Process performance improvement by Hybsi® nanosieve membranes for dehydration by pervaporation

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Process performance improvement by HybSi® nanosieve membranes for dehydration by pervaporation

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The key objective of the International Energy Agency (IEA) for future energy technologies is to reduce CO_2 emissions with ~50Gt/yr by 2050. The 27 EU states decided a 20% boost overall in renewable fuel use by 2020. In another key measure EU leaders decided to cut carbon dioxide emissions by 20% from 1990 levels by 2020. Carbon-neutral bio-based fuels such as ethanol, butanol, and bio-diesel are promising candidates for transportation purposes. Effective and energy-efficient separation technologies to dehydrate the wet fuels are needed for large scale application. It is widely accepted that molecular separation membranes will play a crucial role in this transition to sustainable transportation fuels. Furthermore these membranes can be used in the energy efficient dehydration of all kinds of chemicals.

Pervaporation or hybrid distillation-pervaporation separation processes using membranes are commonly considered options for the energy efficient dehydration of organics. We recently explored the use of organic-inorganic hybrid silica for microporous membranes. These membranes have unprecedented life times of at least 2 years in the dewatering of *n*-butanol at 150°C.[1] These membranes have a good performance in the dehydration of ethanol as well, both under pervaporation and vapor permeation conditions[2]. Here, we report on the optimization of industrial processes using these new membranes. By process simulation and flow sheeting for example the bio-ethanol production process via fermentation has been calculated, new process schemes have been made and the process has been optimized. Calculations show that an important improvement in the energy consumption can be obtained, meeting the future environmental criteria but also leading to important cost price reductions.

1. a) H. L. Castricum, A. Sah, R. Kreiter, D. H. A. Blank, J. F. Vente, J. E. ten Elshof, *Chem. Commun.* **2008**, 1103-1105; b) H. L. Castricum, R. Kreiter, H. M. van Veen, D. H. A. Blank, J. F. Vente, J. E. ten Elshof, *J. Membr. Sci.* **2008**, *324*, 111-118.
2. R. Kreiter, M. D. A. Rietkerk, H. L. Castricum, H. M. van Veen, J. E. ten Elshof, J. F. Vente, *ChemSusChem* **2009**, in press.

ECN

Energy research Centre of the Netherlands

Process improvement by HybSi® membranes in dehydration pervaporation – bio-ethanol production

Henk van Veen, et.al.

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- Background
- HybSi® pervaporation membranes
  - Preparation and performance
- Bio-ethanol production process
- HybSi® membranes in bio-ethanol
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- Conclusions

Background

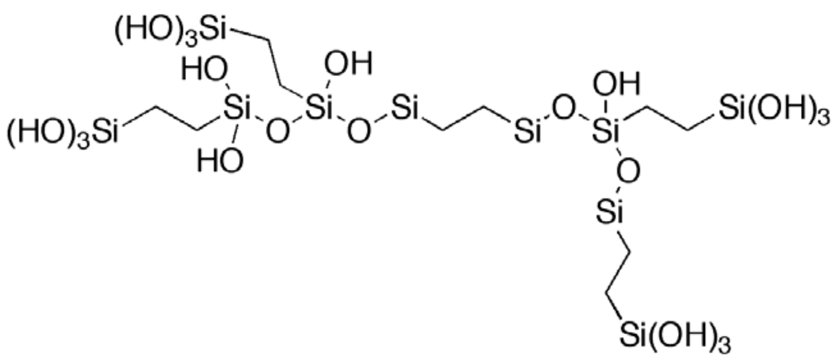
- Objective IEA: reduce CO_2 emissions with 50 Gt/yr by 2050
- 27 EU states: 20% renewable fuels by 2020
- EU: cut CO_2 emissions by 20% in 2020 compared to 1990
- Needed for bio-based fuels
- Molecular separation can play key role, e.g. in dehydration of bio-ethanol
- Need for stable and high flux pervaporation membranes

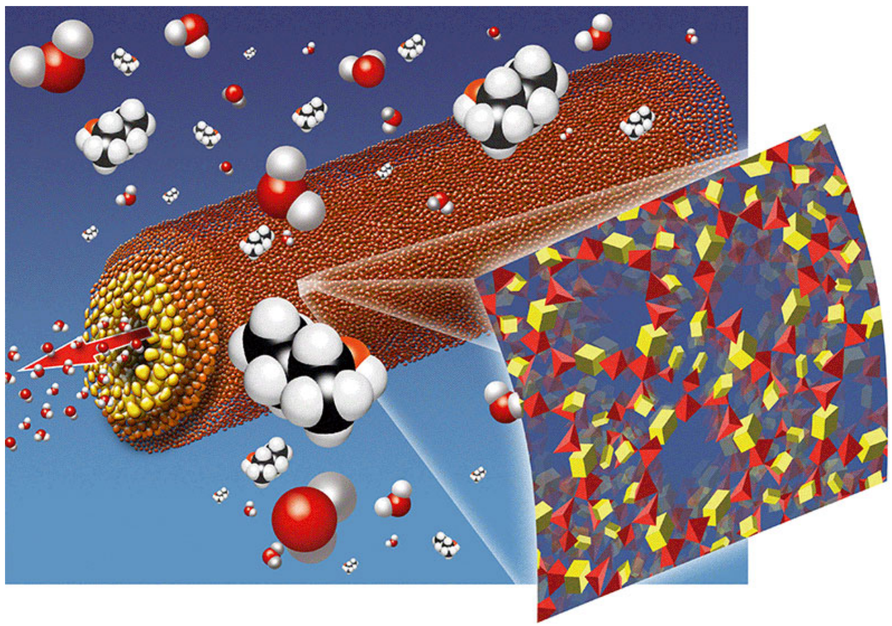
Hybrid membranes from bisfunctional silica precursors HybSi®

Stable membranes: 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)





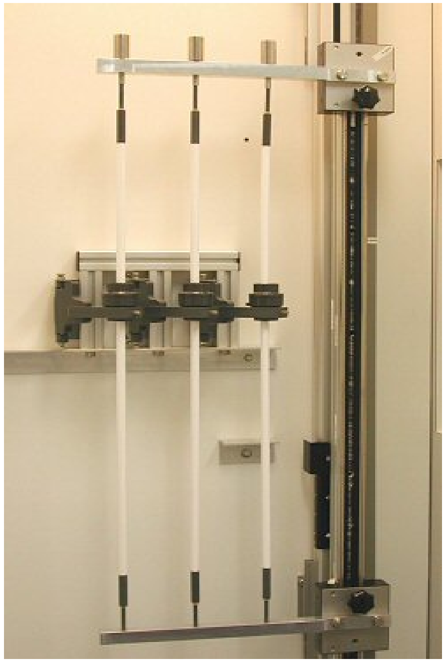
Patented in collaboration with Univ. of Twente and Univ. of Amsterdam (Ashima Sah, Andre ten Elshof, Hessel Castricum, Marjo Mittelmeijer)

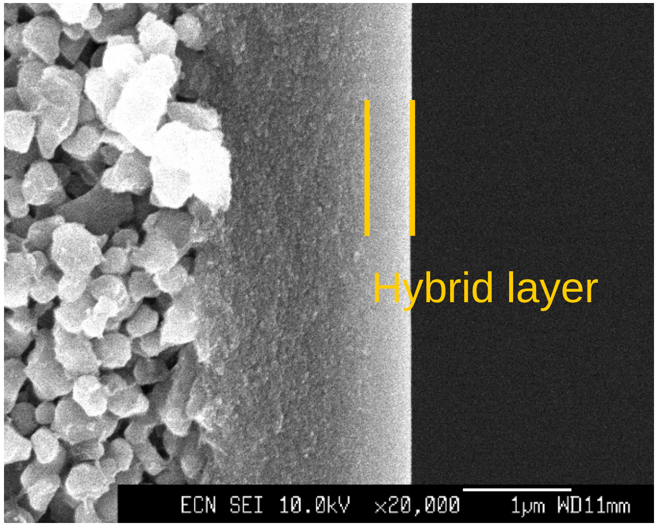
WO2007081212, 2006; *Chem. Commun.* 2008, 1103-1105

Precursors and preparation of HybSi® membranes

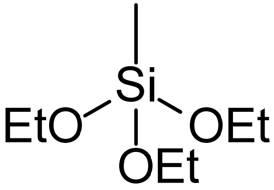
Precursors:

- BTESE + MTES
- BTESE
- BTESM

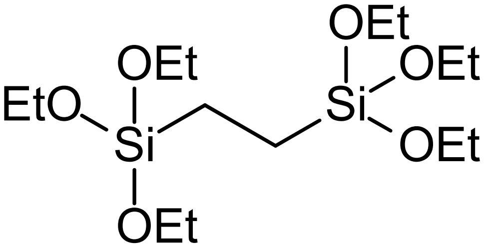




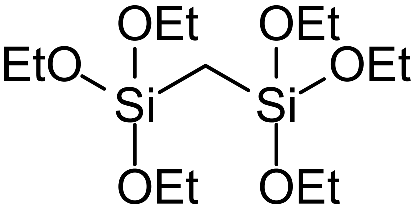
MTES



BTESE



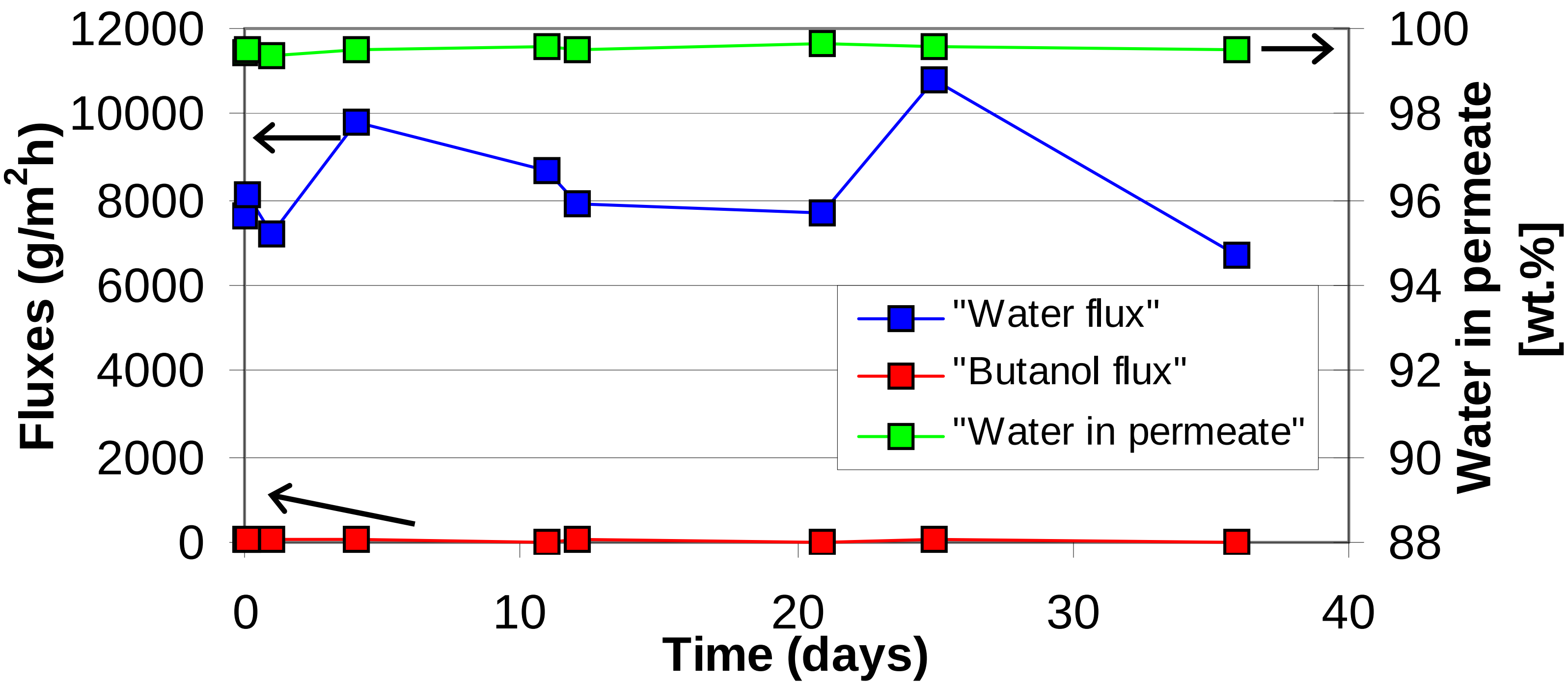
BTESM



Performance HybSi® membranes, 190ºC

Feed = 5 wt.% water in nBuOH
BTESE precursor
stable > 1 month

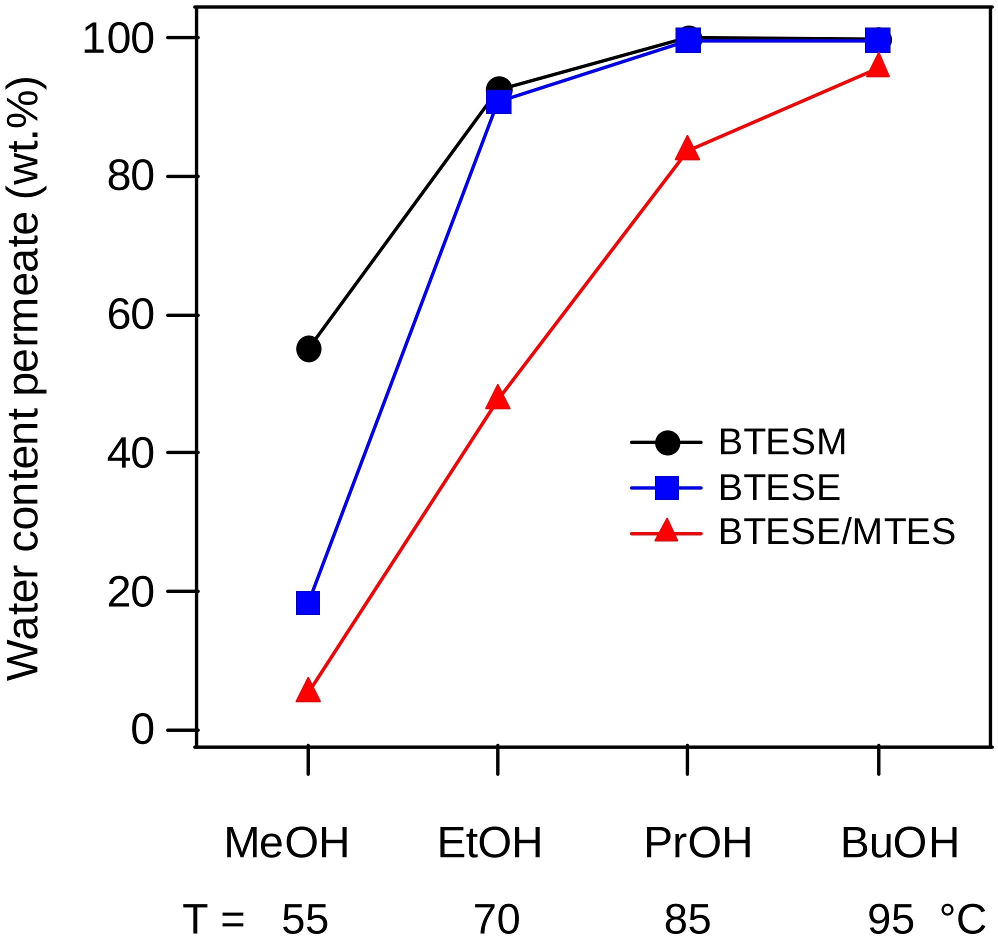
Fluxes and water conc. in permeate vs. time



Tests up to 150°C see:
J. Membr. Sci. 2008, 324, 111-118

Application testing - alcohols

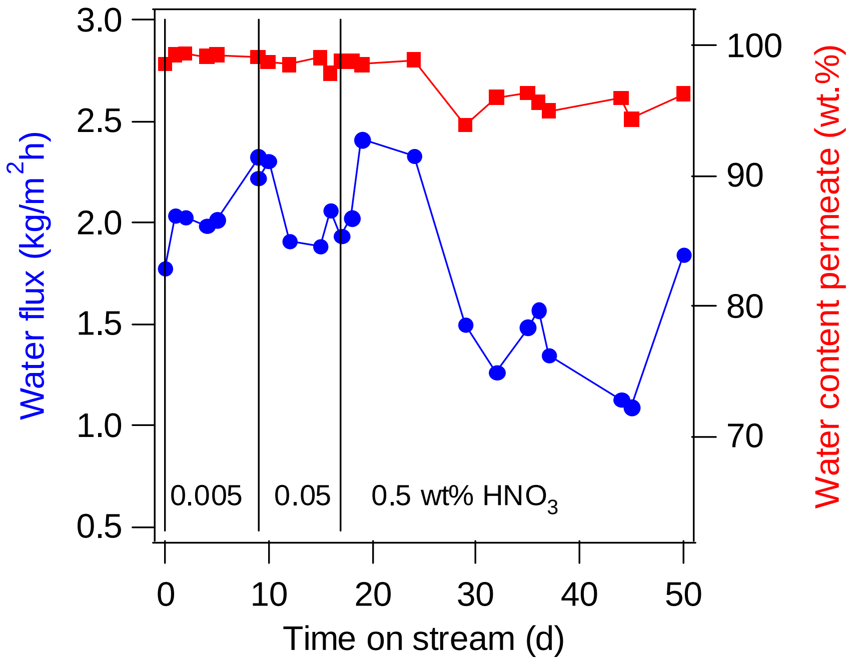
Feed = 5 wt.% water in alcohol



ChemSusChem 2009, *2*, 158-160

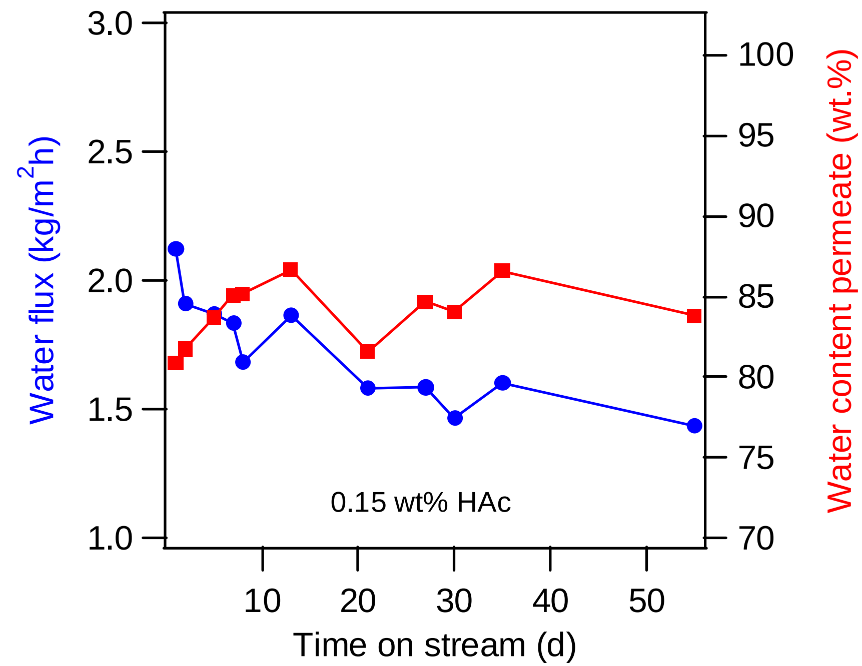
Acid stability

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



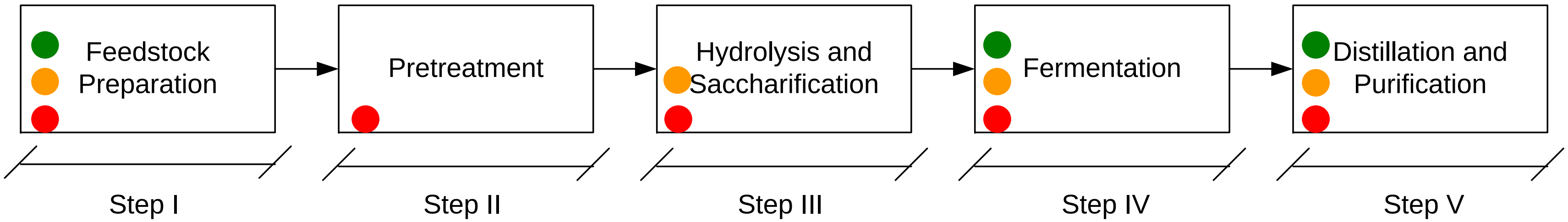
J.Mater.Chem. 2008, *18*, 1-10

Feed : 5 wt.% water in EtOH
0.15 wt% HAc
BTESM

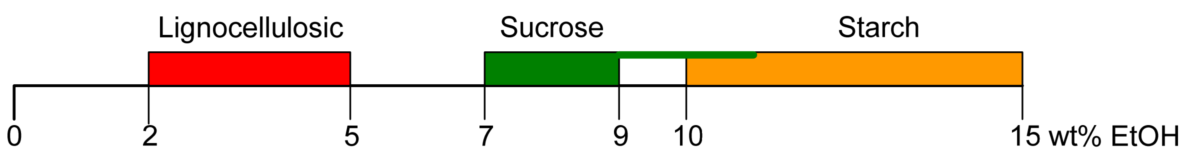


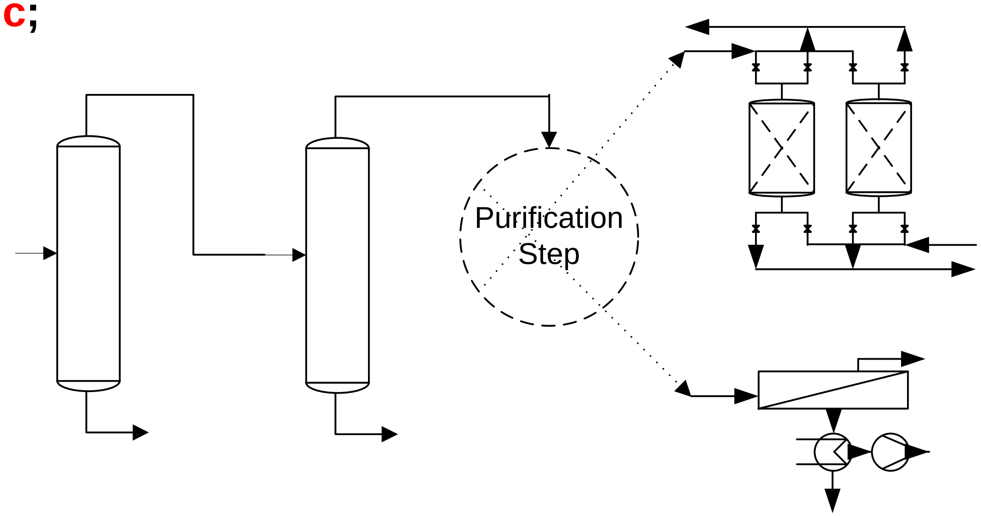
ChemSusChem 2009, *2*, 158-160

Bio-ethanol Production



- **Sugar Crops - Sucrose;**
- **Cereal crops – Starch;**
- **Lignocellulosic biomass - Lignocellulosic;**



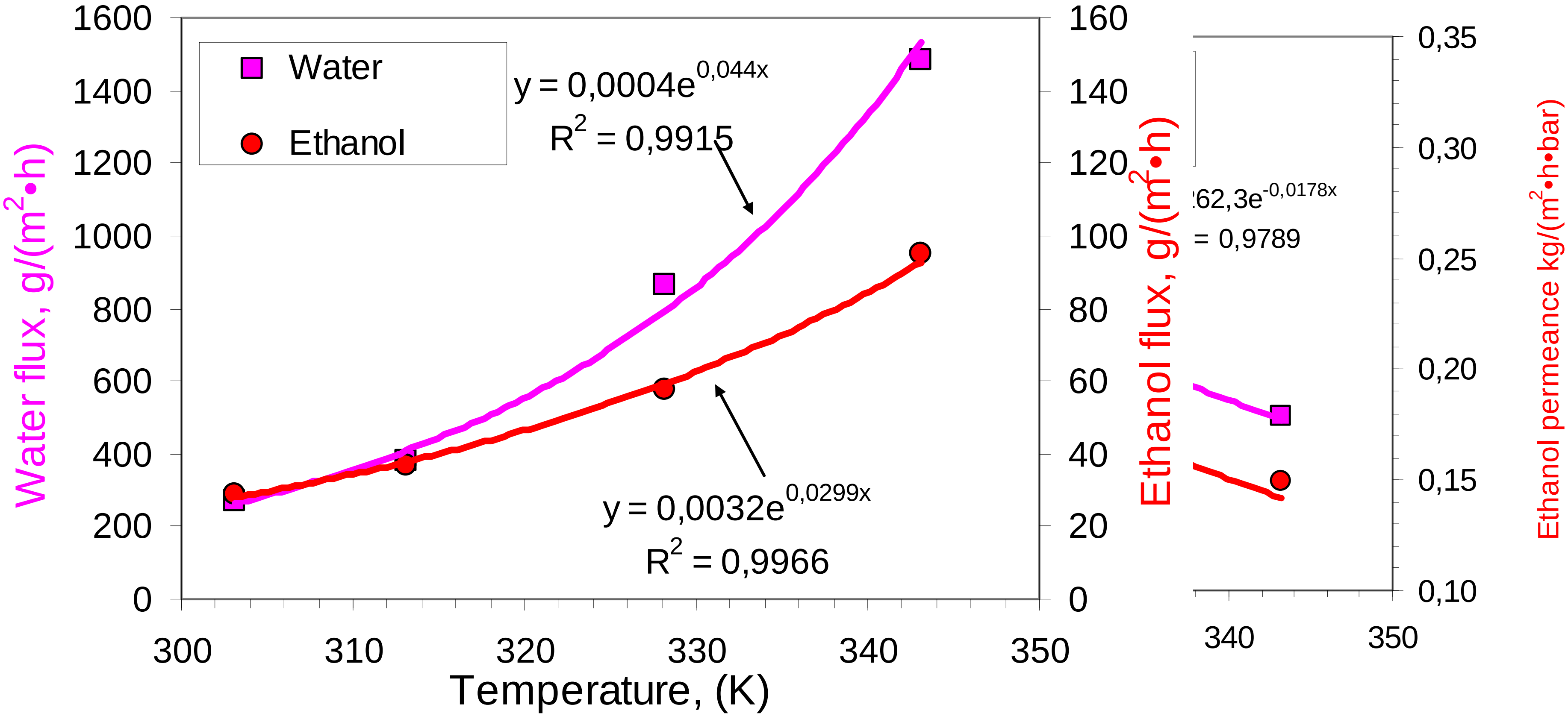


0.995 wt. fraction

Final EtOH concentration

HybSi® Membranes for Bio-ethanol Production: data

Water and ethanol flux and permeance vs. temperature in a binary mixture



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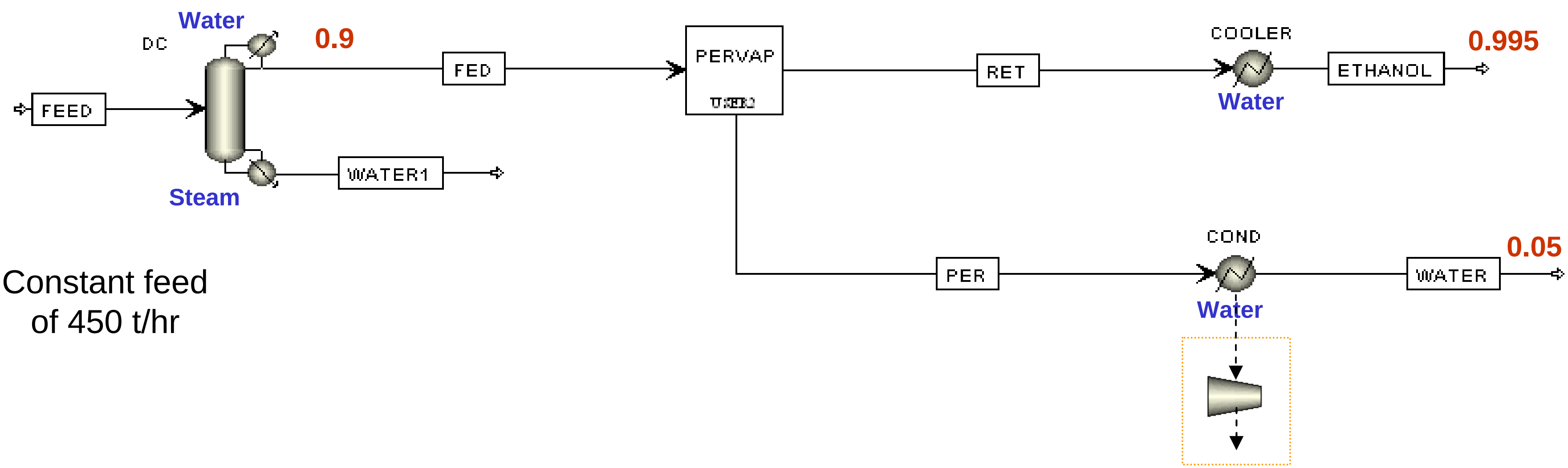
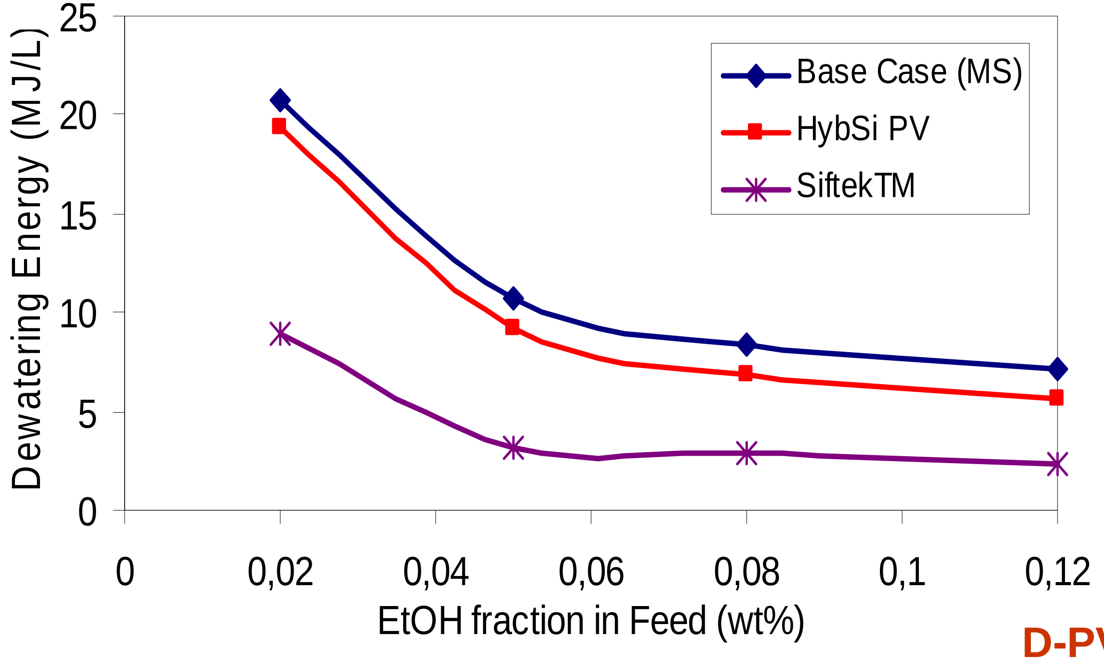
HybSi® Membranes for Bio-ethanol Production: flow sheets



Constant feed of 450 t/hr

Feed Composition (wt fraction EtOH)	Distillation Column		Pervaporation Unit					Total Duty (PJ/Year)	Final EtOH Flow (t/year)	Duty (MJ/L_{EtOH})
	Q_{Total} (PJ/Year)	% Q_{Total}	Condenser	Elec. Vacuum Pump	Q_{Cooler}	Q_{Total}	% Q_{Total}			
			PJ/year							
0.02	1.3	98	0.013	0.000	0.009	0.0	**2**	1.3	54326	**19.358**
0.05	1.8	97	0.039	0.000	0.025	0.1	**3**	1.9	161786	**9.204**
0.08	2.3	95	0.067	0.000	0.043	0.1	**5**	2.4	271984	**6.898**
0.12	2.8	94	0.101	0.000	0.065	0.2	**6**	3.0	415149	**5.627**

HybSi® Membranes for Bio-ethanol Production: energy



D-MS vs D-HybSi PV

D-PV energy savings: 7 to 22%

D-PV without Cooling Water

Siftek™ D-VP vs HybSi® D-PV

- Siftek™ DID NOT consider the cooling water energy;
- Siftek™ is optimized in two membrane steps;

Feed EtOH (wt %)	MJ/L
8	4,6
12	3,5
Siftek™	
10	4,8

HybSi® Membranes for Bio-ethanol Production: economics

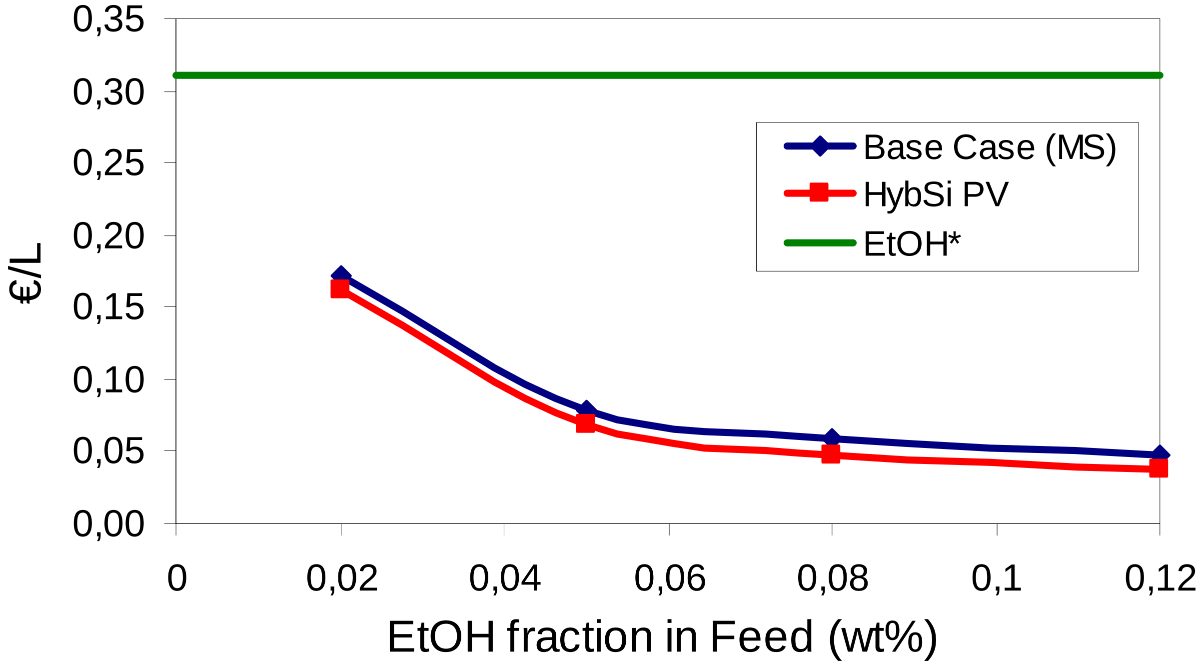
Costs of utilities taken from DACE (Dutch Association of Cost Engineers)

Reboiler (DC) and Heater (MS): Steam;

Molecular Sieve: Natural Gas;

Vacuum pump (PV): Electricity;

Condensers (DC and PV unit) and Coolers (PV and MS units): Cooling water;



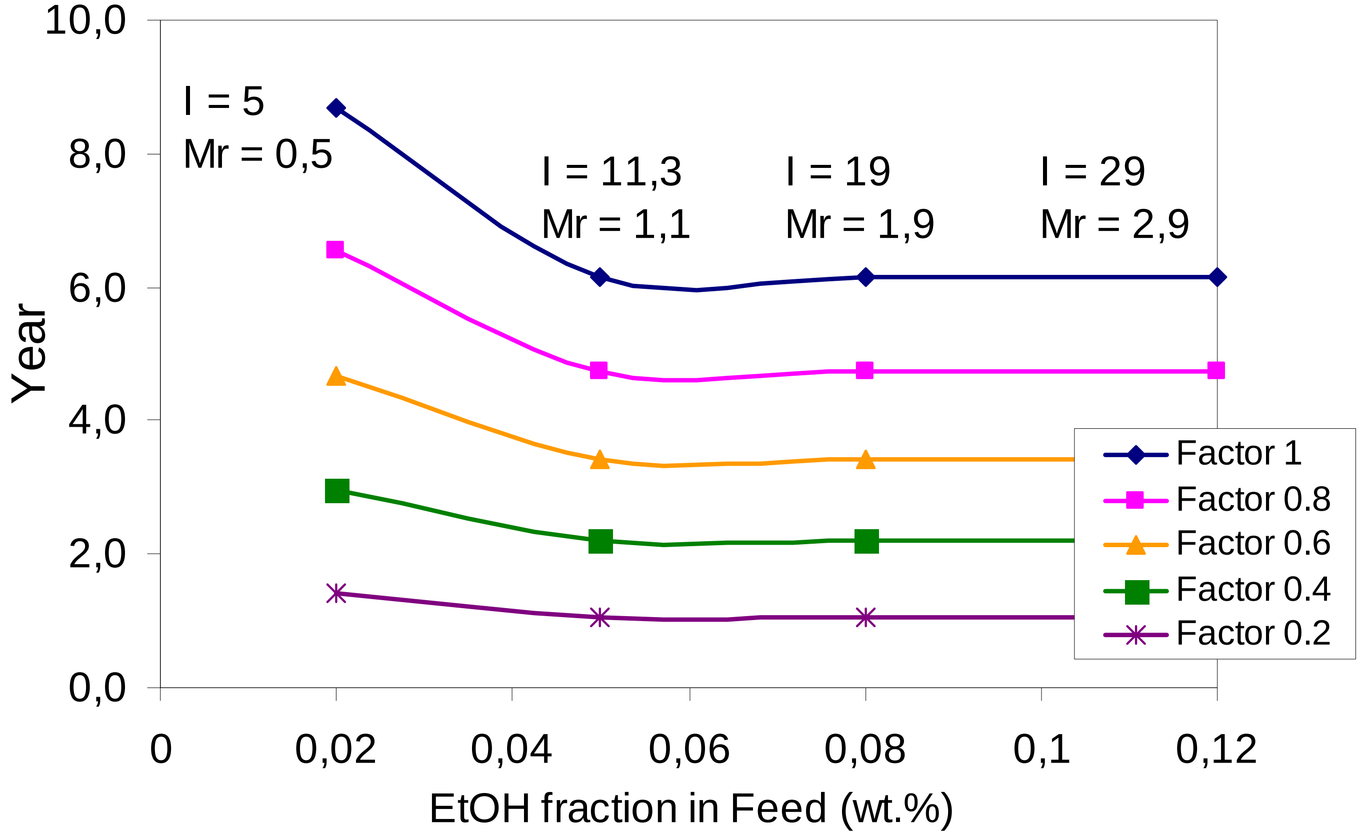
D-HybSi PV cost savings:

6 to 23%;

HybSi® Membranes for Bio-ethanol Production: economics

Payback period

I (Initial investments, M€) and Mr (Membrane replacement, M€/3years)

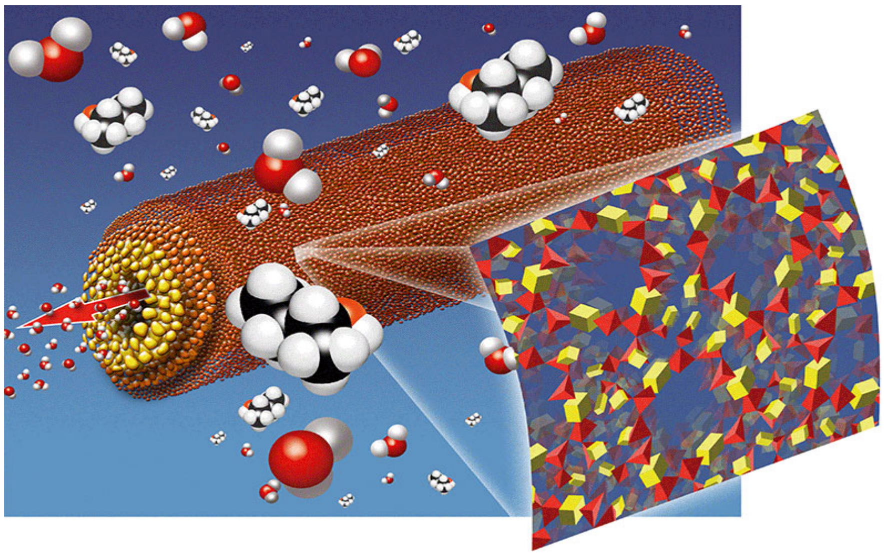


HybSi® Membranes for Bio-ethanol Production
Conclusions for D-HybSi PV vs. D-MS

- HibSi® membrane shows energetic (up to 22%) and economic (up to 23%) benefits in bio-ethanol production
- A payback period of 6 years is realistic, a cost decrease or a flux increase by a factor 2 is wished
- After return of investment: savings from 0.6 to 4.7 M€/year
- Environmental benefits PV vs. MS (not presented):
  - CO_2 emissions: reduction almost 100% leading to extra economic savings from 68 to 520 k€/year)
  - Reduction in cooling water up to 19%

Further information and acknowledgements

HybSi®
Pervaporation Membranes



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J. Mater. Chem., 2008, 18, 2150-2158
J. Sol-Gel Sci Techn, 2008, *48*, 203-211
J. Mem. Sci, 2008, 324, 111-118
ChemSusChem, 2009, *2*, 158-160
Patent: WO2007081212

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