Institute for Sustainable Process Technology

TENMIP Final Report (Openbaar)

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Penvoerder	ISPT
Naam Cluster directeur	Kees Roest
Naam Projectleider	Lies Bonami (Huntsman)
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Partners

HUNTSMAN

SHELL

SolSep BV
Robust Separation Technologies

KU LEUVEN

vito

ECN › TNO innovation for life

UNIVERSITY OF TWENTE.

Publiek eindrapport

1. Samenvatting

a. Uitgangspunten

Within the project 'Testing and Evaluation of Nanofiltration Membranes in Industrial Processes' (TENMIP) it was evaluated if nanofiltration can replace energy intensive distillation. Two Industrial partners (Shell and Huntsman) selected 5 industrial processes for which the separation is difficult and/or energy intensive. Five membrane developers (Univ. Twente, KU Leuven, ECN part of TNO, VITO and SolSep) selected 5 membrane composition concepts within their own range of expertise that could potentially be suitable for the proposed cases. The difficulty lays in small differences in size, shape, polarizability and complexity of the compounds to be separated. Also, the low molecular weight cut-off of less the 300 Da needed for these separations and the high process temperatures (>100°C) are a challenge.

Proven membranes types screened first on model mixtures and tailored to optimize the performance for the selected cases. In this way over 100 screening experiments were done on varying membrane types, cases and/or conditions. The best preforming membranes were selected per case and tested for the process mixtures.

It was shown through tests with model mixtures that it is possible to obtain good separation with a good permeate flow with some membrane types. However, the results could not be reproduced using the actual process mixtures or under actual process conditions. This was probably due to specific differences in composition between the industrial process mixtures and model feeds.

The economics of OSN separation for the 5 industrial processes were calculated, using an excel based calculation tool, and when possible compared to the existing process. It was found that two membranes tested in the model mixtures meet the required separation demand as set by the end-user.

2. Discussie

a. Resultaten

The cases for Shell did focus on the separation of Poly Cyclic Aromatics (PCAs) from a hydro wax stream (hydrocracker bottom product) either by direct removal using membrane separation or by an indirect removal using solvent extraction. For the latter route the recovery of the solvent (solvent-PCA separation) by membrane separation was examined in the project.

In the Huntsman cases, because of the highly reactive nature of isocyanate and EHS concerns, isocyanates can cause allergic reactions, it was chosen to work with model compounds for the screening of the membranes. The model compounds were selected to approximate (regarding MW, geometry, functional groups, polarity) the process compounds as much as possible, but also be safe and easy to use.

Membranes were tailored from five different membrane producers (Univ. Twente, KU Leuven, ECN part of TNO, VITO and SolSep) for these industrial cases.

<u>ECN part of TNO - HybSi membranes</u>

For the hybrid silica membranes tailoring of the membrane was done via two routes. First, the pore size of the tubular ceramic support was increased to reduce the resistance for liquid transport. This was done by increasing the calcination temperature of the gamma-alumina based intermediate layer. Secondly, the incorporation of a micellar structure into the final membrane layer was done to open the pores a bit further.

This should lead to a higher permeance for the solvents, still maintaining the good retention of the HybSi membrane. The component CTAB (cetyl trimethyl ammonium bromide) was used as ionic surfactant to accomplish this. Via these modifications the membrane permeance was increased by a factor of 6. In the different model mixture tests it was shown that for this modified HybSi membrane the permeance is low a room temperature, it very strongly increases with temperature and remains a good retention at high temperature.

University of Twente - Highly crosslinked membranes

Membranes prepared at Twente were tested for cases 1 and 2. The membrane type best-suited for separation in Case 1 is based on grafting of maleic anhydride and shows a permeability of 2.9 $L.m^{-2}h^{-1}bar^{-1}$ and a retention of 91%. The highest permeabilities (around 3.2 $L.m^{-2}h^{-1}bar^{-1}$), coupled to with retentions greater than 60 %, were observed.

The polystyrene grafted membranes also perform well, with a permeability of 1.8 $L.m^{-2}h^{-1}bar^{-1}$ and retention of 87%. The polystyrene graft on the UT-PS membranes can swell, but the porous ceramic membrane architecture remains inert to swelling. The different swelling degree of the PS graft from solvent to solvent was shown to impact the permeability and retention to a limited degree. The maleic anhydride functional groups of the TUD/UT-MA membranes ensure frequent attachment to the external surface, thus preventing excessive polymer swelling.

SolSep - Block-copolymer systems

SolSep has a few platforms to adapt membranes to certain OSN applications. These are typically polymer-based. For the several cases mentioned first overall stability was checked, by combinations of materials, varying polarity as well as ´cross link density` within a certain class of materials optimization of the separation performances is strived for. Based on a proprietary system in which polarity, physical and chemical crosslinks play an important role, membranes were modified and screened for their performance in the five model cases exhibited by the large industries. The model systems were all performed at room temperature. In a few cases were crosslinking was upgraded to the maximum, moderate to good retentions were found on model systems. However, these performances were lowered in the real systems, probably because of the –required- higher temperatures.

KU Leuven - Cross-linked polymeric membranes

All KU Leuven membranes were prepared by simultaneous phase inversion and crosslinking process. The polymer used Matrimid 5218 supplied by Huntsman. The separation performance of these crosslinked membranes was tuned by changing polymer concentration, solvent/co-solvent system, solvent/co-solvent ratio, and evaporation time before phase inversion in the casting solution. The crosslinked membranes were post-treated with different solvents (acetone and ethanol) and were evaluated for different cases in dead-end mode. For cases 1 and 2, these membranes had negative rejections of DPA in heptane and toluene, respectively. For cases 3 and 5, no conclusions could be drawn for the PETB – anisole mixture due to failing analytical methods. However, high rejection of 85 – 95% for the comparable dye Sudan Black together with good permeances (0,92 $L/m^2.h.bar$) were obtained.

VITO - Grignard-grafted ceramic membranes

The surface of commercial 1-channel 0.9 nm TiO_2 membranes sourced from Inopor (surface area of approx. 50 cm^2) was functionalized with various organic groups using both Grignard grafting, an innovative method developed and patented by VITO (FunMem), as well as phosphonic acid grafting, a method known in the art. The support membranes were first properly pretreated to remove adsorbed surface water, after which they were submerged for 48 h in a reaction mixture comprising a specific grafting reagent in diethylether. The reaction was carried out under dry atmosphere at room temperature and the reaction mixture was filtered through the membrane to maximize the contact with the complete pore surface. MgBr salts, formed as side-product of the Grignard reaction, were removed by a proper washing procedure. After washing, the grafted membranes were dried at 60°C under vacuum.

Selected membranes were tested on the synthetic test mixtures suggested by both Shell (Case 1 and Case 2) and Huntsman (Case 4), using a bench-top stainless-steel high-pressure cross-flow test set-up. The trials were performed at low permeate recovery, a cross-flow velocity of approx. 2 m/s, transmembrane pressures of 10-15 bar (using nitrogen gas for pressurization) and temperatures of 50-100°C, depending on the test mixture.

Generally, the modified membranes exhibited a better performance in terms of solvent flux (toluene, heptane, anisole) and solute retention (DAP, TMPD), compared to the unmodified titania membranes used as support. For both Shell cases (Case 1 and Case 2), fluxes as well as DAP retentions were shown to increase with increasing TMP and temperature. Despite being (very) selective (e.g. DAP retentions up to 96%) and chemically stable also at higher temperatures, permeabilities were relatively low under the operating conditions studied (up to approx. 0.8 $l.m^{-2}.h^{-1}.bar^{-1}$, depending on membrane, test mixture and operating conditions).

b. Perspectief voor toepassing

A round robin test has given more confidence for comparing results of different partners and anomalies in the results can reveal hidden problems. It is highly recommended to perform a round robin test at the start of a project when working with various partners and/or set ups.

The use of model mixtures was good from a safety point of view, so a lot of tests could be done. On the other hand, it was shown to be very difficult to reach similar membrane performances for the process mixtures as compared to model mixtures. One reason is for example the strong reactivity of some of the process mixtures that need better membrane pretreatment/drying. Another complexity is that for proper separation of components that are very similar in size other effects like polarity, polarization possibilities and other (temperature depended) specific interactions with membranes gain importance. Hence, these are not easy to mimic using other compounds.

Model mixtures should best be tested at the same conditions as the process mixtures as the performance of the membrane can significantly change when changing the operating conditions, e.g. temperature.

In the end two membranes tested in the model mixtures mixtures (for cases 1 and 3) meet the separation demand as set by the end-user. For case 2 and 5 one membrane is close to meet the demands in the model mixture. For case 4 none of the membranes meets the separation wishes. In the industrial process mixtures no membrane shows a result that meets the predefined criteria.

The current stage of development of all the TENMIP membranes, also the most successful ones, is lab-scale (TRL3-4). To verify the real possibilities membrane production should be lined-up and verified to element-prototype scale (TRL6-7).

c. Eventuele spin-off

UTwente wishes to further develop the membrane chemistries tested in this project in a follow-up project, where these membranes will be up-scaled from flat to tubular substrates.

VITO is currently exploring how the separation properties of the grafted ceramic membranes tested in this project, especially in terms of flux, could be significantly improved by finetuning of the grafting protocol. Important steps were taken towards the scale-up and commercialization of the FunMem technology, and a new semi-automatic installation for simultaneous grafting of up to 5 ceramic membranes at commercial scale was commissioned in 2018. Also, as a side-track from TENMIP, a novel type of grafting was explored, enabling widening of the application scope of the grafted ceramic membranes, amongst others for low MWCO separations in non-polar solvents at elevated temperatures, as studied in this project.

It is possible to obtain high retentions of organic compounds with a MW < 300 Da with some of the tested membranes, even at higher process temperatures, however mostly at the expense of low permeabilities. There is room to optimize that.

3. Bijdrage aan de doelstellingen van de regeling

A main driving force for exploration of membranes for separation of components in the mixtures with close boiling points is the potential energy saving. For current “easy” solvent recovery processes that incorporate distillation, energy reductions of 50-60 % have been calculated when using straight-forward NF. Mixtures that have close boiling points may benefit even more from the use of membranes as the distillation processes are intensive. This has also a techno-economic advantage.

In this project the possibilities were evaluated of organic solvent nanofiltration (OSN) in the lower molecular mass regions (<300 Da), particularly at higher temperatures (close to 100°C and beyond) in real process streams. This was extended to the assessment of close boiling molecules and homologue type of hydrocarbons. In these cases, the molecular weight difference between the molecules is relatively small. One could argue that membranes that should separate organic molecules that differ, say 200 Da, are typically reverse osmosis (RO) membranes for solventsMembranes that can achieve an efficient separation between components with small differences (size, shape, polarizability, complexibility) are not standard and definitely not available commercially at this moment. However, there are a few leads - five different proven membrane types - that set us on track to explore how such a membrane could probably look like.

4. Publieke communicatie / disseminatie

In general, the progress that was made in WP 5 was the facilitation of telco’s, organization and hosting of progress meetings, poster presentation at the ISPT day and facilitation of dissemination of articles and PR material.

Several deliverables have been produced. The kick-off meeting was organized and carried out. A midterm review was organized and carried out. Progress meetings four times a year were organized and carried out. Presentations for all partners were facilitated and published on Promise. Poster presentations were held each year at the ISPT day and will be presented at ISPT day 2019 in November. A progress presentation was kept up-to-date at all times.

We developed PR materials, facilitated communication within the project and wrote progress reports. Several articles were published online including a kickoff article and an article at the end of the report. Furthermore, all communication deliverables, scientific articles, etc. were authorized before release via the ISPT Promise online authorization loop.

All internal communications can be found on the ISPT plaza expect when the content was to confidential to share with other members of the ELS cluster who were not part of the TENMIP project.

- Regular progress meetings (15 Face-to-face or telecon meetings). Minutes of meeting and presentations can be found on the ISPT plaza.
- 3 scientific papers
- 3 poster presentations at ISPT-day (2016-2018)
- final report
- Project end poster at ISPT-day this year in November 2019
- Poster presentation at BMG Membrane Poster Day, June 5, 2018, Leuven (Belgium) (VITO):

Modified ceramic low cut-off nanofiltration membranes for separation in organic solvents at high temperature, Maider Coloma Jiménez, Matthieu Dorbec, Pieter Vandezande, Sara Salvador Cob and Anita Buekenhoudt

- Article in progress:

Testing and evaluation of organic solvent nanofiltration membranes in industrial processes, Renaud Merlet, Louis Winnubst, Arian Nijmeijer, Mohammad Amirilargani, Ernst Sudhölter, Matthieu Dorbec, Sara Salvador

Cob, Pieter Vandezande, Soraya Sluijter, Henk van Veen, Petrus Cuperus, Ingrid Wienk, Yusak Hartanto, Ivo Vankelecom, Patrick de Wit

- Article in progress:

"Temperature and solvent-stable cross-linked polyamide membranes for separating non-polar mixture" The possible authors based on the order would be Subhalaxmi Behera, Yusak Hartanto and I.F.J. Vankelecom.

- Poster at Organic Solvent Nanofiltration 2019 Conference

5. Acknowledgement

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