PDMS organic solvent nanofiltration membranes on ceramic supports

6th International Conference on Organic Solvent Nanofiltration, Saint-Petersburg, Russia, 4-6 June 2017

ECN-M--17-020 - June 2017

PDMS organic solvent nanofiltration membranes on ceramic supports

6th International Conference on Organic Solvent Nanofiltration, Saint-Petersburg, Russia, 4-6 June 2017

Author(s)

H.M. van Veen
M.M.A. van Tuel
K.J. Damen
Y.C. van Delft

Disclaimer

Although the information contained in this document is derived from reliable sources and reasonable care has been taken in the compiling of this document, ECN cannot be held responsible by the user for any errors, inaccuracies and/or omissions contained therein, regardless of the cause, nor can ECN be held responsible for any damages that may result therefrom. Any use that is made of the information contained in this document and decisions made by the user on the basis of this information are for the account and risk of the user. In no event shall ECN, its managers, directors and/or employees have any liability for indirect, non-material or consequential damages, including loss of profit or revenue and loss of contracts or orders.

PDMS organic solvent nanofiltration membranes on ceramic supports

M.M.A. van Tuel[1], H.M. van Veen[1] and Y.C. van Delft[1]
[1]*Energy research Centre of the Netherlands, ECN, Westerduinweg 3, 1755 LE Petten, the Netherlands*

Highlights
1. Retentions of 98% for 800D molecules are combined with permeances of 1.5 kg/m^{2}hbar.
2. Tuning of membrane performance is possible by support choice and coating parameters.
3. Membranes are broad applicable in different solvents and potentially at high temperatures.

PDMS membranes applied on a polymeric supports are well known for their applicability in organic solvent nanofiltration. By coating a thin PDMS layer on a ceramic support these membranes can also be used at higher temperatures and under more demanding conditions like high pressure differences or application in different solvents. Furthermore, the membranes can be stored at atmospheric conditions.

We have applied PDMS layers on two different types of tubular ceramic supports, i) an alpha-alumina support with a pore size of about 0.2 μm and ii) a gamma-alumina support with different pore size ranges between 4-11 nm. The performance of the membranes has been tested in different solvents like acetone, toluene and hexane and in different retention tests:

1. sunflower oil (1.5 wt.%) dissolved in hexane, toluene or acetone. The refined sunflower oil consists of a mixture of triglycerides with a molecular weight of around 800 Dalton and represents applications in the food industry;
2. 0.5 wt.% of a transition metal (Wilkinson) catalyst dissolved in toluene as an example to recover valuable homogenous catalysts used in the chemical industry.

We will show the influence of the different support types and support treatment on the performance of the membranes in the applications presented above. An important result is that after 6 months of atmospheric storage the membrane performance has not changed. The addition of silica based structures in PDMS on the membrane performance will be discussed. Furthermore, we will show the influence of the membrane layer thickness on the performance both in pure solvent testing and in the selected applications. In figure 1 a picture is presented of the feed, permeate and retentate for a PDMS membrane applied on a gamma-alumina support used in the recovery of a Wilkinson catalyst (molecular weight = 925 Dalton) in toluene. The permeance of 1.6 kg/m^{2}hbar for toluene in combination with the retention of 95% is higher than for PDMS membranes reported in literature [1].

Figure 1. Retention test results with 0.5 wt.% homogenous Wilkinson catalyst dissolved in toluene for a PDMS membrane applied on gamma-alumina.

References
[1] L. Gevers, et.al., Journal of Membrane Science, 278, p.199-204, (2006).

PDMS organic solvent NF membranes on ceramic supports

Marc van Tuel, Henk van Veen, Kay Damen, Yvonne van Delft

OSN2017, St. Petersburg, 5 June 2017

ECN

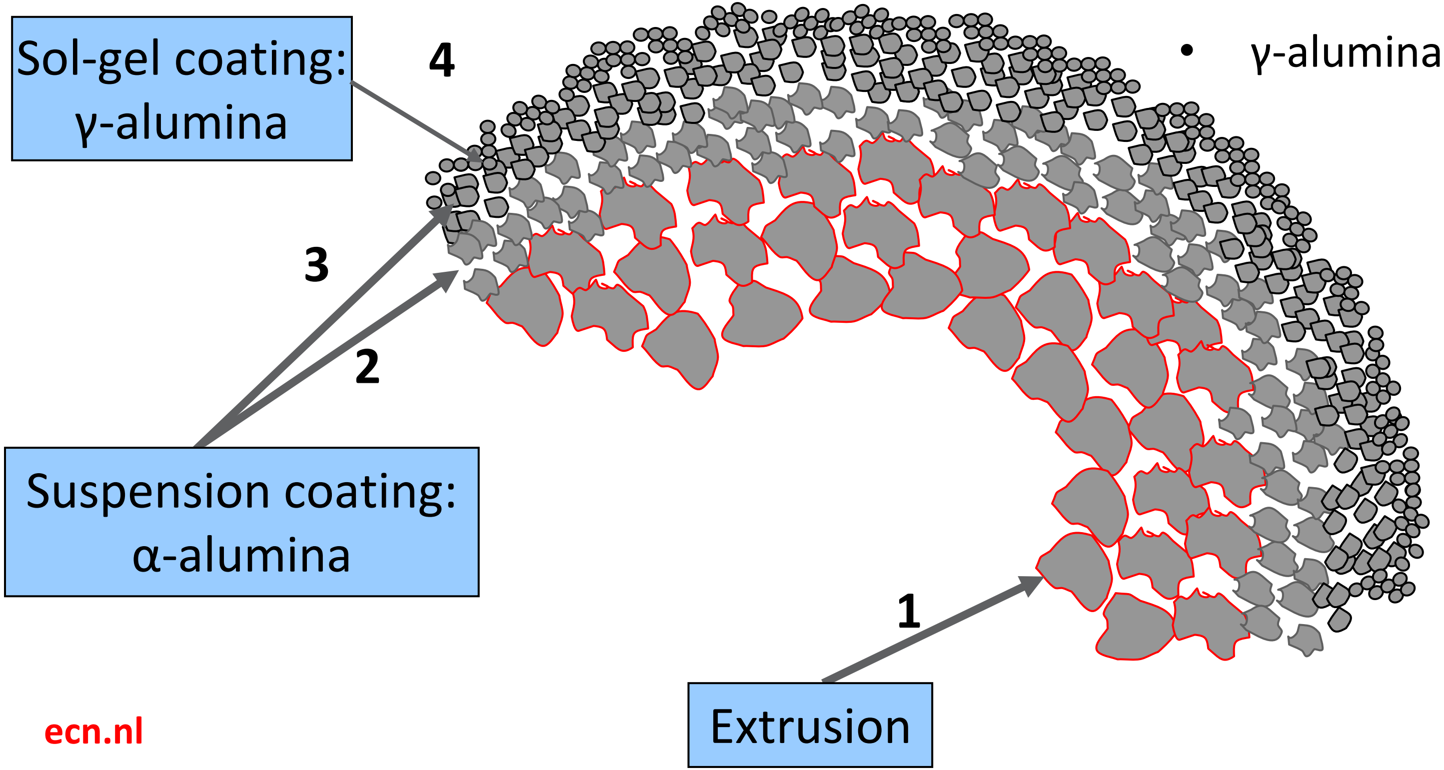
Introduction

- PDMS well known for OSNF
- Markets:
  - recovery of expensive homogeneous catalysts (chemical industry)
  - recovery of edible oils from extractants (food industry)
  - enantiomer separation (pharma industry)
  - recovery of Active Pharmaceutical Ingredients (pharma industry)
  - small organic molecules from solvents, e.g. fermentations (chemical, food, pharma, bio refining)

- Use ceramic support for more demanding applications
- Test influence of different ceramic supports on membrane performance
- Quality test in sunflower oil and homogeneous catalyst recovery
- Higher temperature application: organosolv processing

Ceramic membrane supports

- α-alumina: 0.2 micron pore
- γ-alumina: 4-40 nm pore



PDMS membrane preparation

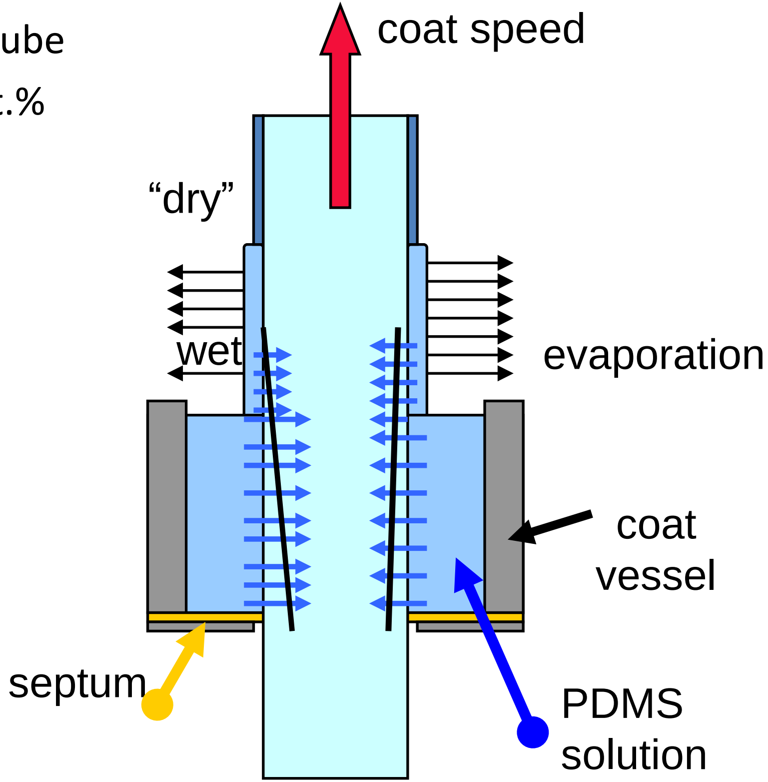
30 cm long ceramic tube

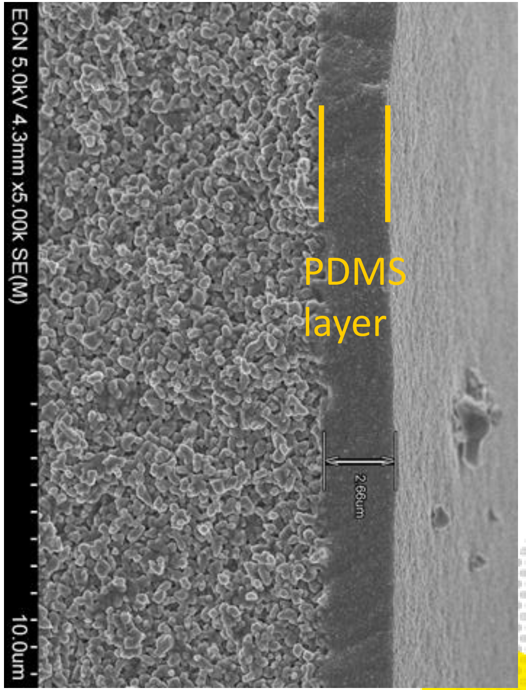
PDMS (A+B): 5-30 wt.%

Solvent: hexane

Dry: 12 hrs @ RT

Heat: 1 h @110°C





α-alumina support

PDMS thickness 2.7 μm

Membrane testing

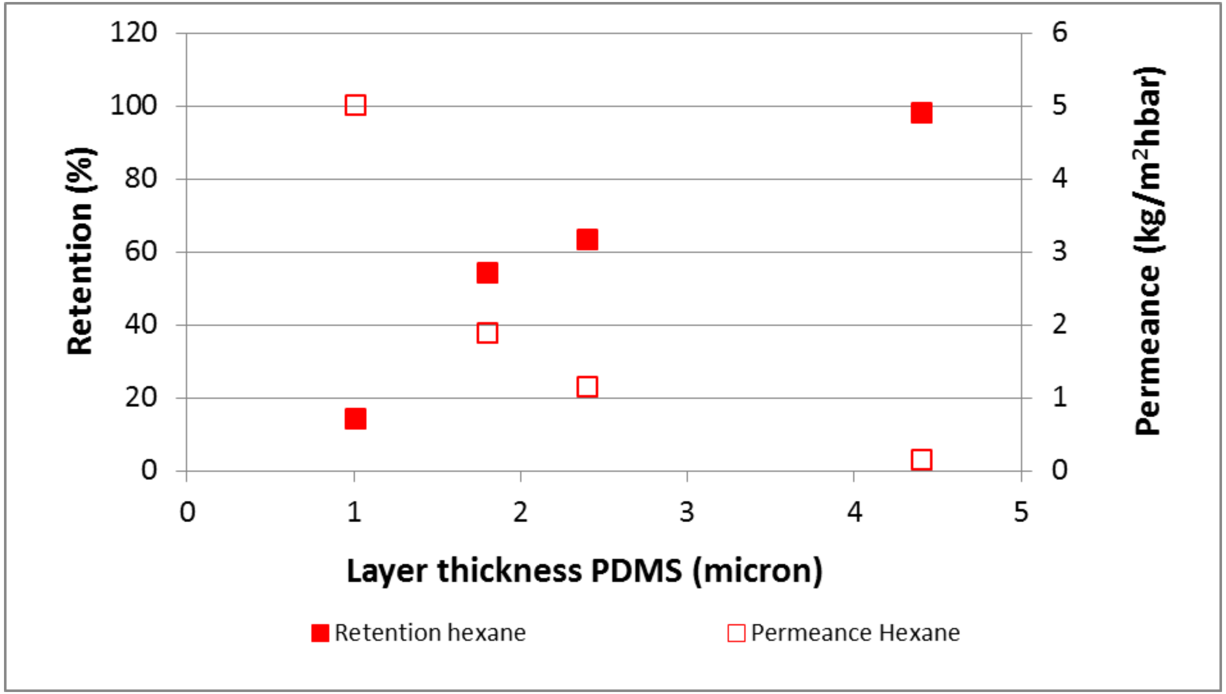
Dead-end (+ small cross flow NF)
max. 25 bar, 150°C (90°C)

Retention test: 1.5 wt.% sunflower oil in hexane or toluene
ΔP = 20 bar

Sunflower oil: mixture of triglyceride (C_{18} with traces of C_{16}-C_{20} fatty acids)
MW ±800 Dalton

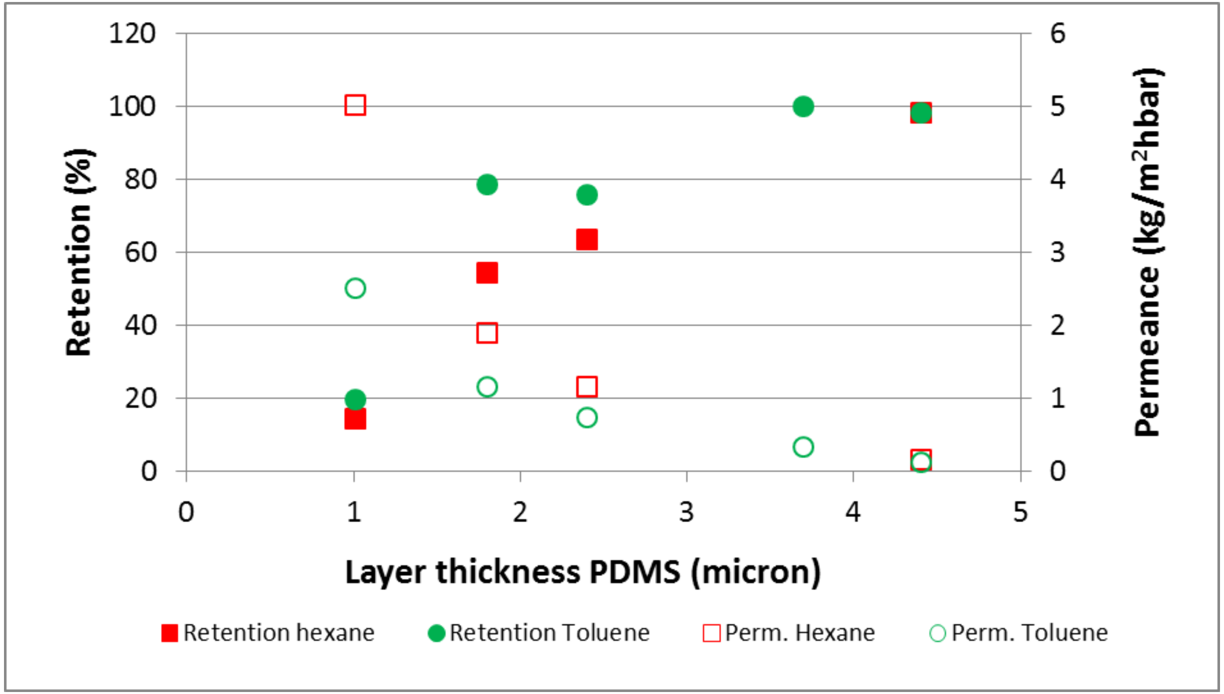
PDMS on α-alumina
(1.5 wt.% sunflower oil in hexane)

Influence of PDMS layer thickness



PDMS on α-alumina
(1.5 wt.% sunflower oil in hexane or toluene)

Influence of PDMS layer thickness

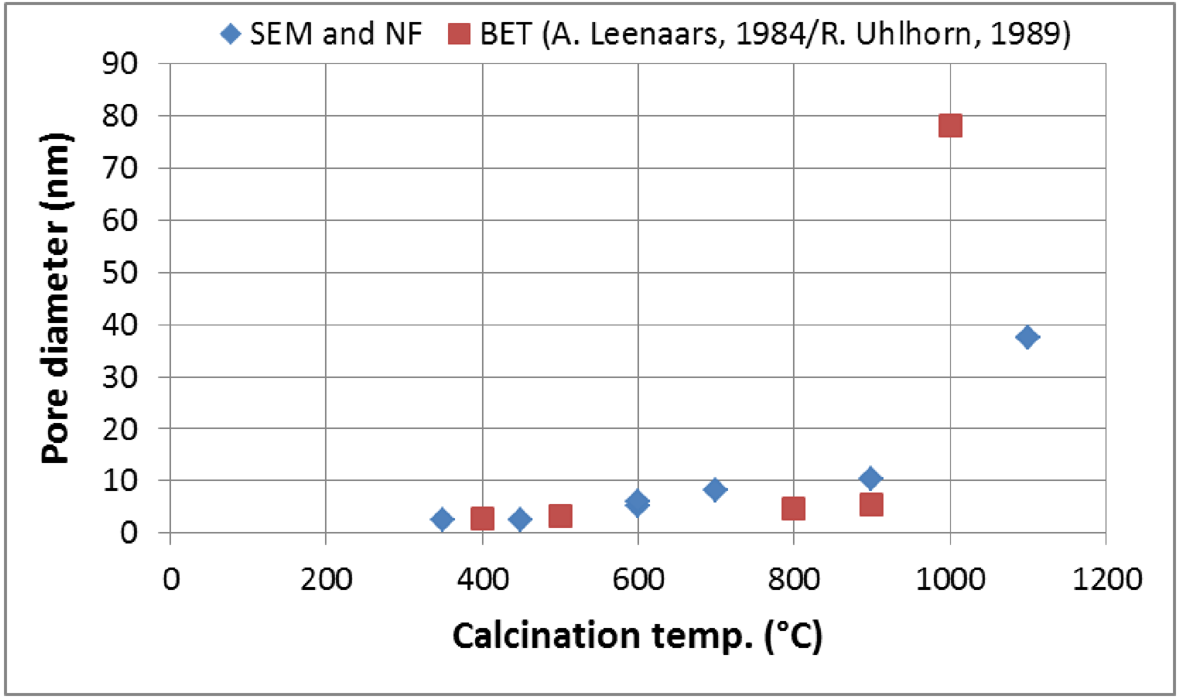


Thickness PDMS on α-Al_2O_3 > 3 micron for retention > 90% → permeance of ± 0.4 kg/m^2hbar

Wish: decrease layer thickness of PDMS still with good retention

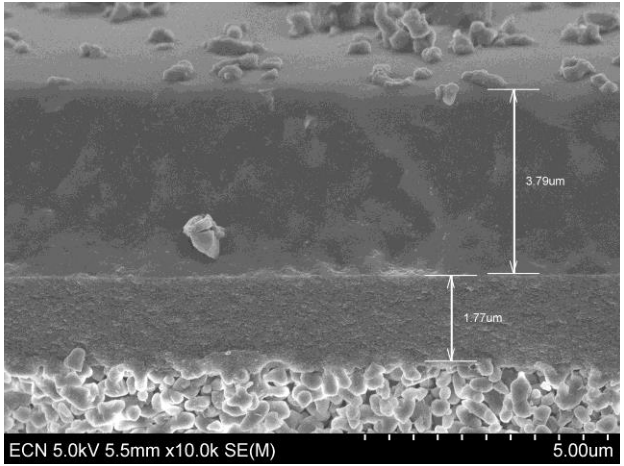
γ-alumina supports

Change of γ-alumina pore diameter by calcination at higher temperatures

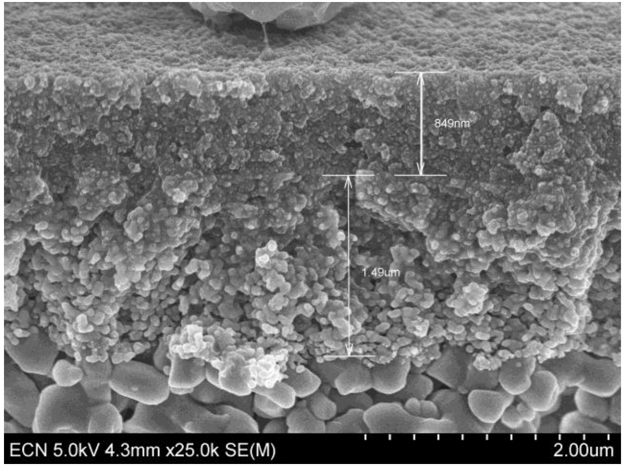


ecn.nl

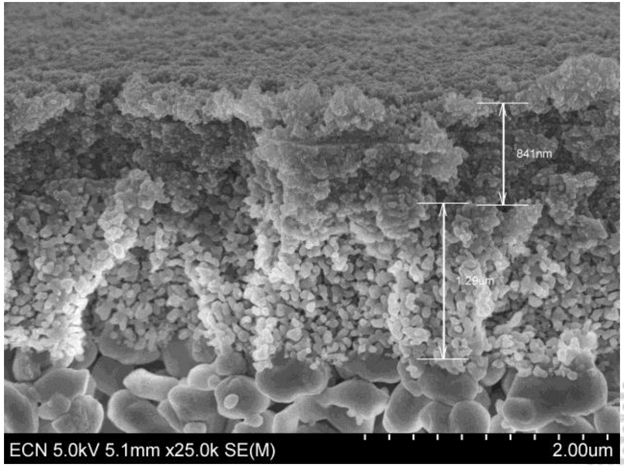
γ-alumina supports



700°C – 2x dilution



1100°C – 4x dilution

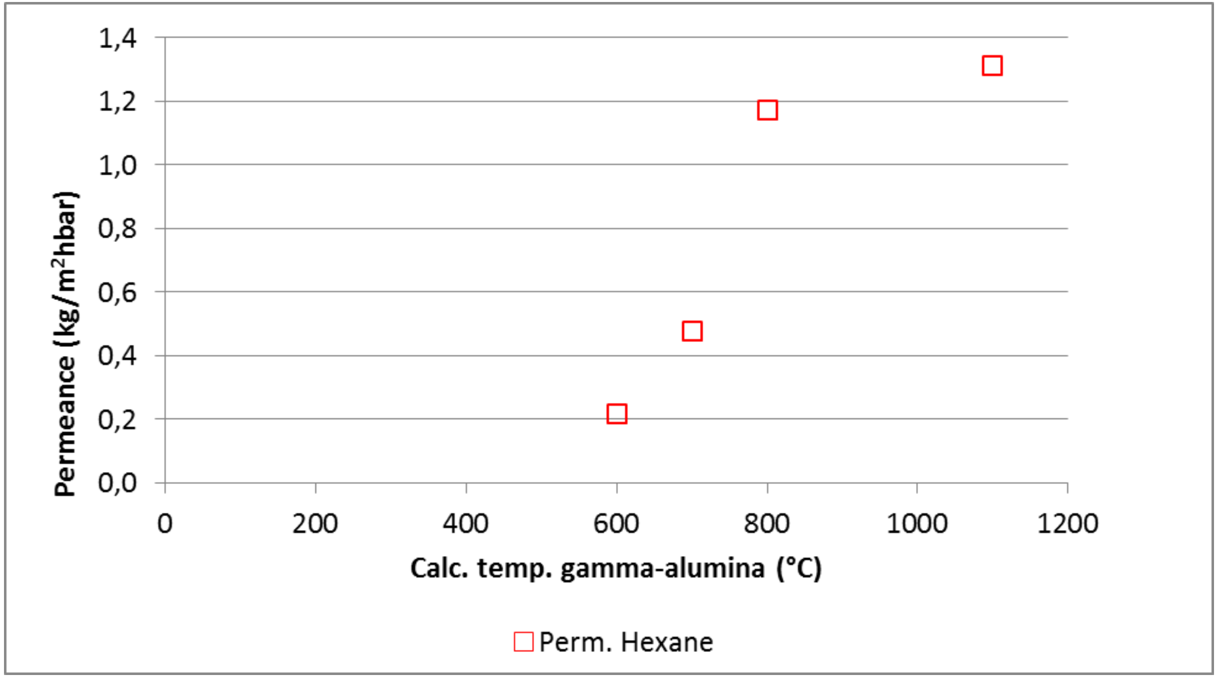


1100°C – 6x dilution

Higher calcination temperature gamma-alumina and more diluted PDMS solution: more open polymer structure and partly infiltration into the support

PDMS on γ-alumina
(pure hexane)

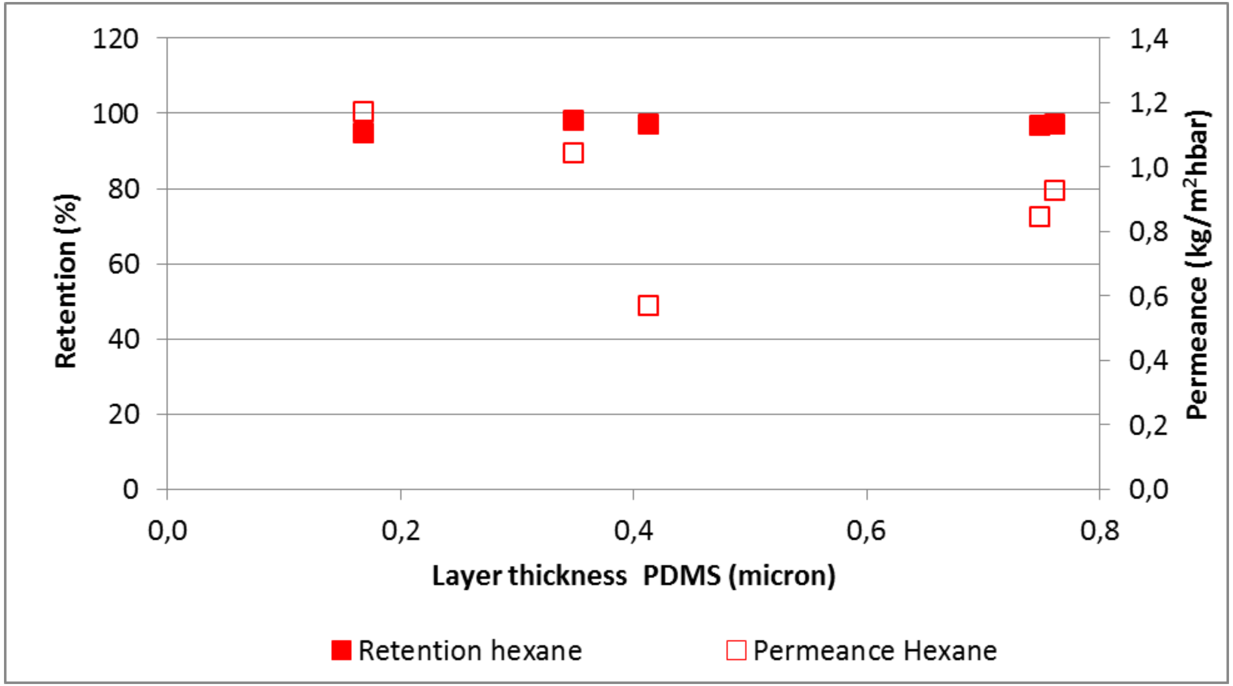
Influence of calcination temperature on hexane permeance



Use gamma-alumina calcined at 1100°C!

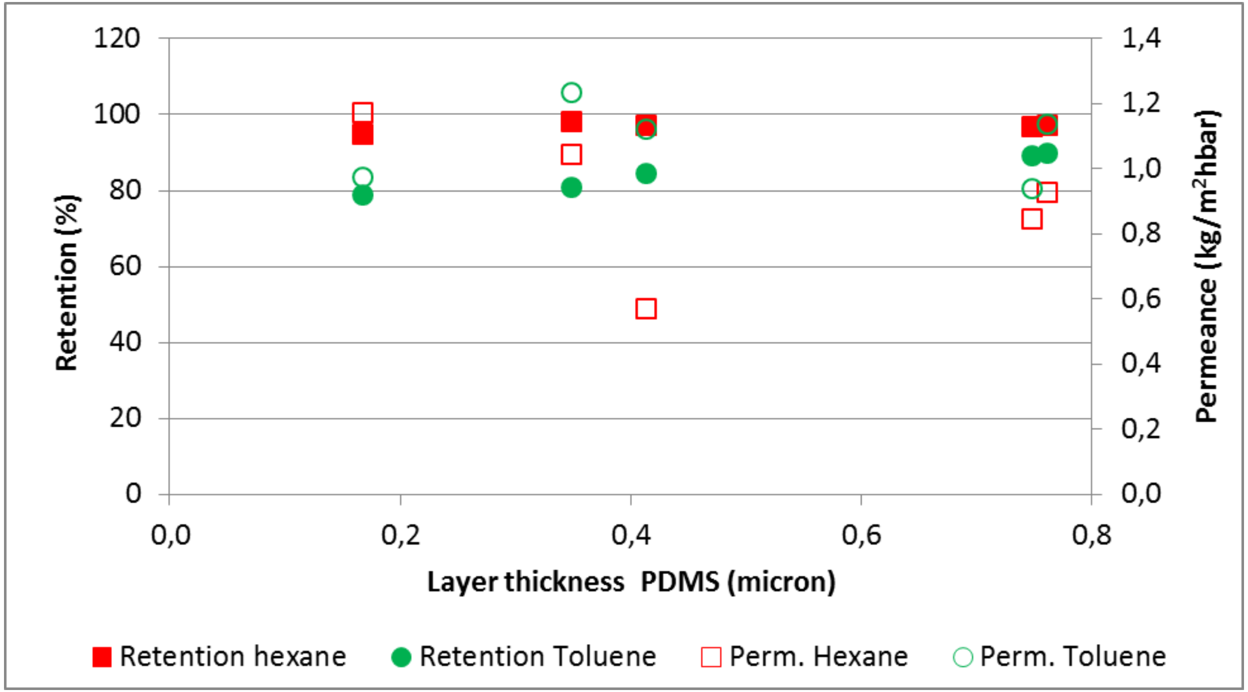
PDMS on γ-alumina
(1.5 wt.% sunflower oil in hexane)

Influence of PDMS layer thickness



PDMS on γ-alumina
(1.5 wt.% sunflower oil in hexane or toluene)

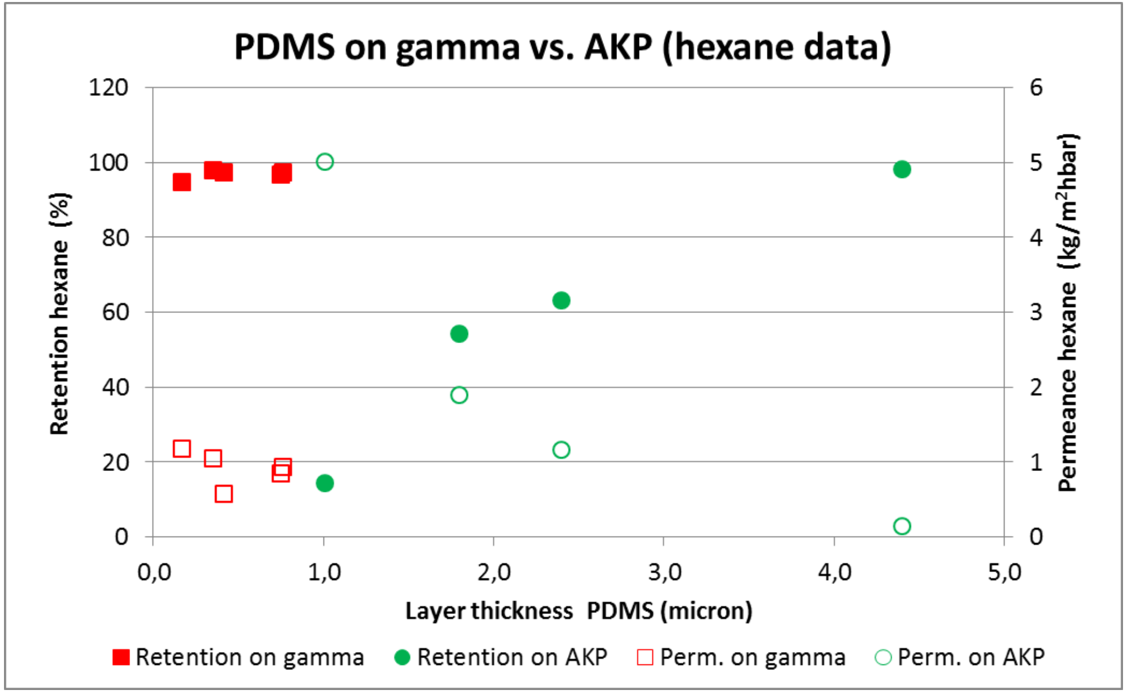
Influence of PDMS layer thickness



Thickness PDMS on γ-Al_2O_3: 0.2 micron for retention > 96% and permeance of 1.2 kg/m^2hbar in hexane

PDMS on α-alumina vs. γ-alumina
(1.5 wt.% sunflower oil in hexane)

Influence of PDMS layer thickness



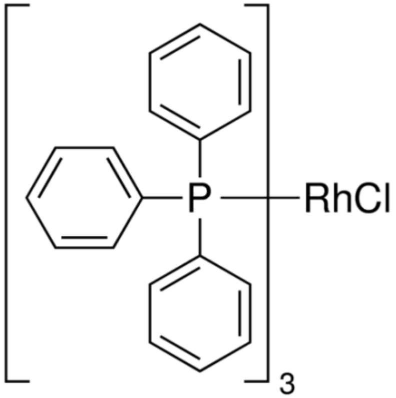
For high retentions + good permeance gamma-alumina as support is preferred over alpha-alumina

Homogeneous catalyst testing

PDMS on γ-alumina in homogeneous catalyst recovery

Wilkinson catalyst used in e.g. hydrogenation reactions

Rhodium(I) tris(triphenylphosphine) chloride, 925 g/mol) recovery as example (1 wt.% in toluene)



PDMS membrane pre-test in 1.5 wt.% sunflower oil in hexane:

1.2 kg/m^2hbar and 95% retention

PDMS on γ-alumina in homogeneous catalyst recovery

Wilkinson catalyst (925 g/mol) in toluene: 1.6 kg/m^{2}hbar and 95% retention

PDMS on γ-alumina in homogeneous catalyst recovery

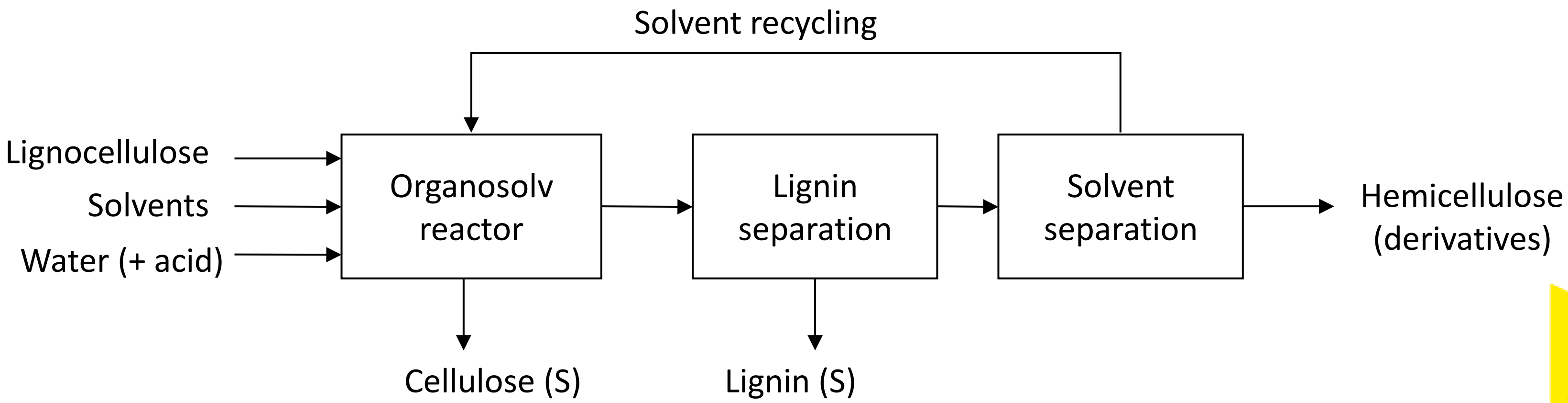
Wilkinson catalyst (925 g/mol) in toluene

Membrane	description	Toluene perm. (kg/m^2hbar)	Retention (%)	Ref.
PDMS	On PAN polymer support	1.2	78	Gevers, JMS 2006
PDMS + ZSM5	On PAN polymer support	0.6	98.5	Gevers, JMS 2006
PDMS + USY (silica)	On PAN polymer support	0.2	98	Gevers, JMS 2006
MFP50	Commercial PDMS membrane from Koch	0.5	81	Gevers, JMS 2006
This work	PDMS on gamma alumina	1.6	95	This work

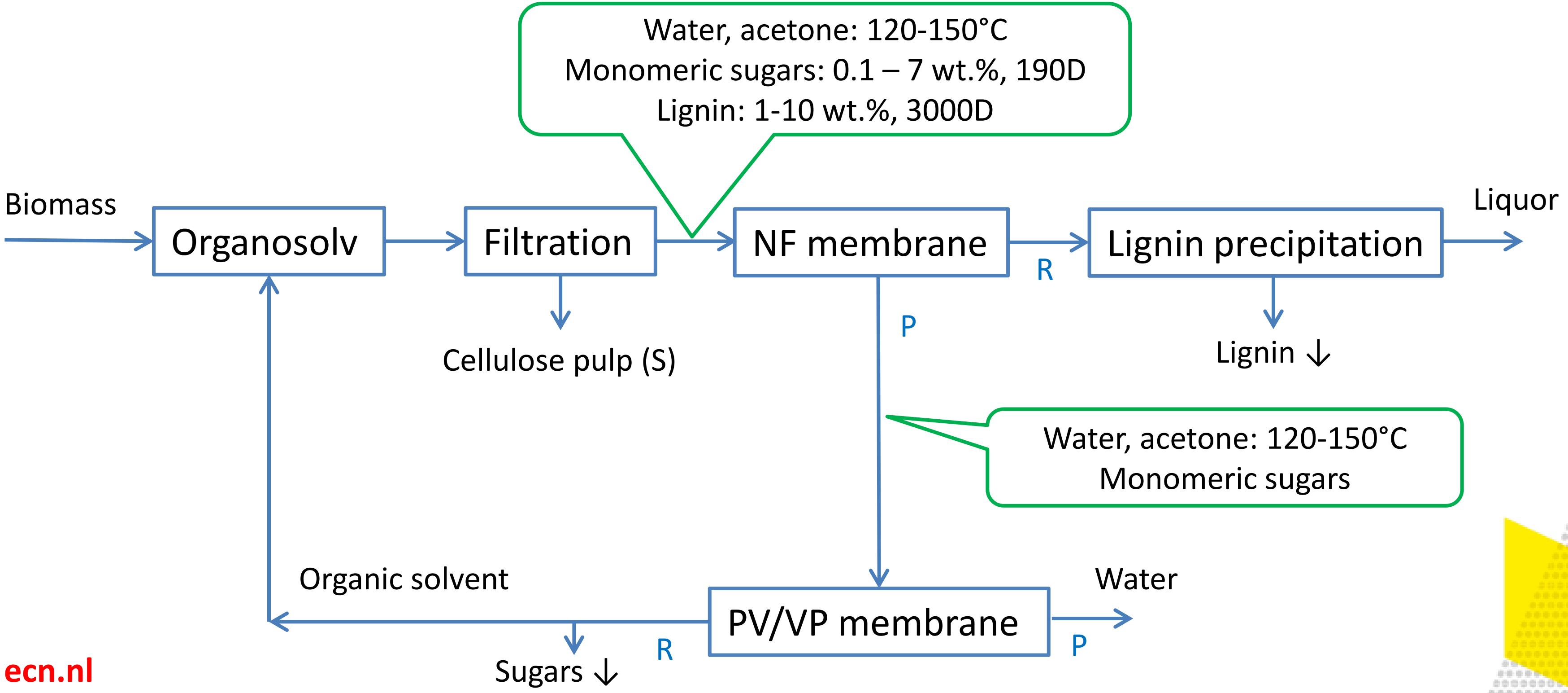
Move towards higher temperature use

Organosolv processing

- Pretreatment technology for lignocellulosic biomass into cellulose, hemicellulose and lignin
- Mixture of water and organic solvent like ethanol or acetone at 140-220°C

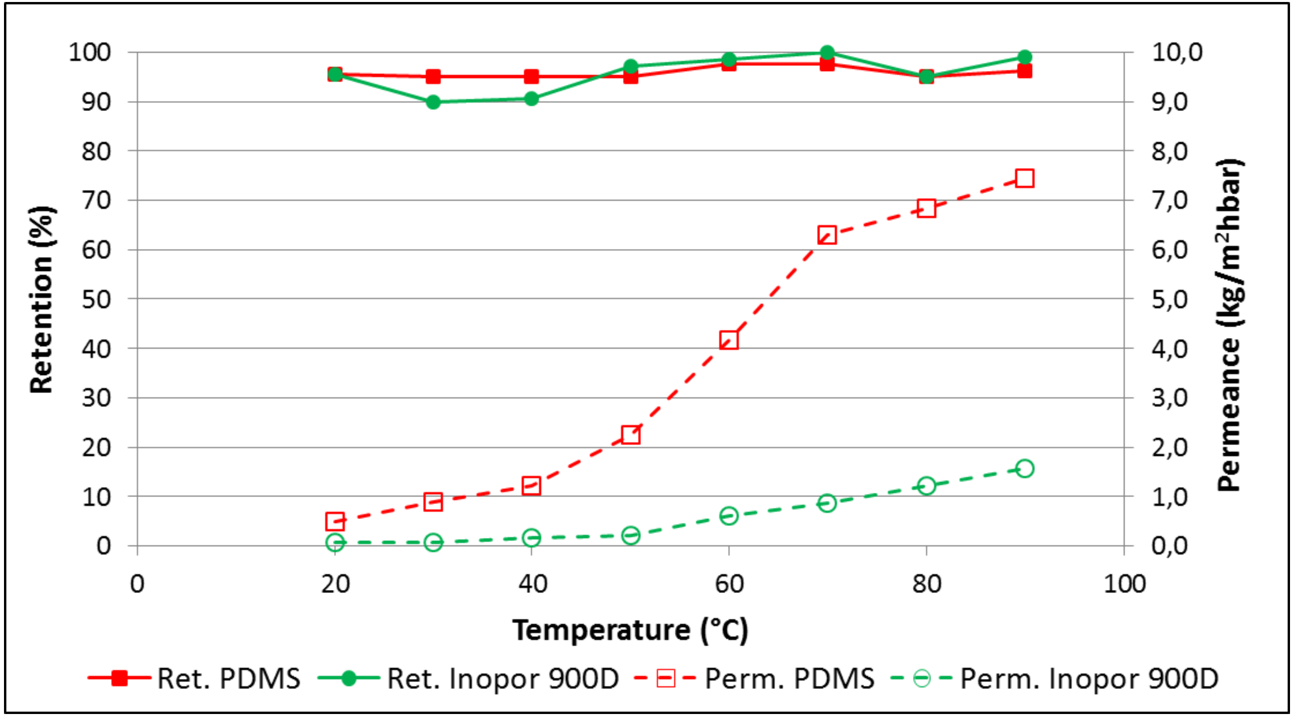


Organosolv processing: ECN patented idea



Organosolv processing first (model) tests

Acetone + PEG900, ΔP = 10 bar



First results PDMS on ceramic support are very promising

Conclusions

- Good performances of PDMS on tubular ceramic supports
  - Sunflower oil in hexane and toluene
  - Wilkinson catalyst in hexane
  - Gamma-alumina support better than alpha-alumina
- First results of ceramic supported PDMS in (model) organosolv processing are promising
  - Retention in wished range, permeances much higher than commercial (ceramic) membranes

Acknowledgements:

- Financial support from Dutch Ministry of Economic Affairs (EZ) is gratefully acknowledged
- Part of this work has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No. 731263 (project Ambition, HORIZON 2020 Call-LCE-33-2016)

Energy research Centre of the Netherlands
PO Box 1
1755 ZG PETTEN
The Netherlands

Contact
+31 (0)88 515 4949
info@ecn.nl

www.ecn.nl