TNT
"Through and through" grafting of Ceramic Membranes

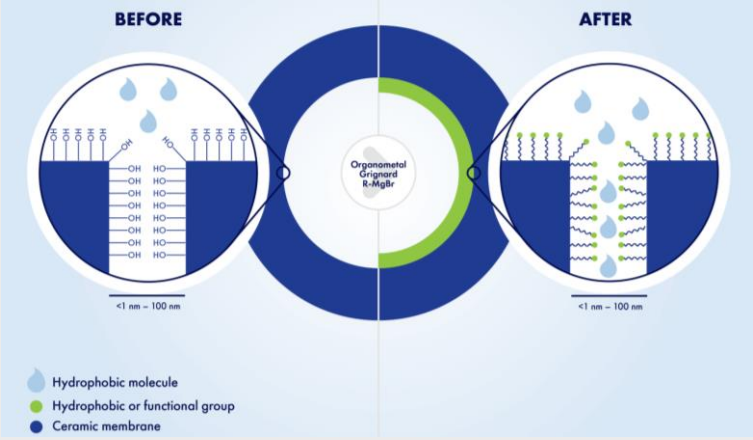
TNT aims to increase fluxes of non-polar solvents by grafting both the filtration layer and the support material of tubular ceramic membranes.

THE CONTEXT

A-membranes is a startup company which has acquired the rights to the technology to graft ceramic membranes using organometal (Grignard) chemistry, partially owned by INNOMEM partner Vito. A-membranes is currently investing in the development and implementation of an industrial process for the grafting at high MRL level.

The benefits of Grignard grafting organic moieties to the surface of ceramic membranes has been demonstrated in numerous academic publications and in industrial demonstrations as well. However, the technology has limitations. The current state of Grignard modifications only grafts organic moieties on TiO2 or ZrO2 filtration layers. No moieties are attached on standard Al2O3 supports keeping their original polar behaviour. This leads to relatively low, non-economical flux levels in applications with less-polar solvents as e.g. n-hexane or petroleum-derivates, caused by the lack of affinity of the unmodified and polar Al2O3 support material, working as a "brake" to the flux.

To remediate this issue, the TNT project aims to test the feasibility to graft TiO_2 supported ceramic membranes "through and through".



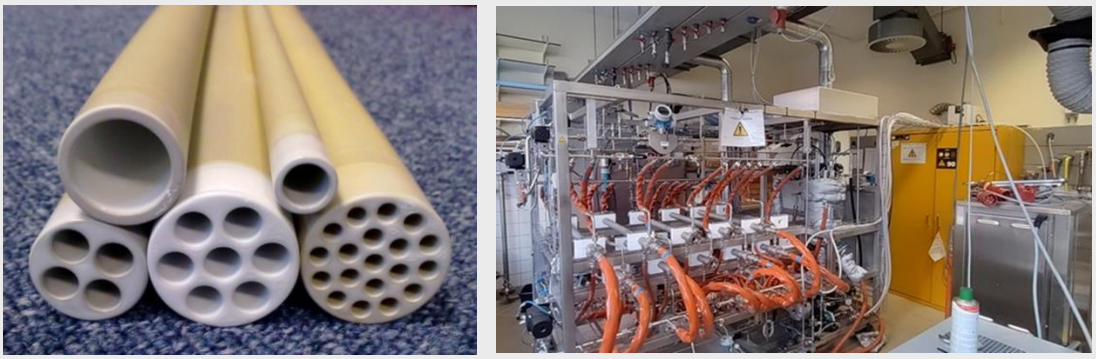
Effect of Grignard grafting of native ceramic membranes, leading to membranes with increased performance in solvents, decreased fouling, or tuneable surface chemistry (a-membranes.com).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 862330

THE CHALLENGE

Fraunhofer IKTS has developed tubular titania ceramic membrane supports and nanofiltration (NF) and ultrafiltration (UF) membranes derived from them. In the TNT Demo-case Project partner VITO will try to graft these innovative full TiO2 membranes "Through & Through", i.e. not just the outer filtration layers but the interior macro-porous TiO2 as well, and this when using the Grignard grafting technology developed at VITO and transferred to A-membranes.

With this project, A-membranes seeks to compare filtration results of these grafted mono-membranes to the results obtained in some well-documented cases on comparable grafted Al2O3/TiO2 membranes. We anticipate seeing increased flux levels for lower polarity solvents. This will undoubtedly increase both the technical and economic application window for the technology. Tests will be performed both on UF and NF membranes, to understand also if the narrowing of the pore size could have an impact on the efficiency of this "support grafting", due to e.g. sterical effects.



Full TiO_2 ceramic membranes (left) and grafting Pilot Line (right) used in the TNT project.

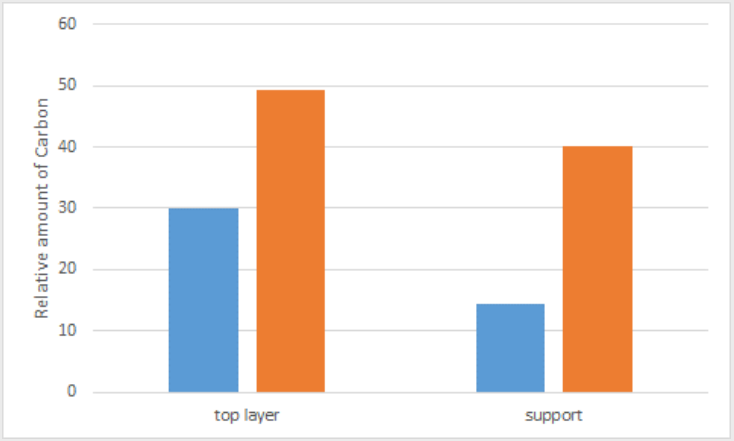
THE RESULTS

Fraunhofer IKTS produced a set of different TiO_2 supported NF and UF membranes with pore sizes varying from 0,9 nm to 30 nm. These were delivered to VITO for grafting tests.

Subsequently, VITO did a series of grafting experiments, varying the grafted groups (methyl and phenyl) and the grafting solution concentration. Next to the Grignard method, also phosphonic acid grafting was used, in order to introduce hetero-elements (i.e. P) instead of only carbon, for easier visibility in spectroscopic characterisation. All membranes were analysed for their water flux and water contact angles, and top layers as well as support layers were analysed with electron microscopy looking at structures and elemental analysis (SEM, EDX). This revealed clear evidence of through and through Grignard grafting, and allowed to derive the optimal grafting procedure.

In a next step, VITO produced several TNT grafted UF and NF membranes, and sent them over to Fraunhofer for filtration testing in different apolar solvent-based model mixtures, mimicking a variety of industrially relevant applications. The current results already confirm that fluxes of apolar streams are indeed increased compared traditional grafted membranes. More extensive testing is ongoing.

Disclosure or reproduction without prior permission of INNOMEM is prohibited



Amount of carbon analysed using SEM-EDX on a native membrane (blue), and a methyl Grignard grafted membrane (orange), measured on the top layer and on the support.

CONCLUSION

The following promising conclusions can be drawn from the TNT project:

- TiO_2 supported ultrafiltration and nanofiltration membranes can be successfully grafted "through and through" ", i.e. not just the outer filtration layers (top layers) but the interior macro-porous TiO2 support as well.
- SEM-EDX analysis of the top layers and the support show clearly increased carbon contents after methyl Grignard grafting
- First filtration results with apolar solvent-based model mixtures, mimicking a variety of industrially relevant applications, show increased fluxes for TNT grafted membranes
- This will allow A-membranes to increase their market for grafted membranes to e.g. the edible oil market, pyrolysis oil from plastics, petrochemical applications, food and beverage market etc.

TECHNIQUES USED

In the TNT project the following services and capabilities of the INNOMEM OITB were used:

- Production of TiO_2 supported NF and UF membranes by INNOMEM partner Fraunhofer.
- Grafting of ceramic NF and UF membranes at INNOMEM partner Vito.
- Testing of grafted ceramic NF and UF membranes with solvent-based model mixtures, performed at INNOMEM partner Fraunhofer.

For more information, you can get in touch with us by sending an email Hannes.richter@ikts.fraunhofer.de or bart.coen@a-membranes.com

Disclosure or reproduction without prior permission of INNOMEM is prohibited