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Comparing the Performance of Organic Solvent Nanofiltration Membranes in Non-Polar Solvents

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Supporting Information
available online

Organic solvent nanofiltration (OSN) is gradually expanding from academic research to industrial implementation. The need for membranes with low and sharp molecular weight cutoffs that are able to operate under aggressive OSN conditions is increasing. However, the lack of comparable and uniform performance data frustrates the screening and membrane selection for processes. Here, a collaboration is presented between several academic and industrial partners analyzing the separation performance of 10 different membranes using three model process mixtures. Membrane materials range from classic polymeric and thin film composites (TFCs) to hybrid ceramic types. The model solutions were chosen to mimic cases relevant to today's industrial use: relatively low molar mass solutes (330–550 Da) in n-heptane, toluene, and anisole.

Keywords: OSN membranes, characterization, solvent-interaction, model case, industrial application

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1 Introduction

Organic solvent nanofiltration (OSN), concerns itself with non-aqueous separations via a membrane. OSN is typically used for two purposes: (1) help to re-use a solvent or (2) concentrating- or recycling- a solute [1,2]. OSN has

attracted interest from both academics and businesses since its first proven commercial success, the MAX-DEWAX[®] process of 2001 [3]. Since then, a variety of applications in chemical-related, pharma and food industries has been displayed [4–7]. It is worth to mention that OSN is not focused on a single solvent like water, but includes work in a wide

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range of organic solvents. This has consequently led to a variety of OSN membranes reported in literature, each designed for “optimal performance” in specific solvent/solute mixtures. As affinities between membrane, solute and solvent vary, accurate comparison of membrane performance data when either or both the solvent and solute are changed is rarely possible [1,8]. Hence, experimental screening trials are essential for the scale-up of any laboratory-developed OSN membrane technology.

Currently, no widely accepted method for systematic OSN membrane testing is in place. This is not due to a shortage of proposed solutions. Many solutes have been advocated as cornerstones of ideal standard testing method but none can be regarded as universal. For instance, dyes often carry a charge, which makes it often difficult to discriminate between membrane adsorption and retention [9]. Also, ranges of oligomers have been proposed as “model solutes”. For example, polyethylene glycol (PEG) [10], polypropylene glycol (PPG) [11], polystyrene (PS) [12], and polyisobutylenes (PIB) [13–15] were all coined as ideal testing solutes. However, it is clear by now that such polymers themselves influence OSN performance. Consequently, combinations of these with various solvents, cannot be used as the single screening method for all OSN applications. Thus, testing a representative solvent-solute pair of similar chemical make-up and affinity close to the target case(s) seem to be more accurate and employed in this work.

Some of the most challenging separations occur in aromatic and aliphatic solvents. Many traditional membrane materials are not necessarily stable in these solvents. Classic polymer membranes may show poor performance because of swelling. Ceramic membranes, though stable, are as such not suited for non-polar solvent filtration due to their highly hydrophilic surface [16]. As a result, a variety of specialized membrane materials have been developed for use in the mentioned solvents.

The goal of this study was to compare the performance of OSN membranes developed by five project partners across three model cases, representative of demanding industrial process separations. The model cases were chosen to (a) provide laboratory-safe equivalents of mixtures used in industry and (b) to protect proprietary industrial process mixtures. All cases ask for membranes that can work in the molecular mass range of 250–550 g mol⁻¹.

The model cases are listed in Tab. 1. To accurately compare the permeance and retention of the various membranes and testing equipment used by the project partners, a round-robin test was first conducted on the same commercial OSN membrane.




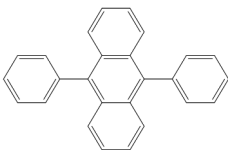
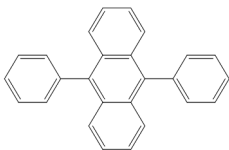
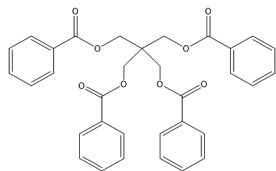
The other membranes used in this study were ranging from classic poly imide membranes and TFCs to modified ceramic membranes. The membranes and some of their relevant material properties are summarized in Tab. 2. The synthesis routes of these membrane fall outside the scope of this article and can be found in the Supporting Information.

To ensure a fair comparison across the testing equipment, a commercial membrane was first tested on each setup under the conditions of case 1. Those are the first results presented in Results and Discussion section. The performances of membranes for the other cases is presented after that.

2 Materials

The solvents used for membrane fabrication and membrane testing were sourced from various manufacturers. Unless otherwise indicated, solvents were analytical grade (99%) or above and used without further purification. The solutes used for cases 1, 2, and 3 were 9,10-diphenylanthracene (Sigma, ≥ 99%), and pentaerythritol tetrabenzoate (Sigma, ≥ 96%), all used without further purification. Solvent, solutes and concentrations used are given in Tab. 1.

Table 1. Solvents, solutes, and screening conditions of cases 1, 2, and 3.

	Case 1	Case 2	Case 3
Solvent	Toluene 92 Da 	n-Heptane 100 Da 	Anisole 108 Da 
Solute	 9,10-Diphenylanthracene 330 Da, 100 ppm	 9,10-Diphenylanthracene 330 Da, 100 ppm	 Pentaerythritol tetrabenzoate 553 Da, 0.2 wt.%
Conditions	20 °C, 20–30 bar	20 °C, 20–30 bar	50 °C, 20–30 bar

Ideally, the solute is to be retained while the solvent is free to pass through the membrane.

Table 2. Characteristics and provenance of the membrane types tested.

Sample family	Partner	Availability	Membrane architecture	Material		Max <i>T</i> [°C]
				Support	Selective layer	
ECN-Hybsi-NF	ECN-TNO	Semi-commercial	Ceramic-based hybrid	α -Al ₂ O ₃ / γ -Al ₂ O ₃	BTESE & CTAB	150
ECN-PDMS	ECN-TNO	Semi-commercial	Ceramic-supported polymer	α -Al ₂ O ₃ / γ -Al ₂ O ₃	Cross-linked PDMS	150
ECN-PI	ECN-TNO	Semi-commercial	Ceramic-supported polymer	α -Al ₂ O ₃ / γ -Al ₂ O ₃	Polyimide	150
KUL-PI	KU Leuven	Laboratory	ISA	Non-woven	Matrimid/polyimide	> 80
Solsep	Solsep™	Custom-made for project	TFC	Polyimide	Proprietary	80–120
TUD/UT-MA	University of Twente/Technical University of Delft	Laboratory	Ceramic-grafted polymer layer	α -Al ₂ O ₃ / γ -Al ₂ O ₃	Poly(alkene-co-maleic acid)	> 50
UT-PS	University of Twente	Laboratory	Ceramic-based hybrid	α -Al ₂ O ₃ / γ -Al ₂ O ₃	Polystyrene grafted-from γ -Al ₂ O ₃	100
UT-POSS	University of Twente	Laboratory	TFC	PAN	polyPOSSamide	160
VITO-FunMem	VITO	Semi-commercial	Ceramic-based hybrid	TiO ₂	Proprietary Grignard-grafted	150

3 Methods

A variety of membrane test setups were used. Both dead-end and cross flow setups were used with tubular or flat membrane geometries. The different set-ups used are listed in Tab. 3.

Table 3. Equipment configuration used by each partner.

Partner	Cross Flow (CF) or Dead-End (DE)	Geometry
University of Twente	CF	Flat sheet
VITO	CF	Tubular single-channel
ECN-TNO	DE	Tubular single-channel
Solsep	DE	Flat Sheet
KUL	DE, stirred	Flat sheet

Retention is expressed as a percentage solute removed from the retentate. Solute concentrations were determined by measuring the UV-Vis absorbance with a spectrophotometer. Calibration curves were made to ensure linear fitting over the solute concentration profile.

4 Results and Discussion

Literature comparisons of dead-end vs. crossflow configurations for OSN are scarce. The two analyses found [34,35]

suggest that diverging retention or permeance across different set-up configurations is seen only at high solute concentrations. Solutions of 50 mM of linear-chain tri-alkylamines in toluene suggested somewhat lower retentions in a cross-flow configuration than in dead-end configuration [34]. Another study [35] did not report significant differences in retention when comparing cross-flow and dead-end setups. In both cases, permeance decreased with increased solute loading, which confirmed an influence of mass transfer and suggest at least some concentration polarization.

The set-up configurations employed in this study are diverse, not only in terms of dead-end vs. cross-flow, but almost in every aspect, e.g., membrane cell geometry, means of pressurization, control instruments, sampling and test volumes, effective area. The solute concentrations used are ~ 5–10× lower than the examples discussed in [34,35] and the solute concentration is kept constant from set-up to set-up. Therefore, the impact of concentration polarization on either permeance or retention was expected to be minor, and independent of the set-up configuration. In case 3a concentration of 0.2 wt % (2000 ppm) was used across all set-ups, and therefore dead-end setups may have experienced lower than expected retentions.

Even within the same type of set-up configuration, other factors like the cell shape or cross-flow velocity might influence the membrane performance as well. However, an extensive study by Böcking et al. [36] showed that permeance and retention data are more connected to the characteristics of the membrane than to the set up.

For the round-robin test, a commercially available membrane (NF030105TMP19), provided by SolSep B.V., was used in the set-up of each partner. The test was carried out

with the Case 1 mixture. Overall, retention was measured after discarding the first few milliliters of permeate and the permeate was periodically recycled into the feed, effectively keeping feed solution at a near-constant concentration. Tests were done in duplicate on each set-up and all results are plotted in Fig. 1.

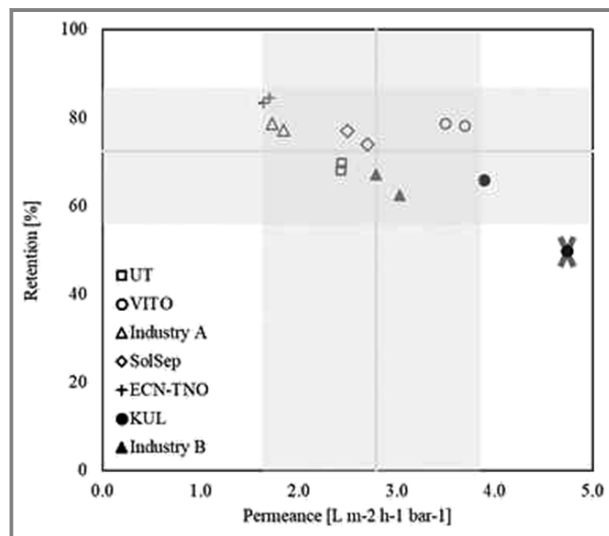


Figure 1. Round robin test results of commercial membrane (NF030105TMP19) supplied by SolSep tested on a case 1 feed at 10 bar of transmembrane pressure and room temperature. Open symbols represent cross-flow setups, filled symbols represent dead-end set-ups. The exception (X) was discarded when calculating the average P and R and their standard deviations. Horizontal and vertical lines and shaded area represent mean and standard deviation respectively. Error bars representing measurement uncertainty are omitted for clarity.

The mean permeance and retention are $2.80 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and 73 % with standard deviations of $0.9 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and 9 %, respectively. The data points shown in Fig. 1 at ca $2.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and 83 % were obtained from a module designed for dead-end set-ups but connected to a cross-flow setup. Hence, also such a setup gave results within the same significance interval. At higher recoveries, retentions may start to be concentration dependent, especially for dead-end set-ups. For all measurements, a Z-score is computed in order to assess the reliability of the measurement. Except for the outlier discussed previously, all Z-scores are below an absolute value of 2, indicating satisfactory results (see Supporting Information Tab. S2).

From the statistics we conclude that we can compare the experimental data between the set-ups as presented in the following section.

4.1 Results of other model systems and optimized membranes

Retentions as a function of permeance are plotted for cases 1 and 2 in Figs. 2 and 3, respectively. The membrane type

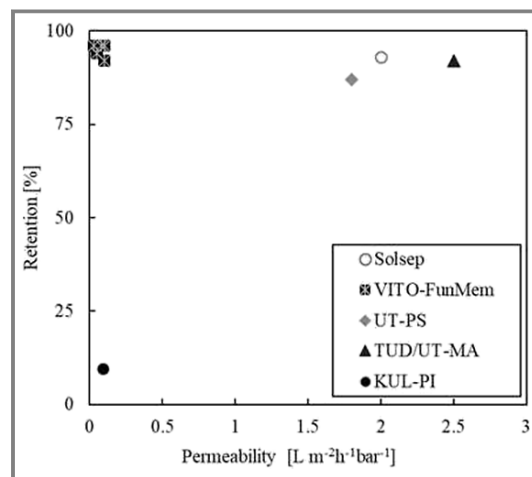


Figure 2. Permeance and retention results of case 1 experiments: toluene with 100 ppm DPA (333 g mol^{-1}). Each datapoint represents the average of three different measurements, for clarity error bars are omitted from this graph.

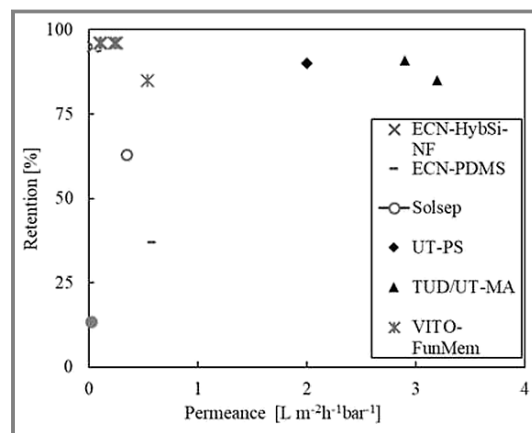


Figure 3. Permeance and retention results of case 2 experiments: n-heptane with 100 ppm DPA (333 g mol^{-1}). Each data point represents the average of three different measurements, for clarity error bars are omitted from this graph.

best-suited for separation in case 1 (100 ppm of DPA, MW 333 Da, in toluene) is TUD/UT-MA (red triangles) with a permeance of $2.9 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and a retention of 91 %. The highest permeances (around $3.2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) with retentions larger than 60 %, were observed for the TUD/UT-MA and UT-PS membranes. Classic phase inversion PI membranes (KUL-PI) shown low retentions. In further optimization trials such PI membranes exhibited negative retentions ($\sim -30 \%$), which is not uncommon for such materials [13, 36, 37].

Case 2 uses the same solute dissolved in n-heptane instead of toluene. As shown in Fig. 3, retention larger than 90 % was observed only for a few membranes. The membrane of VITO performed similar to case 1: high retention and low permeance. The SolSep NF-TM1 showed a permeance of $2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ coupled with a retention of 93 %.

However, the Solsep membrane NF-TM#2 that performed well in case 2 (n-heptane) only yielded a permeance of $0.35 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and a retention of 63 % in case 1. Again, the same KUL-PI membranes exhibit negative retentions (from -9 to -16 %) and low ($< 0.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) permeances. The UT-PS hybrid ceramic membrane showed a permeance of $1.8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and retention of 87 %, while TUD/UT-MA yields a permeance of $2.5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and a retention of 92 %.

It seems that retention of “classic” polymer membranes is more prone to interaction between solvent and polymer material. The ceramic-based, polymer-grafted membranes are less influenced by swelling which results in more pronounced retention for VITO, UT-PS and TUD/UT-MA membranes. The modified ceramic membranes show interaction with the solvent, but this seems to be minor. The selectivity-permeance trade-off that is often seen in other membrane systems can also be seen here.

Case 3 involves solvent and solute molecules that are quite similar. This may induce anomalous swelling of polymers. The retention measurements were performed at elevated temperatures (50 – 60 °C), and the results are shown in Fig. 4. A same trend as observed for case 2 was found: if the retention was high, the observed permeances were low. Most selective were the VITO-FUNMEM membranes with retention of ca. 78 % at permeance of ca $0.15 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. The hybrid membrane of ECN showed comparable results, with $0.18 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and 69 % retention at 60 °C. Also here: membranes that have interaction with solute/solvent but low or negligible swelling are the most selective. It should be noted that the membranes of case 3 were also tested at room temperature instead of at 50 – 60 °C and had zero to negligible permeances.

As a follow-up to this work, several of the best-performing membranes benchmarked within this study were selected for continued testing on mixtures of industrial interest.

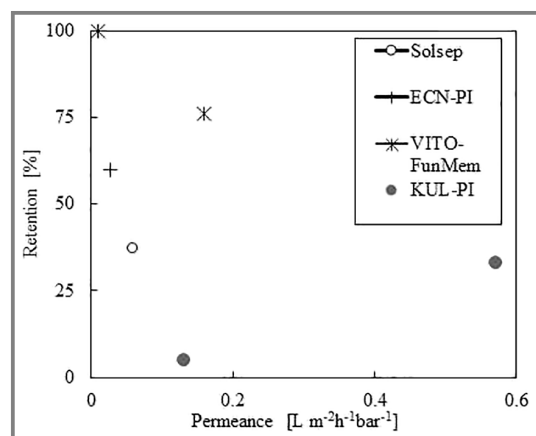


Figure 4. Permeance and retention results of case 3 experiments: anisole with 2000 ppm pentaerythritol tetrabenzoate ($\text{MW} = 553 \text{ g mol}^{-1}$). Each datapoint represents the average of three different measurements, for clarity error bars are omitted from this graph.

5 Conclusions

Several OSN membranes were tested on three industrially-relevant model mixtures by 5 different partners. The mixtures were solutions of n-heptane, toluene or anisole with low molecular weight poly aromatic compounds of molecular weight in the range of 330 – 550 Da. These are representative for certain industrial commodities and target was a maximal solute retentions (> 90 %) at reasonable permeance ($P > 1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$). Set-ups included cross-flow and dead-end configurations. A round-robin test with the same membrane by all partners confirmed that the results of different setups could be compared.

The optimized membranes were characterized in terms of retention and permeance. There was not a single membrane that could be used for all different model cases. Across all 3 cases, the membranes with polymeric supports had larger performance variations than the membranes with ceramic supports. Some of the polymeric membranes were only chemically stable for a specific case. Ceramic-based variants were stable but sometimes give nil-permeance as caused by their inertness. When polymeric membranes worked, they tend to give higher permeances. Until membrane-solute interactions become predictable, these results demonstrate the need for customized testing with representative synthetic mixtures when benchmarking OSN membranes for industrial processes.

For a full evaluation of membrane performance work with real process mixtures remains imperative to verify and develop the industrial application. As results obtained with proprietary industrials mixture are rarely disclosed the comparison of membrane performances on real mixtures stays difficult. Therefore, the gap between lab and industry will remain to be bridged using synthetic model mixtures.

One could argue whether a characterization system with a homologous range of polymers is better. In OSN the desired separations are mostly oriented towards separation of single molecules- and not eg ranges of polymers. Also, these homologue ranges bias the separation by their nature. Hence, we would advocate to spend more time to develop permeation methods using industrial relevant single solutes.

Note: this work was included in the oral presentation of F. P. Cuperus given at DGMT of March 23, 2021.

Supporting Information

Supporting Information for this article can be found under DOI: [10.1002/cite.202100032](https://doi.org/10.1002/cite.202100032). This section includes additional references to primary literature relevant for this research [24–40].

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Symbols used/acronyms

BTESE	bis(triethoxysilyl)ethane
CTAB	acetyl trimethylammonium bromide
DI	de-ionized
HAD	1,6-hexanediamine
NMP	N-methylpyrrolidone
PAN	polyacrylonitrile
PDMS	polydimethylsiloxane
PI	polyimide
POSS	polyoctahedral silsesquioxane
PS	polystyrene
THF	tetrahydrofuran
TFC	thin-film composite

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Comparing the performance of organic solvent nanofiltration membranes in non-polar solvents

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Research Article: A variety of organic solvent nanofiltration membranes were screened and characterized for three industrial model cases. The influence of setups and membrane type on the results were statistically verified and commented.



Supporting Information
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