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TNO report

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Organic solvent nanofiltration membranes on low cost ceramic supports (COSMOS)

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UNIVERSITY OF TWENTE. COORSTEK Shell Institute for Sustainable Process Technology

Samenvatting

Introductie
Een significant deel van het energiegebruik in de procesindustrie wordt gebruikt voor scheidingen. Membraantechnologie heeft de potentie om de huidige inefficiënte distillatieprocessen te vervangen of aan te vullen en hiermee op het energieverbruik van de industrie te verminderen. Om de implementatie van dergelijke technologieën te bespoedigen is zowel een kostenreductie en verhoging van de kwaliteit en betrouwbaarheid van membranen van belang.
COSMOS ontwikkelt stabiele keramische membranen, die kleine moleculen (molecuulmassa van 200 – 800 gram per mol) kunnen scheiden uit organische oplosmiddelen. Deze keramische membranen hebben het voordeel dat ze stabiel zijn in de meeste organische oplosmiddelen en bestand zijn tegen hoge temperaturen, wat nodig is voor de toepassing binnen met name de petrochemie.

Doelstelling van het project
Het COSMOS project heeft als doel stabiele keramische en hybride membranen, die voldoen aan de wensen en eisen van de eindgebruikers, te ontwikkelen en op te schalen. Bovendien richt het zich op een reductie van de productiekosten van dergelijke membranen. Twee specifieke toepassingen worden geëvalueerd: polycyclische aromaten (PCA) verwijdering en concentratie van eetbare oliën en aceton recycling in de voedingsindustrie.

Resultaten
De belangrijkste resultaten binnen het project zijn:
- Een kostenreductie van keramische membranen door dragers op grote schaal en geautomatiseerd te produceren (CoorsTek) en het aantal stappen om een geschikt membraan te maken te verlagen.
- Een nieuwe generatie georganiseerde mesoporeuze silica membranen (MSMs) aangebracht op een poreuze dragen door middel van Stöber-solution pore-growth approach.
- Thermisch stabiele membranen gebaseerd op hybdride silica en polyimide aan de binnenkant van keramische dragers met een selectiviteit voor moleculen kleiner dan 330 Dalton (MWCO < 330 Da), klaar voor verdere opschaling.
- PDMS membranen aan de binnenkant van keramische dragers met een selectiviteit voor moleculen met een gewicht van 800 Dalton, klaar voor verdere opschaling.
- Techno-economische evaluatie voor de twee toepassingen:
  - Veelbelovende business case voor de PCA casus bij hoge concentratie factoren.
  - Het economische voordeel van de energiebesparingen van de eetbare olie casus is momenteel niet voldoende voor een haalbaar proces.
- Een roadmap naar de toepassing van de keramische membranen, inclusief de volgende stappen in vervolgprojecten en missende partners voor commerciële toepassing.

Contents

1 Project details

Project title	Organic solvent nanofiltration membranes on low cost ceramic supports (COSMOS)
Project number	TEEI117016
Coordinator	TNO
Project period	01.10.2017- 31.06.2021
RVO Program line	1b. Heat: – Efficient process technology (efficient separation technology as alternative for distillation)

This project is funded by the Dutch Ministry of Economic Affairs, National Regulations EZ-grants, Topsector Energie executed by the Rijksdienst van Ondernemend Nederland.

Project partners:

Organisation	**location**	**Main contact**	**e-mail**
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2 Background and objectives of the project

2.1 Introduction

Within the process industry, nearly 25% of the energy is used for (thermal) separation processes. The main separation process used is distillation, which has a low energy efficiency. It is well known that membrane processes are significantly more energy efficient compared to distillation. Organic Solvent Nanofiltration (OSNF), specifically, is a very energy efficient alternative for energy intensive separations like distillation. Yet it is presently limited to separations with relatively large (size) differences between the solvent and the component(s) to be separated (typical Molecular Weight Cut Off (MWCO) > 500 Da). Expansion of OSNF to separations in lower molecular mass regions (< 300 Da) will open up a plethora of possible applications in industry, leading to significant energy savings. Another challenge is to develop membranes capable of performing these separations at elevated temperatures (> 100 °C), and separate based on small differences (e.g. size, shape, polarity) between the components of a mixture.

Within the project "Organic solvent nanofiltration membranes on low cost ceramic supports (COSMOS)", hybrid silica-based NF membranes with a MWCO of < 300 Dalton as well as for a less challenging application of MWCO ~800 Da in the food industry are developed. Due to their unique solvent resistance, we have selected hybrid silica membrane materials as a basis for developing solvent stable nanofiltration membranes that meet the demands as set by the industry. The general idea of the COSMOS project is to use sol-gel technology to modify the structure of hybrid silica-based membranes to make organic solvent nanofiltration (OSNF) membranes with tuned retention in OSNF and test these membranes in selected industrial mixtures. Furthermore, existing polymers are applied to the ceramic supports.

The sol-gel and polymer membrane technology is combined with the ceramic membrane support developments running at CoorsTek in Uden. CoorsTek uses their large scale ceramic processing facility for preparation of ceramic membrane supports and has taken major steps in setting up the infrastructure for single-channel, multichannel and hollow fiber supports (Figure 1). Their large scale production, advanced quality control, and the fact that they normally deal with large quantities of ceramic components will lead to high quality, tuneable and low cost supports.

Figure 1: Illustration of large scale production infrastructure of CoorsTek (left) and multichannel or multitube supports (right).

OSNF membranes R&D in the Netherlands is focused largely on fundamental development of membranes (TRL 2-4). Scaling-up of these and other membranes is still required. The developments of low cost ceramic supports at CoorsTek combined with selective membranes developed in this and previous projects, allow for scale-up of these membranes and low cost solutions for the mentioned highly demanding applications. In the case of OSNF, the membrane costs in combination with stability and lifetime are limiting factors that need to be solved to come to implementation.

2.2 Project objective(s)

The aim of COSMOS was to scale-up hybrid silica and polymer-based OSNF membranes to 0.1 m^2 of membrane area using low cost, high quality ceramic supports. By this, a breakthrough is obtained in stable low cost organic solvent nanofiltration membranes and the position of the Dutch industry in playing a major role in production of these membranes. This project aims at developing a 40% more efficient separation process via replacement of thermal separation by pressure-driven separation processes. For efficient separation of the selected aromatic and aliphatic mixtures the membranes targets are i) a permeance of ≥ 1 $L/m^2.h.bar$ and ii) a retention of 200 Dalton at temperatures up to 140 °C. For the concentration and recovery of edible oils in the food industry ii) a retention of 800 Dalton is sufficient.

This project will support the implementation of organic solvent nanofiltration membranes on low cost high quality ceramic (hollow fiber and multichannel) supports in higher temperature applications in the (petro)chemical and food industry. The combination of higher temperatures, solvents and a retention of 200 Dalton is novel and has not been done and established before.

3 Method and results

3.1 Method

The project consisted of six interrelated work packages (WP) as depicted in Figure 2.

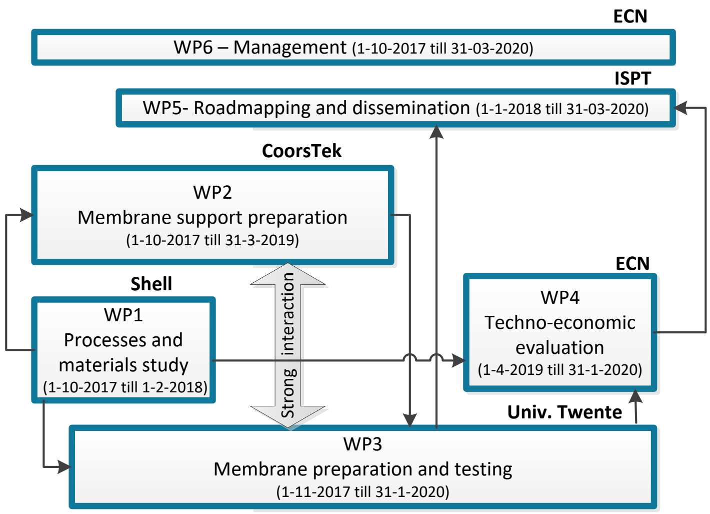

Figure 2: Project overview showing the different work packages and their interrelations.

First, specific applications around the cracker and in the food industry were selected by Shell and TNO, respectively. In WP2, CoorsTek manufactured low cost hollow fiber and multi-channel ceramic supports using their unique large scale production facilities. UTwente and TNO set-up techniques for applying hybrid silica and polymeric nanofiltration membranes on the ceramic supports. The membranes have been characterised by flux and retention measurements with model mixtures (WP3). An evaluation has been made of the techno-economic potential in the end-user processes including the energy savings options (WP4). A roadmap and strategy towards membrane production scale-up and implementation has been set-up in WP5. The ISPT network has been used to disseminate results and connect the technology to the program and its ELS cluster roadmap.

3.2 Results

WP1: Processes and materials study

Goal:

- Specify application requirements for membrane development and testing.

Results:

- Factsheet case 1.
- Factsheet case 2.
- Model mixture selection.
- Literature overview, material selection and modification strategy.

<u>Factsheets</u>

The end-user Shell in combination with TNO set specific process applications on which the membrane development and testing was focused in COSMOS. Shell recognizes many opportunities using OSNF for the separation of aromatic and aliphatic mixtures around the cracker and refinery applications in general. They defined a specific representative case, case 1: Poly Cyclic Aromatics (PCA) removal from waxy hydrocarbon stream. A factsheet was set-up containing details on i) the composition and flow rates of the process streams ii) product purities and volume requirements iii) molecules to be separated including setting model mixtures and marker molecules, iv) recycle options possible within the process, v) wishes on side stream (re-)use, vi) process conditions, vii) a general flowsheet of the existing process and of the wished nanofiltration based process including main mass and heat balances and economics, viii) sample delivery to the testing partners, ix) safety information of the applications (MSDS).

TNO formulated a second use case from the food industry, based on process information available from the EEMBAR project (ISPT-BL-20-12): edible oil concentration and acetone recovery process (Figure 3). In the process from Bunge IOI Loders Croklaan, a mixture of 10 % shea nut oil/shea olein in acetone, or palm oil is concentrated and acetone is recycled. The capacity of the process is 20 ton/hr of 10 wt.% oil in acetone. Details and assumptions were described in the factsheet.

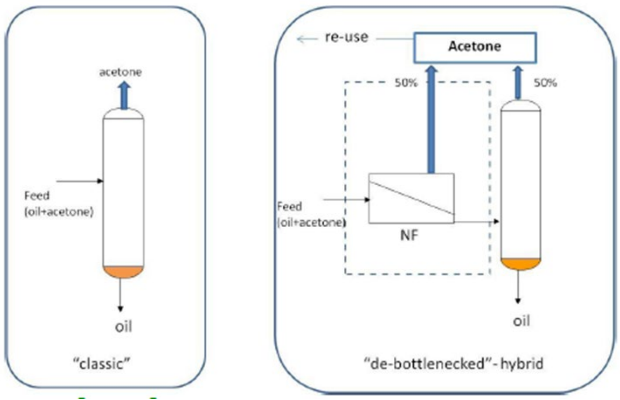

Figure 3 Block scheme or flowsheet of part of the present process (left) to be evaluated and the new NF process (right) (info taken from EEMBAR project poster ISPT Day 2017).

<u>Model mixture selection</u>

Standard test procedures (including analysis, pressures and temperatures) were agreed upon and documented to test the properties of novel membranes first:

- Full retention curves using various polyethylene glycols (PEGs) for membranes of which the retention is unknown.
- Targeted retention measurements with marker PEG of specific size.

Testing of the PCA removal case was limited to PEG (200 Dalton) in acetone and toluene at temperatures up to 90 °C. Within the TENMIP project, a model mixture DPA (diphenylantracene) in toluene was also defined. For the edible oil application tests, sunflower oil (10%) in acetone was selected as model mixture. The results of these tests are described accordingly in WP3.

<u>Materials overview and decisions</u>

A literature review on hybrid silica precursors, additives, pore formation molecules (co-polymers, surfactants, micelles, thermal degradable additives, etc.), sol-gel chemistry and pore transport of liquids in meso and microporous systems was performed by TNO and UTwente. Together with the process input, this led to the following strategy for membrane modification. For the case of PCA removal, hybrid silica membranes having a MWCO of 250 Da and developed previously, were selected as base membrane. However, the permeance of these membranes should be improved. Therefore, at the UTwente, the organisation and alignment of the mesopores was investigated. At TNO, the bis-tri-ethoxy-silyl-ethane (BTESE) precursor combined with the templating agent cetyl trimethyl ammonium bromide (CTAB) from now on called *OSNF-HybSi,* was selected for the PCA removal case. For the edible oil application, the polymeric membranes crosslinked polydimethylsiloxaan (PDMS) and Polyimide (PI) on the ceramic CoorsTek supports were chosen.

WP2: Membrane support preparation

Goal:

- Preparation of high-quality low-cost support, including intermediate layers to obtain defect free membranes.

Results:

- Single channel supports available for first coating experiments.
- (Limited number) of intermediate layers on ceramic supports to obtain defect-free membranes.
- Hollow fiber and multichannel ceramic supports that can be used for low cost OSNF membranes.

<u>Single channel support fabrication</u>

CoorsTek manufactured several single channel alumina supports. Especially, the strength of the supports was improved. The 0.2 and 0.6 µm supports were selected and as they represent the pore sizes that are required for defect-free membranes, and delivered to TNO. These supports are all stable up to 1200 °C.

<u>Intermediate layers</u>

The traditional ceramic supports used at TNO require several layers before the selective top-layer can be applied successfully, leading to high quality membranes. The pores of the extrusion-based support are too wide to directly apply the dense top layer. Therefore, first one or two α-Al_2O_3 (AKP) layer are applied, followed by a γ-Al_2O_3 layer, as depicted in Figure 4. These additional steps add to the cost of the final membrane, thus in the COSMOS project we aimed at reducing the number of intermediate layers by tuning the recipes.

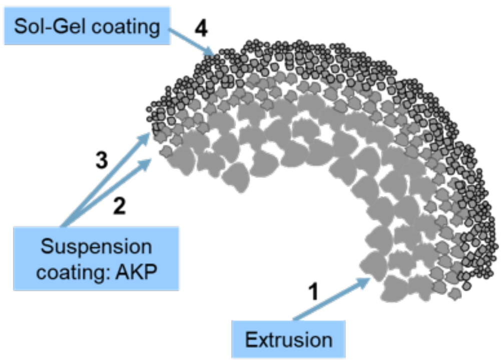

Figure 4: Build-up of the ceramic membrane supports.

First, the amount of intermediate layers and thus required coating steps have been reduced for the 200 nm support (Figure 5) on the outside of tubular supports. No AKP layer was required to obtain a defect-free gamma layer on this support. For the support having a larger pore size (600 nm) the gamma layer infiltrated in the pores and 2 AKP layers were found to be required.

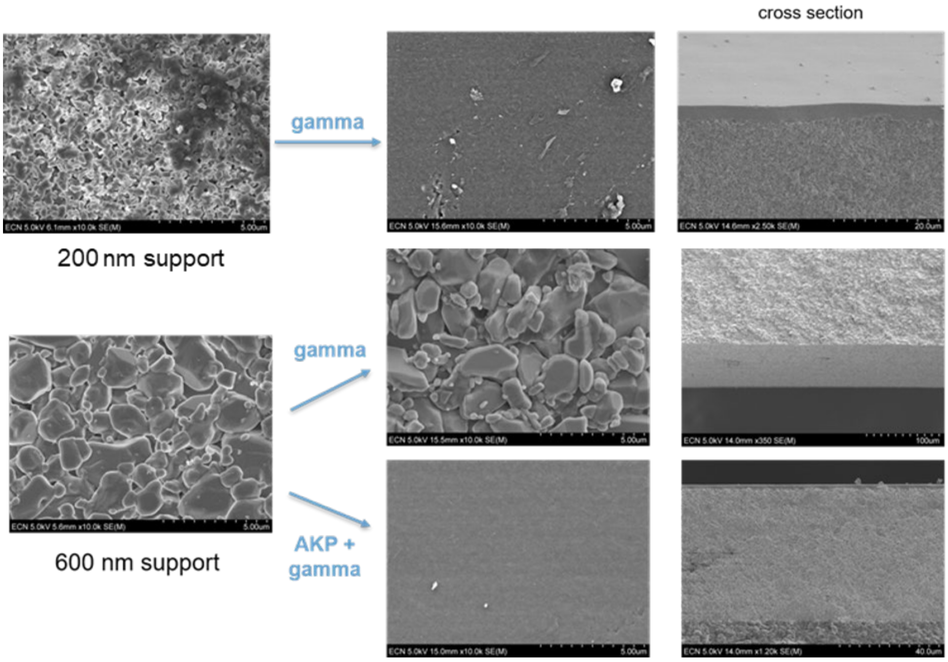

Figure 5: Overview of route to good OSNF membrane support, SEM images of surface and cross-section layers.

Subsequently, the intermediate layers were coated on the inside of the supports to allow for scale-up in multitube modules or multichannel supports. Therefore, the coating set-ups were adapted (Figure 6). Coating using a peristaltic pump led to significant defects in the membrane support, which was attributed to gas bubbles in the sol. Using communicating vessels and adapted coating procedure high quality supports were obtained after sintering at 600 °C, as was confirmed by visually inspection and characterisation by bubble point (BP), SEM and Helium flow.

Figure 6: Set-up for coating on the outside (left) and inside (right) of tubular supports.

<u>Hollow fiber and multichannel ceramic supports that can be used for low cost OSNF membranes:</u>

Hollow fiber (~2 mm diameter) and multichannel (small scale) ceramic supports can be produced at CoosTek, but were not delivered to TNO for coating as more effort was required to tune the recipes to obtain good membranes on the single-channel supports. The current recipes are expected to be reasonably easily translated to hollow fiber supports. The advantages and disadvantages of the different configurations have been investigated and are discussed in WP4.

WP3: Membrane preparation and testing

Goal:

- Development of membranes for the selected applications requiring retention of 200 and 800 Da and permeance of 1 $L.m^{-2}.h^{-1}.bar^{-1}$.

Results:

- Hybrid silica on flat-disk.
- OSNF membranes based upon i) hybrid silica applied on the inside of a multichannel ceramic support and ii) polymeric layers applied on the inside of a hollow fiber ceramic support. (Multichannel and multitube).
- Reports describing the functionality of the membranes in the two applications.

<u>Hybrid silica membrane development on flat disks</u>
In this activity, silica-based membranes on flat disk supports have been developed. To combine high-flux and high-rejection properties, membranes consisting of uniform and vertically organized mesopores are promising systems for OSNF. To this end, a new generation of mesoporous silica membranes (MSMs) has been developed, in which an organized mesoporous layer is directly formed on top of a porous ceramic support via a Stöber-solution pore-growth approach (Figure 7) instead of the conventional evaporation-induced self-assembly (EISA) method.

First, tetraethoxysilane (TEOS) based membranes were prepared[1]. By using a template (structure directing agent) and this precursor under basic-catalyzed sol-gel conditions, it was possible to form mesoporous silica materials with tailored pores shapes (2D/3D hexagonal) and diameters (1-10 nm). During further treatment, the template is removed to generate corresponding pores in the final material. Relevant characterization methods have been used to demonstrate the growth of the membrane separation layer and the effect of reaction time and the concentration of the reactants on the microstructure of the membrane.

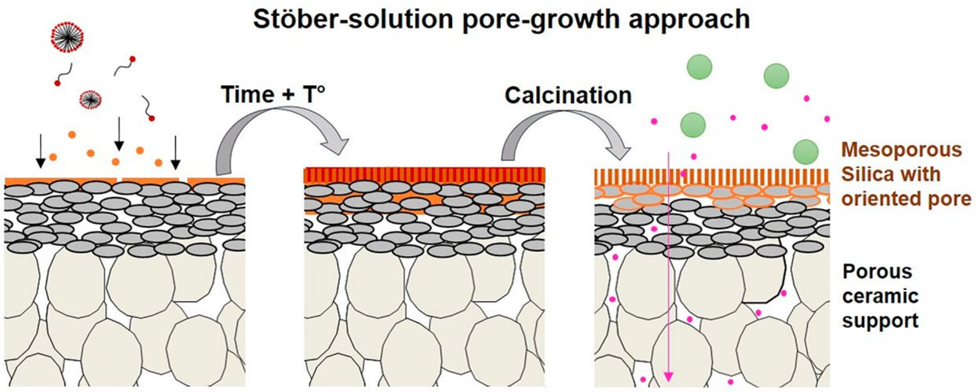

Figure 7: Schematic representation of Stöber-solution pore-growth approach.

Using this method, we prepared silica-based membranes consisting of accessible pores with a diameter of 2.5 nm. Compared to previous studies using the EISA

[1] Pizzoccaro-Zilamy, M.-A.; Huiskes, C.; Keim, E. G.; Sluijter, S. N.; Van Veen, H.; Nijmeijer, A.; Winnubst, L.; Luiten-Olieman, M. W. J. New Generation of Mesoporous Silica Membranes Prepared by a Stöber-Solution Pore-Growth Approach. *ACS Appl. Mater. Interfaces* **2019**, *11* (20).

method to prepare MSMs, an important increase in water permeability was observed (from 1.0 to at least 3.8 $L.m^{-2}.h^{-1}.bar^{-1}$), indicating an improved pore alignment. However, the molecular cut-off measurements (MWCO ≈ 2300 Da) were outside of the NF range (MWCO> 1000 Da).

When using BTESE as hybrid silica precursor and additives/templates via oil in water templated basic-catalyzed sol-gel synthesis, the membrane *MHSM-B1* with a pore size between 1 and 2 nm was obtained. Relevant characterization methods have been used to demonstrate the growth of the membrane separation layer and the effect of reaction time and the concentration of the reactants on the microstructure of the membrane. Compared to our previous studies on mesoporous silica membrane, a similar water permeability was obtained (3.5 instead of 3.8 $L.m^{-2}.h^{-1}.bar^{-1}$). Most importantly, we showed that it is possible to prepare hybrid silica nanofiltration membranes with high retention for PEG with a molecular weight of < 600 Dalton Figure 8). This preliminary work showed that the Stöber-solution pore-growth approach is also applicable to organosilica systems.

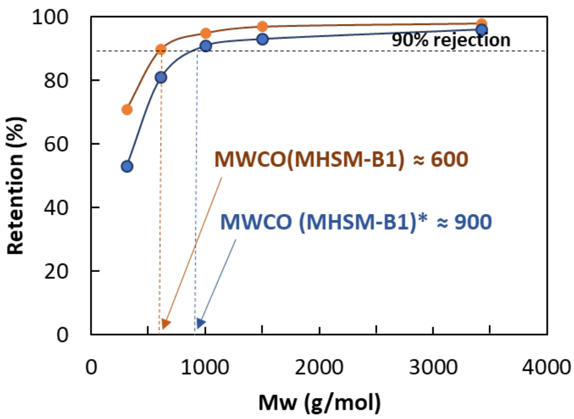

Figure 8. Polyethylene glycol MWCO measurements for the mesoporous hybrid silica membrane, HSM-B1.

This work was replicated by a student and also by TNO. However, it turned out to be difficult to reproduce the results. This is attributed to poor adhesion to the support and collapse of the membrane structure due to decomposition of the organic part of the hybrid pore walls during surfactant removal between 300-500 °C. In the follow-up project PoSimem (see 4.2) that has recently started, the goal is to control the layer formation and tailor the layer thickness, pore size, and membrane morphology as well as improving the interaction between support and membrane.

<u>Hybrid silica membrane development on tubular supports</u>

In order to tailor hybrid silica membranes, the incorporation of a micellar structure into the final membrane layer was applied to open the pores, which should lead to a higher permeance for the solvents, while retaining acceptable retention. The recipes for coating the *OSNF-HybSi* top layers on ceramic supports were adapted to result in high quality supports on the inside of CoorsTek supports. Coating was performed using the set-up described earlier. The resulting membranes were characterized and tested as is described below.

<u>Polymeric membrane on ceramic tubular supports</u>

PDMS and PI were selected as promising candidates for the separation of edible oils from acetone. Previous research showed that PDMS has the appropriate MWCO. It was found that a γ-Al_2O_3 layer is essential to obtain good membranes using PDMS. For PI, two different concentrations (1 and 2 wt.%) were selected for coating using the same installation as for the Boehmite and hybrid silica membranes. Both led to sufficiently good membranes, but the concentration had a significant influence on the layer thickness (Figure 9) and consequently on permeance, as described below.

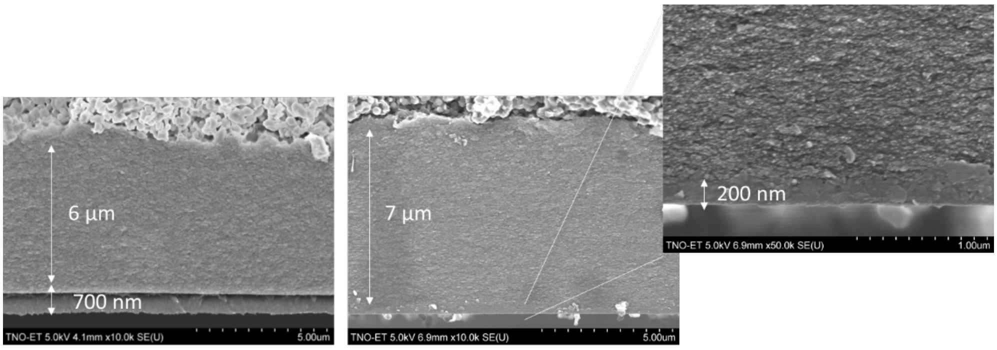

Figure 9: SEM images of cross sections of PI membranes on ceramic supports including layer thicknesses: 2 wt.% left and middle and 1 wt.% right.

<u>Testing of membranes</u>

The NF filtration set up at TNO was adjusted to enable testing of membranes with the selective layer on the inside of tubular supports and at high temperatures. A new module, temperature control unit handling up to 130 °C and 30 bar, and an HPLC pump for cross-flow of 40 mL/min were purchased and incorporated in the installation.

OSNF-HybSi

In previous model mixture tests, it was shown that for the *OSNF-HybSi* membranes the permeance strongly increases with temperature and retains good retention values (e.g. for DPA) at high temperatures. This trend was also observed using the *OSNF-HybSi* membrane on the inside of the CoorsTek supports. However, in this case, the retention also increases at higher temperatures. This is attributed to minor defects in the membrane, that allow both the solvent and marker molecules passing across the selective layer at lower temperatures, whereas at higher temperatures the transport through the mesopores starts resulting in selective separation. For PEG400 in acetone, 99% retention was observed with a permeance of 0.2 $kg.m^{-2}.h^{-1}.bar^{-1}$ at 90 °C. For DPA in toluene, 79% retention was measured with a permeance of 0.08 $kg.m^{-2}.h^{-1}.bar^{-1}$ at elevated temperature. These permeances are less than the ones measured in the TENMIP project, but comparable to the numbers obtained with OSNF-HybSi membranes on the outside of CoorsTek supports. This is attributed to the resistance for liquid transport caused by the pore size of the γ-Al_2O_3 intermediate layer and can be improved, for example, by increasing the calcination temperature of the gamma-alumina layer.

Testing polymeric membranes on ceramic supports for edible oil case

The PDMS membranes showed good retention of sunflower oil (85%) in toluene with a permeance of 0.5 $kg.m^{-2}.h^{-1}.bar^{-1}$, approaching the target of 1 $L.m^{-2}.h^{-1}.bar^{-1}$. PDMS is known to swell in solvents changing the MWCO and permeance accordingly. Unfortunately, the membrane leads to an MWCO of 2000 Da in acetone, which makes it unsuitable for the food application.

PI on ceramic supports was found to be a promising candidate for this separation. 98% retention of PEG1000 was measured for the membrane based on the 2 wt.% recipe. Even PEG400 was surprisingly retained with up to 98% at 90 °C. As expected, a higher permeance is observed for the 1 wt.% recipe with a thinner top layer than the 2 wt% membrane, even reaching 1 $kg.m^{-2}.h^{-1}.bar^{-1}$ at 110 °C in this model mixture. This successful membrane (PI 1 wt.%) was therefore also applied in the model mixture DPA in toluene. Here, it showed a similar trend to the OSNF-HybSi membranes of good properties at elevated temperatures with 90% retention, but a disappointing 0.06 $kg.m^{-2}.h^{-1}.bar^{-1}$ permeance at 130 °C. Commercial PI-based membranes are available from Evonik with MWCO values of between 150 and 400 Da (Starmem™122 and 240, Duramem™150, 200 and 300). However, these membranes have reported stability for operation at temperatures up to only 50 °C. The PI membranes were tested for up to four days without decline in performance.

WP4 Techno-economic evaluation

Goal:

– Evaluation of economic feasibility for application of the novel OSNF membranes in the selected processes, including requirements on the membrane processes and materials.

Results:

– Report on techno-economic assessment for two applications.

The economics of nanofiltration membrane based separation processes have been calculated for the cases defined in WP1.

PCA removal from waxy hydrocarbon stream

For the PCA case, the economic based target should be to just reach the technical specifications of the hydrowax (retention of 90%) at a concentration factor as high as possible. At a permeance of 1 $kg.m^{-2}.h^{-1}.bar^{-1}$ and a retention of 90%, a concentration factor of 12 is needed to come to an attractive Return on Investment (ROI) of 2 years (Figure 10). From an economic point of view, this is an attractive process. Previous test data using model mixtures have shown that a permeance of 2 $kg.m^{-2}.h^{-1}.bar^{-1}$ in toluene and a retention of 98.6% for the model component DPA at 90 °C is possible, thus these requirement are met. However, these results have not been reproduced since then.

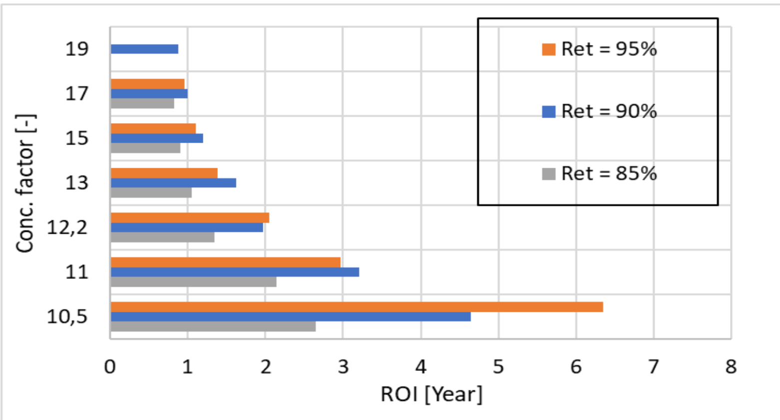

Figure 10: ROI as a function of the concentration factor for the PCA case at various membrane selectivities.

Edible oil concentration and acetone recovery process

For the second case, the economic benefit should come from energy savings of a hybrid OSNF-distillation process compared to the conventional acetone-oil distillation process. Indeed, for a recovery of 50% by OSNF significant energy savings of 13

TJ/year and corresponding cost savings can already be obtained. The numbers obtained here are comparable to what has been calculated in previous projects. However, the membrane area required for this leads to high costs. To achieve an attractive ROI, we found high demands on the membrane permeance, preferably > 5 $kg.m^{-2}.h^{-1}.bar^{-1}$. Furthermore, increasing the concentration factor leads to more acceptable ROIs. This application is pursued and investigated in more detail in the ISRO project.

WP5 Roadmapping and dissemination

Goals:
- Identification of steps and time required for successful implementation of ceramic-supported hybrid silica OSNF.
- Dissemination of the project results.

Results:
- A roadmap to come to implementation of low cost OSNF membranes on ceramic supports.
- Publications, posters and presentations with the main project results as communication to all relevant stake holders.
- ISPT newsflashes e.g. at the start and closure of the project.

Roadmap

Using the input from all partners and the ISPT liquid processing cluster, a roadmap for the further development and commercial implementation of the ceramic-supported hybrid silica and polymeric OSNF membranes was prepared (Figure 11 and 4.2). Energy savings of several hundreds of PJ/year are possible in the petrochemical and food industry. An important consideration for scale-up is the choice of module configuration. Within COSMOS a study was performed on the advantages and disadvantages of several membrane configuration types.

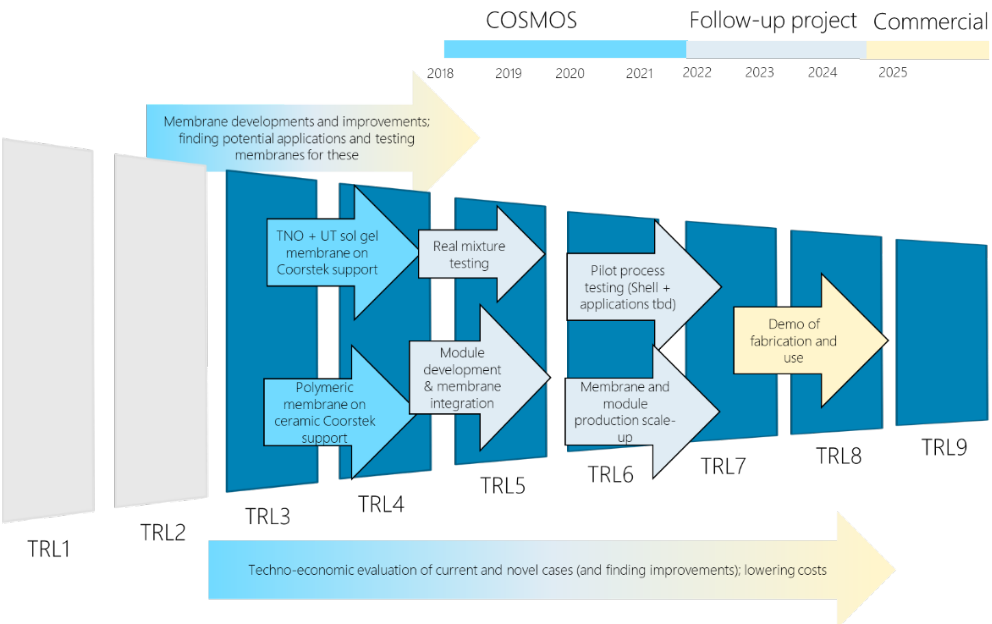

Figure 11: Roadmap for the implementation of ceramic supported hybrid silica and polymeric OSNF membranes.

Dissemination

Dissemination is described in Section 6.

WP6 Management

Goal:

- Project progress management, reporting and control of the project finances.

Results:

- Yearly progress reports and financial statements.
- Final project report.

The COSMOS project was coordinated by TNO. Several project meetings and teleconferences were organized in order to monitor the progress, discuss findings/ results and define iteration strategies. Dedicated meetings were organized around WP3 with mainly TNO and UTwente. At the end of the project, brainstorming sessions were organised in order to prepare for follow-up projects.

All presentations, actions, decision and reports were logged and first stored on the ISPT plaza that was accessible for all team members. At the end of the project, ISPT transferred to Microsoft Teams as data storage system. All documents can be found there and are stored for a minimum of 5 years.

4 Bottlenecks and follow-up

4.1 Bottlenecks

During the project some challenges were encountered which are described below. Despite these challenges the COSMOS project has achieved the main deliverables and goals.

Technical challenges
The following technical and scientific issues were encountered during the project:

- The new recipes for the MSMs using the Ströber approach with BTESE was found to be difficult to reproduce. Therefore, we did not proceed with applying these on tubular supports and relied on the previous hybrid silica procedures. The follow-up project PoSimem is focused on getting more insight in this synthesis route and improve the membranes.
- More effort was needed to adapt the intermediate and final layers to the inside CoorsTek supports. At the start of the project, a step-wise approach was taken: first coating on the outside of CoorsTek, then continue on the inside. This resulted in more effort and time spent on these developments and the target of 0.1 m2 and multichannel was not achieved. However, the current recipes are expected to be reasonably easily translated to hollow fiber supports. Also, a study was performed on the advantages and disadvantages of several membrane configuration types

Operational challenges:
The main operational challenges in the project were caused by the outbreak of the COVID-19 epidemic. Limited access to the labs led to delays linked to the activities concerning hybrid silica membrane preparation and testing at TNO. Time extensions were utilised to deal with these delays. In addition, many conferences were postponed or cancelled due to COVID-19. This had an impact on the dissemination of the project results as described in Section 6.

The Corona crisis also led to strong changes in financial streams and income. This is expected to have an impact on e.g. (future) spending in further R&D. This complicated the assessment of the road mapping activities, needed further R&D, and implementation steps are more difficult to predict and potentially complicates involvement of companies for follow-up projects.

4.2 Follow-up of the COSMOS project

Following the results on the Stöber route within COSMOS, a follow-up project proposal was initiated by Twente and awarded by NWO. The project called ‘Periodic organosilica nanofiltration membranes (POSiMem), recently started. It focuses on the design of novel NF membranes composed of periodic organosilica networks and 2D/3D hexagonal nanochannels, synthesized directly on top of a porous ceramic support. The following approaches are used to modify porous ceramic supports to accomplish the preparation of stable and reproducible NF membranes:

1. Engineered 2D/3D hexagonal nanochannels using a modified Stöber-solution pore-growth approach to prepare reproducible layers with tunable pore diameter (from 0.8 to 2.0 nm) and stable structure.

2. Prepare periodic organosilica membranes with vertically aligned micro/ mesopores covalently attached to the support by conducting a pretreatment of the porous ceramic supports with specific linkers. In this way, we will prepare micro- and mesoporous membranes resistant to washing and testing.

In this project the partners UTwente, ISPT, Shell and TNO together with Sikemia and Pervatech, will continue the collaboration and focus on material development and fundamental understand on the diffusion of the molecules through the membrane, specifically at elevated temperatures.

The business case for the PCA removal case is very promising. For the second case, the economic benefit should come from energy savings of a hybrid OSNF-distillation process compared to the conventional acetone-oil distillation process. We found strict demands on the membrane performance to get to a viable process. However, within the ISRO project this process is investigated further and Bunge Loders Crocklaan and Solsep are developing this process further.

The COSMOS consortium is in the progress of setting up a follow-up project going to higher TRL levels. In WP5, a roadmap was set-up and key next steps were defined: testing the developed membranes using real process mixtures instead of model mixtures and the module development. Depending on the process the best module configuration needs to be determined. The choice for the configuration will have a significant effect on the scale-up. At CoorsTek, the manufacturing with a capacity of 200 m^2 membrane area per week of single tubes/hollow fibers is ready. For the large scale production of multichannel membranes, R&D is required. In addition, it is expected that the coating process is more difficult for a multichannel as the capillary suction of the channels is not the same for each channel.

Another key parameter to be considered is temperature. For high temperature applications (for which ceramic membranes are very suitable) the module assembly needs to be further developed. These activities will be taken up in follow-up projects and are estimated to take 2-3 years.

If successfully, the next step should be pilot testing for the envisioned applications, leading ultimately to commercial implementation. Here, for example, the cleaning of the membranes (backwashing) should be investigated. In addition, the module and membrane production should be scaled-up further, staying at a membrane price < 1500 Euro/m^2. Simultaneously, membrane development and research will be ongoing to increase the fundamental understanding and techno-economic analyses are updated to define essential parameters to reach the business case.

Most partners required for the development and commercial implementation are already in the consortium and interested in a follow-up of the COSMOS project. However, system integrators and a pilot owner/developer are desired to strengthen the consortium. Furthermore, additional applications are desired for the wide-spread implementation of the technology and to fulfil the potential in terms of reduced energy requirements and the contribution to reduced emissions from the process industry. To this end, potential partners, e.g. in the food and pharma industry, are actively contacted and dissemination of the COSMOS results are important to raise the interest within the process industry.

5 Contribution to objectives of the program

The COSMOS projects contributed to the following program lines:

- Programmalijn 1b: Efficiënte procestechnologie:
By the ceramic support production developments at CoorsTek and the reduction in the amount of layers required to obtain a defect free membrane, COSMOS enables a cost reduction of ceramic supports which enables the application of membrane technology in the process industry. In addition, novel membranes have been developed that can meet highly challenging demands of the e.g. petrochemical industry. By these developments in OSNF accelerated implementation and corresponding improvement of the energy efficiency of industrial processes can be achieved. Energy savings of several hundreds of PJ/year are possible in the petrochemical and food industry by replacing thermal separation processes by pressure driven processes world-wide.

- Programmalijn 2: Elektrificatie van processen: Another advantage of pressure driven processes is that they can be driven by (renewable) electricity.

In COSMOS the Dutch knowledge position in membrane technology is strengthened. On one hand, fundamental knowledge on tuning membrane properties is gained at the University of Twente. On the other hand, steps are made in the scale-up of affordable ceramic membranes in order to accelerate the implementation (estimated to be possible as early as 2025). Expansion to other applications in the petrochemical and food industry can have a significant effect on the energy savings (up to 2-8 PJ/year) and corresponding CO_2 emissions (130-520 kton/year) in the Netherlands in 2030.

6 Dissemination

At the start of the project a newsflash of the COSMOS project was launched by ISPT on their website and the publication “Goedkope keramische membranen voor een marktdoorbraak” at RVO based upon an interview initiated by RVO with the former project manager of the COSMOS project, Henk van Veen. A general project description was also made available at RVO and ISPT.

The COSMOS project was presented in the ISPT network at the ISPT poster day 2017, ISPT-ELS cluster 2018, ISPT poster day 2018, ISPT poster day 2019 and ISPT-ELS cluster 2020. The results were presented at the following international conferences: ECERS conference in Turin June 2019 and OSN2019 in Enschede October 2019. Papers were submitted and accepted at World Filtration Congress in San Diego, the Int. Conf. Inorg. Membr. In Taipei and the MELPRO conference in Prague, but these were postponed due to COVID-19. The project has been presented online at the Industrial Energy-Related Technologies and Systems (IETS) collaboration Annex XVII “Membrane Processes in Biorefineries” in 2021.

The work of UTwente resulted in a peer-reviewed publication “New Generation of Mesoporous Silica Membranes Prepared by a Stöber-Solution Pore-Growth Approach” in ACS Appl. Mater. Interf. in 2019[7], and the Bachelor Thesis of Pieter J.C.A. van Beurden ‘Hybrid silica membranes for solvent nanofiltration’.

All communications can be found on the ISPT Microsoft Teams storage system (see below).

7 Signature

Petten

TNO

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on 15-09-2021

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Y.C. van Delft
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