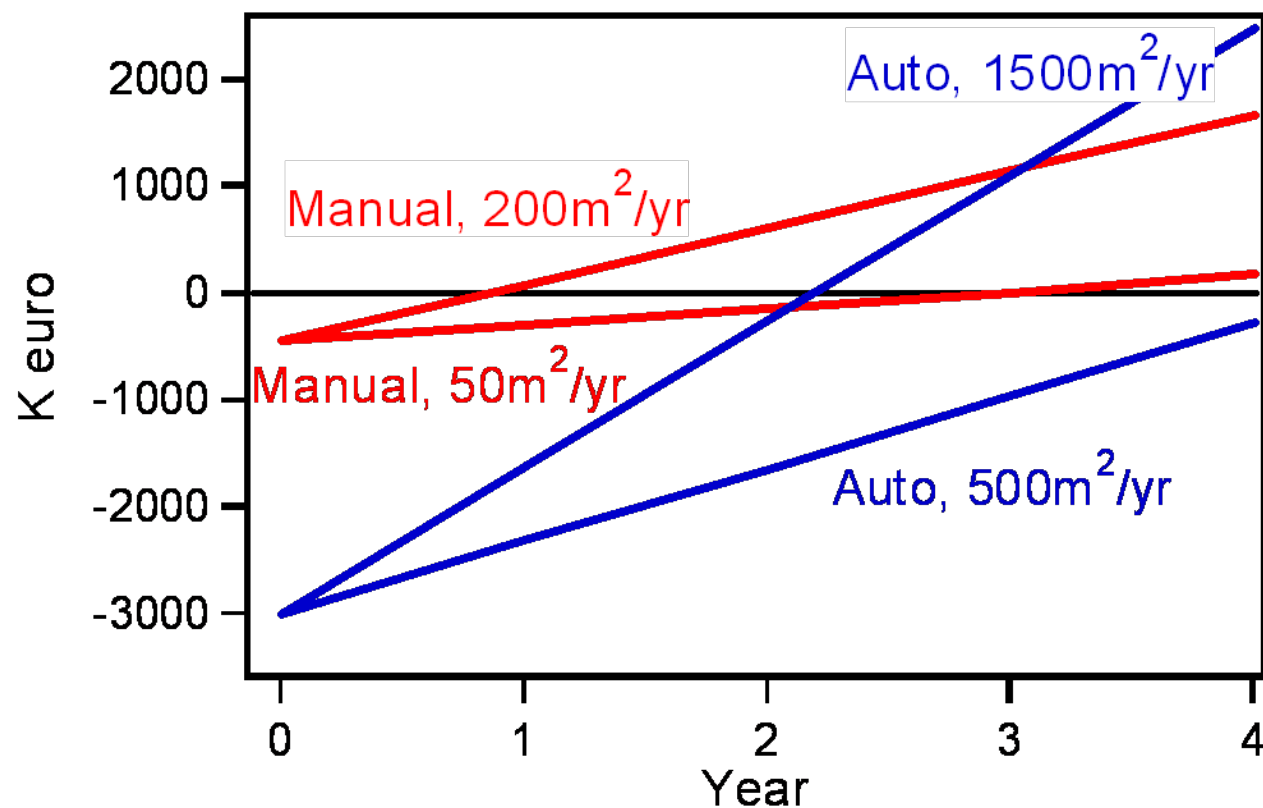
Hybrid material with:

Si – O – Si

Si – CH<sub>2</sub> – CH<sub>2</sub> – Si bonds



## Value for the manufacturer



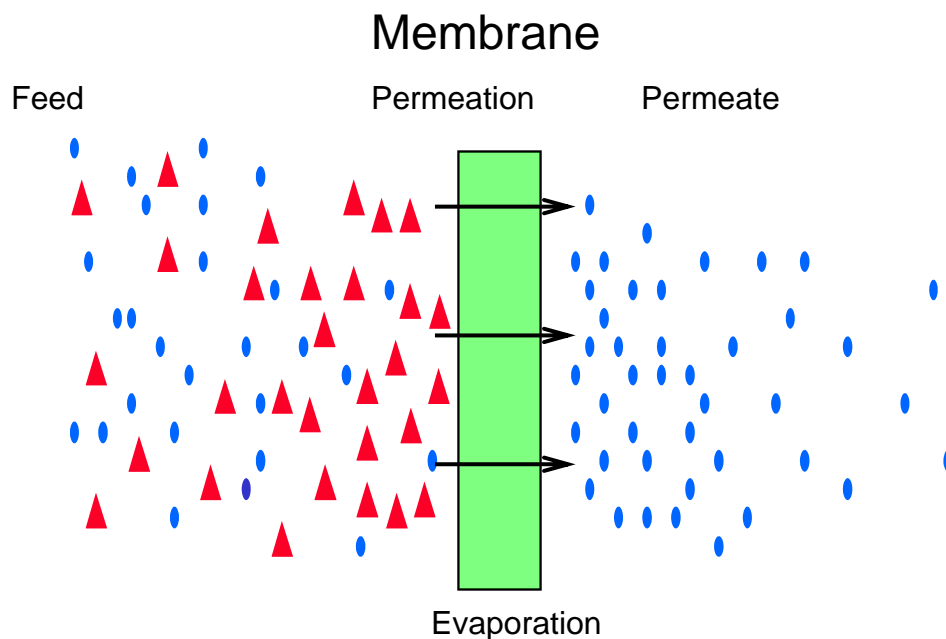
Market size: 5,000 – 20,000 m<sup>2</sup>/yr; 12,000 – 500,000 tubes / yr

## Value for the end-user

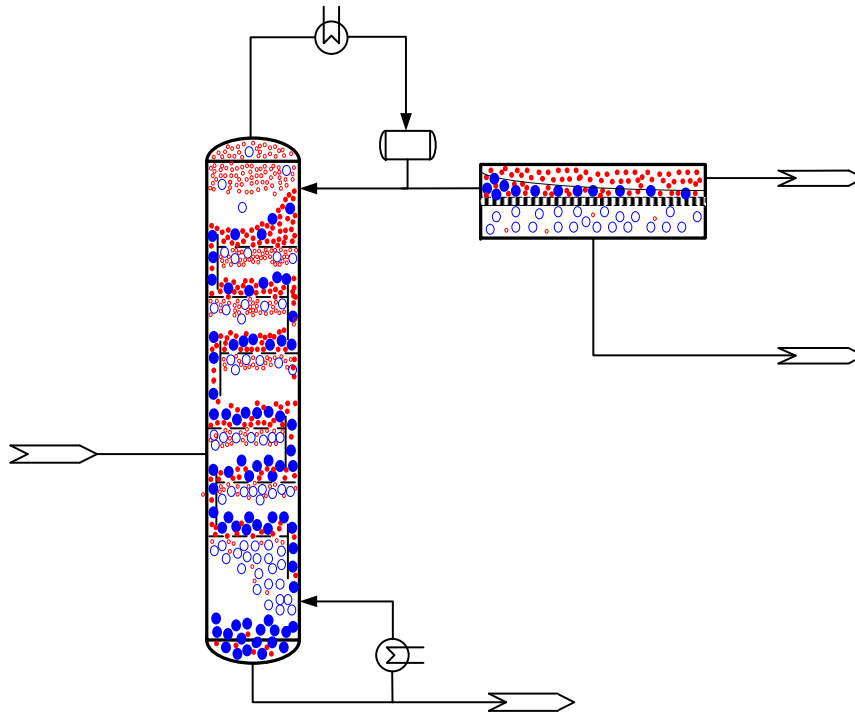
Application	Conventional process	Energy savings	Costs savings	Pay back period
Bio-ethanol	Distillation + mol sieve	30%	20% (2-3 €/ct/l lower EtOH production cost)	3 years
Acetone	Distillation	40%	25%	2 years
Esterification reactions	Distillation (batch process)	50%	30%	± 1 year
Methanol from toluene	Extraction + distillation	50%	30%	± 1 year

## Pervaporation

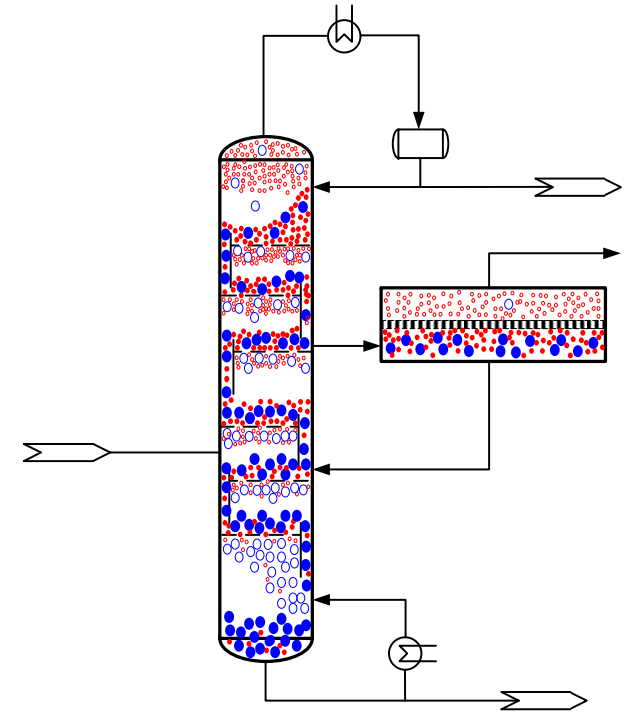
- Selective evaporation via a membrane
- Much higher energy efficiency than distillation



## Prime applications



Separation of azeotropes



Capacity increase through debottlenecking



## The opposition

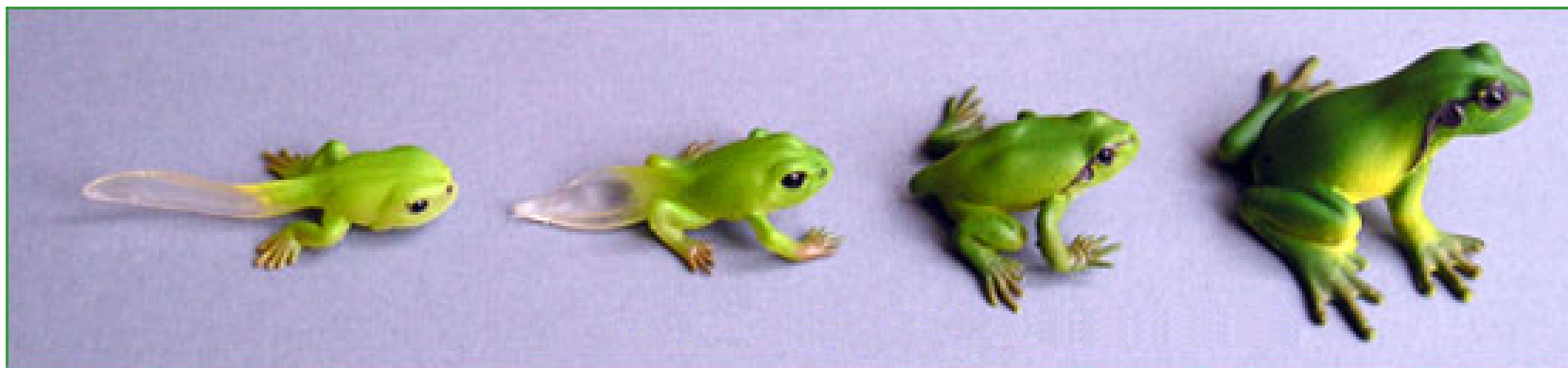
Commercially available pervaporation membranes

- Polymers
  - PVA (Sulzer Chemtech)
  - Polyimide (Vaperma)
- Ceramics
  - Zeolite A (Mitsui, Mitsubishi, Inocermic, Zeolite Solutions)
  - SiO<sub>2</sub> (Pervatech)

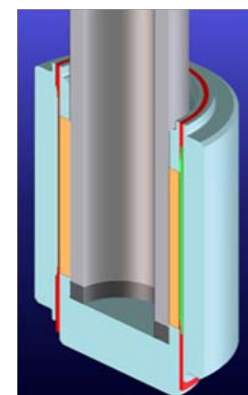
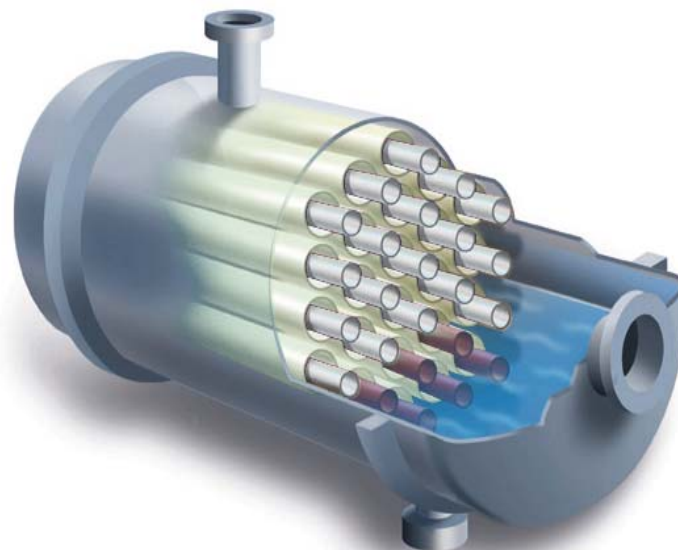
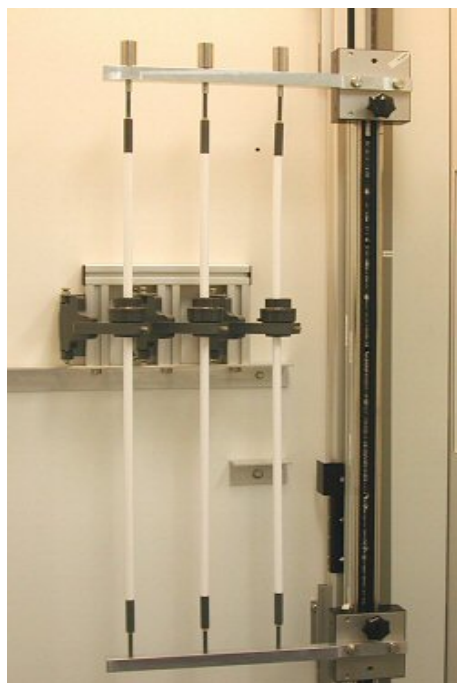
## Towards a generally accepted technology

- 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

## From infancy to maturity



## Where did we start? Status 2003



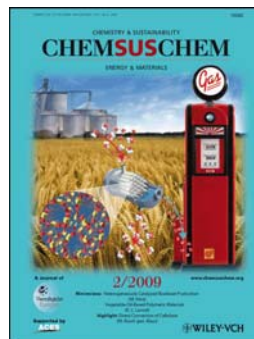
# Looking back

*Ideation*

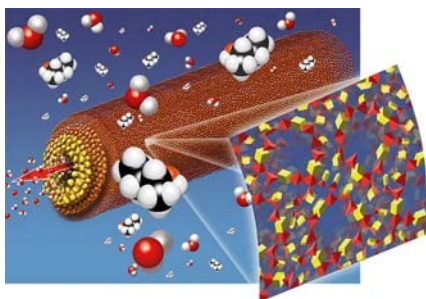


*First attempts  
(UT)*

*First publication:  
“hot article”*



*First membrane tubes + testing  
(UT & ECN)*



*HybSi day  
HybSi “the movie”*



*Patent 1 filed*

*Patent 2 filed*

*Patent 3 filed*

2003

2005

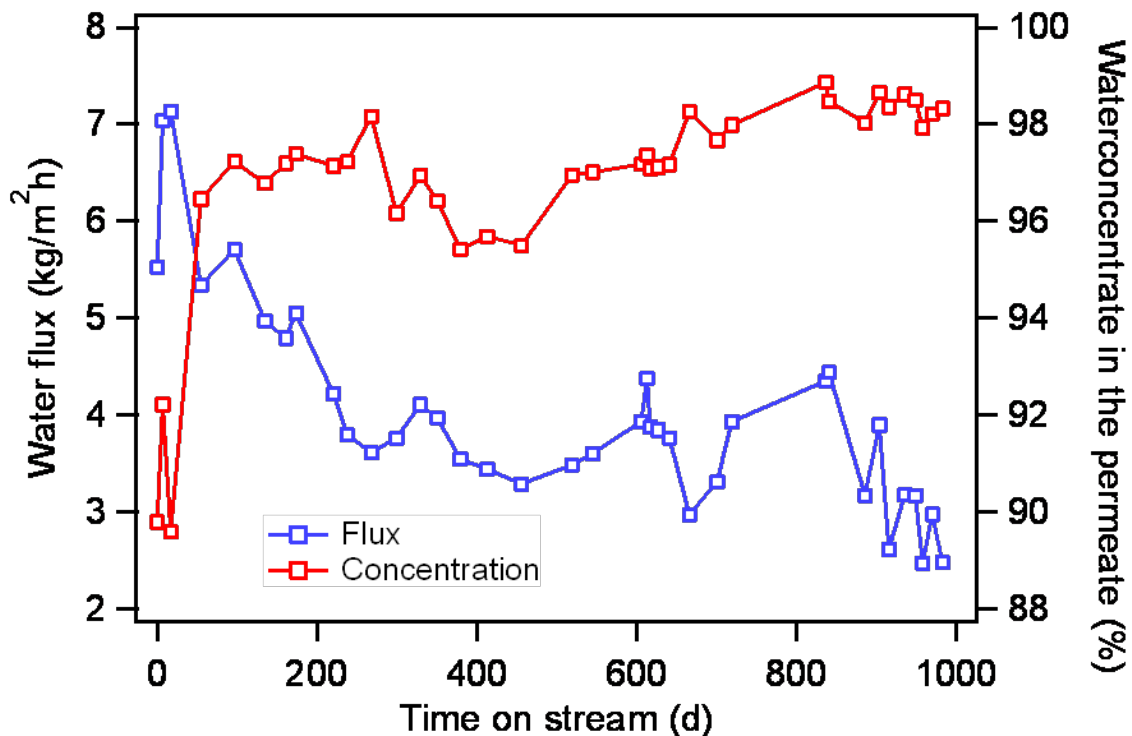
2007

2009

2011

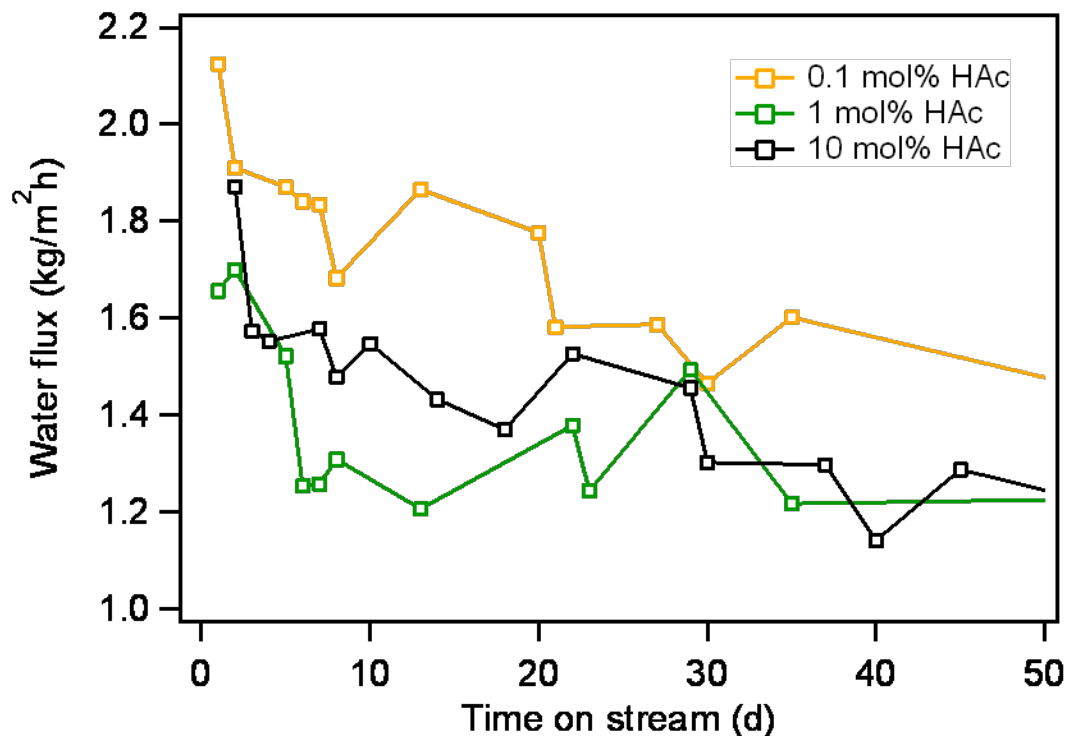
## Long term performance

- 150°C
- 3% H<sub>2</sub>O in BuOH
- Measurement stopped after 1000 days



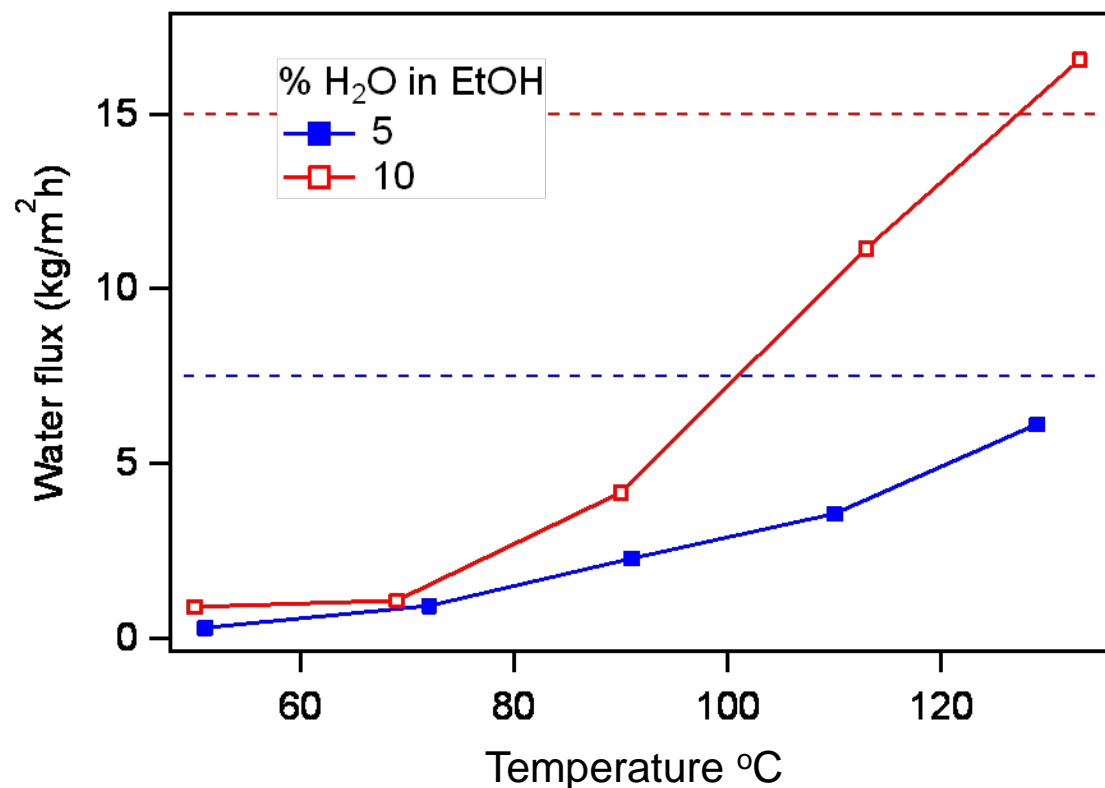
## Acid resistance (HAc in EtOH)

- Various levels of HAc in EtOH
- 70°C
- 5% H<sub>2</sub>O in EtOH



## High temperature performance

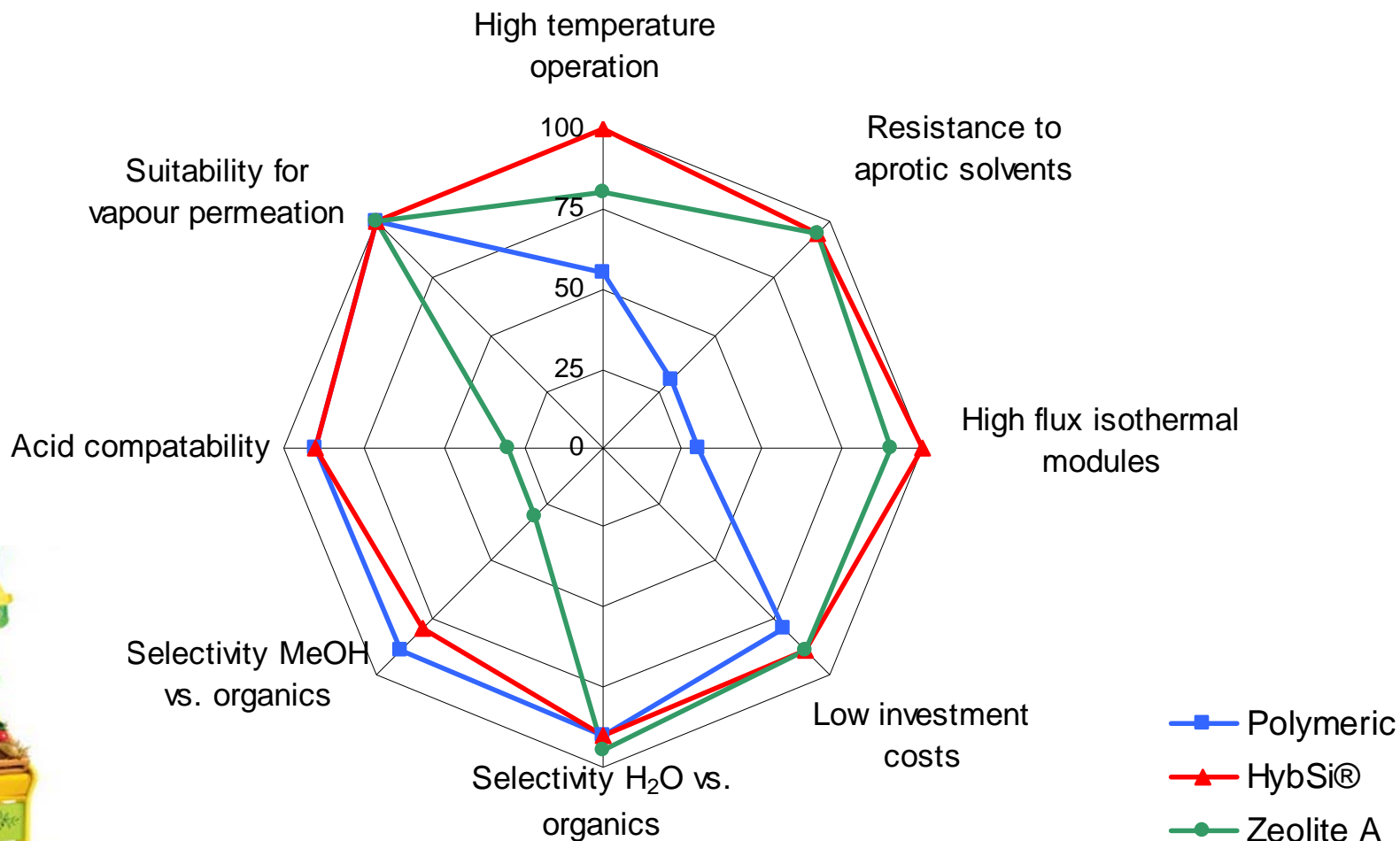
- Ethanol dehydration
- 5 or 10% H<sub>2</sub>O in Ethanol



## HybSi<sup>®</sup> advantages over commercial products

- Higher application temperatures
  - 190°C
- Higher resistance against acids and alkalines
  - $\sim 2 < \text{pH} < \sim 8$
- 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

# HybSi® advantages over commercial products



## Implementation trajectory

- Formation of value chain
  - end-user
  - system builder
  - membrane manufacture
  - Knowledge provider
- Three letter of interest system builders:  
interest ranges from 300 m<sup>2</sup>/yr to several 1000m<sup>2</sup>/yr
- Running actions for external parties:
  - Delivery of lab modules
  - In house application tests
  - On site pilot testing



## Industrial pilot test

- Consortium:
  - Trion Partners, Air Products, Sulzer Chemtech, and Deltalinqs
- 30m<sup>3</sup> of end of pipe fuel
- from 30-35% to ~2% water
- 1m<sup>2</sup> membrane area
- Winter 2011
- Lab result promising!



## What has ECN to offer?

### Non-exclusive license on

- Broad patent portfolio:
  - Materials on various HybSi<sup>®</sup> membranes
    - Hollow fibres, multichannel, external surface tubes, (especially for production > 200 m<sup>2</sup>/yr)
  - Sealing technology & module concept
- Know-how
  - Coating technology
  - Sol-gel procedures
- The names and logos
  - HybSi<sup>®</sup>
  - ECN technology inside

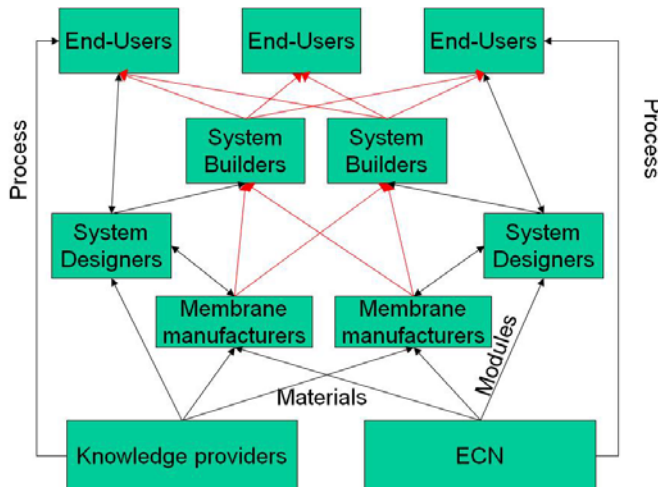


## What more has ECN to offer?

- Contract research
  - Fine tuning membranes
  - Process testing
  - Process simulations and design
- Technological website
  - [www.hybsi.com](http://www.hybsi.com) (>50 unique visits per week)
- Large industrial network
- Parties with proven commercial interest
- Existing e-mail distribution list

## Industrial involvement

- Commitment from **end users**
  - Tests & module sales
  - Process analyses
  - Letters of Intent to come to actual utilisation
- Interest from **OEM**
  - Letters of interests
  - Active participation



- Contract with **manufacturers**
  - First licence granted to Pervatech

## Acknowledgements

- Industrial collaborators & clients

- Sabic
- Huntsman
- Air Products
- DSM
- Sulzer Chemtec
- Pervatech
- Trion partners

- Financial support

- STW
- AgentschapNL
- DSTI

- Knowledge network

- University of Twente
- University of Amsterdam
- TNO



Membrane Technology Group

[www.ecn.nl/memtech](http://www.ecn.nl/memtech)

## HybSi® ready for take off



### Scientific Papers

*Chem. Commun.*, 2008, 1103

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

*ChemSusChem*, 2009, 2, 158-60

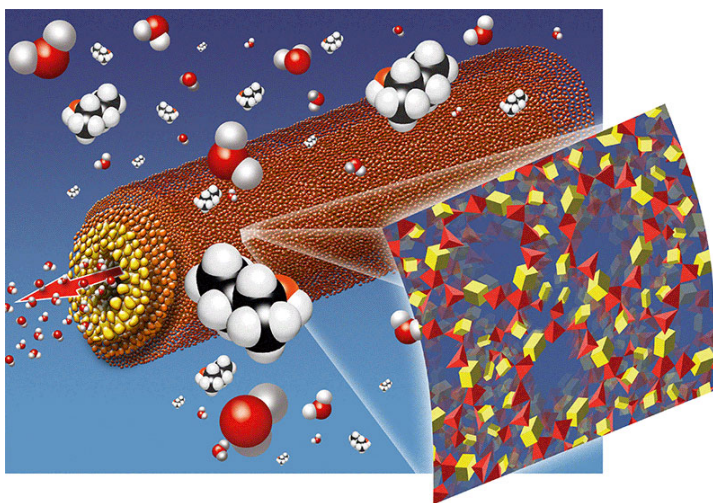
*J. Mater. Chem.*, 2008, 18, 2150

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

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

### Patents

WO/2007/081212 ; WO/2010/008283; WO/01/62371; WO/01/63162



[www.hybsi.com](http://www.hybsi.com)



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