



Welcome

Welcome to this summer edition of the newsletter of the Membrane Science and Technology group and the European Membrane Institute of the University of Twente. In this newsletter we would like to inform you about the latest developments in our group.

Since the start of the year, we had two PhD defenses and there are two more to come in October. Beata Koziara will defend her thesis on October 9 and investigated the use of sulfonated poly ether ether ketone as membrane material for the dehydration of super critical CO₂. It mainly focuses on relaxation and plasticization phenomena in the polymer but also presents a detailed process design. Harro Mengers will defend his thesis on October 22 and his work is dedicated to the development of a membrane reactor process for the direct conversion of CO₂ into valuable products used in the chemical industry and addresses mass transfer modeling, membrane development and a detailed process design including economic evaluation. You can find a summary of both researches in this newsletter.

In addition, you can read about the principle and possibilities of Flow Field Flow Fractionation (Flow-FFF), a chromatography-like technique to analyze and characterize components present in water with respect to their size (distribution) and interactions. It is a technology suitable for the broad analysis of soluble and colloidal components, covering the full size ranges of natural colloids, and natural and manufactured nanoparticles. It offers a tool to better understand the role of specific components or interactions on membrane fouling

and fouling mechanisms.

The item 'It all started in Twente...!' contains a contribution of a person many membrane people in the field will know from his time at the University of

Twente or from his current position at GE Water & Process Technologies in Oakville, Canada: Geert-Henk Koops. You will read some recognizable and funny stories about the old days in Twente.

Finally, we would like to inform you about five short, 15-minute, basic membrane lectures broadcasted by the University of the Netherlands (UvN). With these lectures, the general public gets a glimpse on what membranes are, how they are made, and what you can do with them. You will find more information about the lectures and where to watch them in this newsletter.

For now we hope you will enjoy reading this newsletter. In case you have additional questions or you would like to receive further information or one of our publications, please feel free to contact us at msttnw@utwente.nl or +31 53 489 2950.

On behalf of all members of the group, I wish you a wonderful summer season. We hope to meet many of you after summer again, at e.g. Euromembrane in Aachen.

Prof. Dr. Kitty Nijmeijer



Follow MST on Facebook!



Interested in the latest news of our Membrane Science and Technology group? Follow us and like us on Facebook (www.facebook.com/membranetechnology). There you will find all our most recent publications, PhD defenses, and MSC colloquia, as well as the more social aspects of our group. Enjoy!

Membrane reactors for the direct conversion of CO₂ to dimethyl carbonate

(Defence date: October 22, 2015)



Harro Mengers

Due to the increasing oil prices the chemical industry searches for alternative feedstock for the production of chemicals. CO₂ is considered as an interesting alternative for environmental and economic reasons. Using CO₂ as feedstock not only decreases the demand for fossil fuels, it also reduces the anthropogenic CO₂ emission into the atmosphere, it is nontoxic and since it is considered as waste product it is a cheap feedstock. Worldwide 30.4 Gt of CO₂ is produced by human activity [1], of which 5-10% can be used for the production of chemicals [2]. Figure 1 gives a few examples how CO₂ can be used as feedstock, such as for the dry reforming of methane to make syngas [3], the production of methanol from hydrogen [3] or the production of carbonates [4].

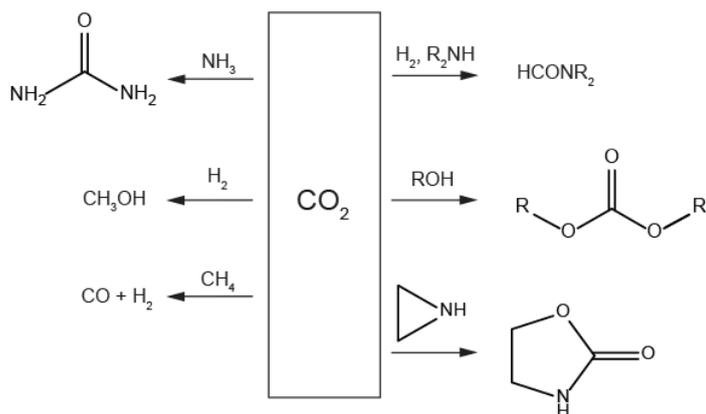
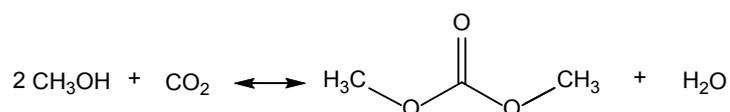


Figure 1: Few examples of organic synthesis starting from CO₂ [4].

Because of the advantages of the use of CO₂, the direct conversion of CO₂ and methanol to dimethyl carbonate (DMC) caught much interest.



In the search for so called “Green Chemistry” DMC is considered as a promising chemical because of its low toxicity and fast biodegradability. It finds major applications in the production of polycarbonates, as methylation agent, in the use as solvent for lithium ion batteries and potentially as fuel additive [4-9]. The drawback of the direct conversion

of CO₂ to DMC is that thermodynamic equilibrium is in favor of the reactants ($K_{eq} \approx 10^{-5}$ at 298 K and 1 atm) and it is difficult to convert CO₂ into DMC at sufficiently high yields. To resolve this, membrane reactors are proposed. The combination of a reactor and a membrane facilitates the instant removal of products (e.g. H₂O) from the reaction mixture, preventing an equilibrium to establish and as such enhancing the conversion of CO₂. Since the use of membrane reactors for this application are rather unexplored, the aim of this research was to investigate the potential of membrane reactors for the direct conversion of CO₂ to DMC.

Catalytic membrane reactors

Maxwell-Stefan theory taking into account multi-component mass transfer characteristics and drift fluxes is used to compare the performance of two membrane reactor configurations to selectively remove water vapor from equilibrium limited reactions:

- Catalytic membrane reactor (CMR); in which reaction and separation coincide.
- Inert membrane reactor (IMR); in which reaction and separation distinct.

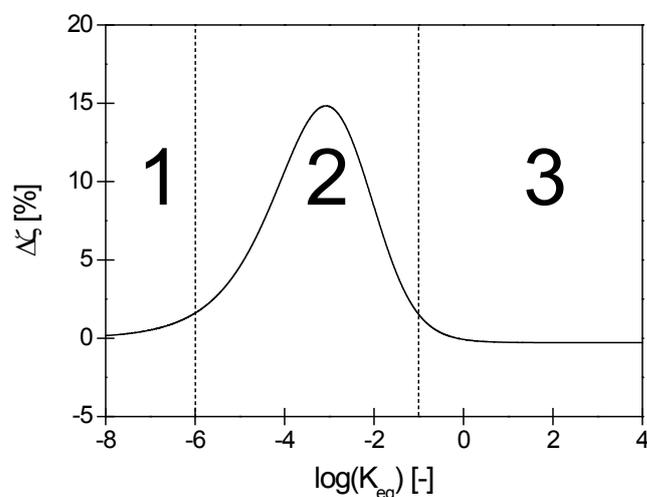


Figure 2: The difference in conversion between the CMR and IMR ($\Delta\zeta = \zeta_{CMR} - \zeta_{IMR}$) as function of the equilibrium constant (K_{eq}) [10].

Figure 2 shows the difference in conversion of both membrane reactor configurations ($\Delta\zeta = \zeta_{\text{CMR}} - \zeta_{\text{IMR}}$) as function of the value of the equilibrium constant. It clearly shows that especially in regime 2 it is favorable to apply CMRs over IMRs. Since in CMRs catalyst and membrane are integrated, water is more effectively removed resulting in higher conversions in regime 2. However, the location of the optimum strongly depends on different process and material properties, such as the mass transfer coefficient over the boundary layer, water permeability of the membrane, residence time, reaction rate constant and membrane area/volume ratio (A/V) [10]. In regime 3 (e.g. esterification reactions) the conversions obtained in CMRs and IMRs do not differ and because IMRs are easier to implement, they are preferred over CMRs.

Membranes for the production of DMC

Based on Figure 2, it is considered beneficial to perform the direct conversion of CO_2 into DMC in a CMR ($K_{\text{eq}} \approx 10^{-5}$). Besides, increased water permeation of the membrane results in higher conversions for the equilibrium limited reaction. Double layer sulfonated poly(ether ether ketone) (SPEEK)/chitosan composite membranes are developed by casting a layer of chitosan on top of a SPEEK film. These materials are chosen because SPEEK is known to be highly permeable by water vapor and able to retain CO_2 [11], and chitosan is known to retain methanol [12]. Figure 3 shows that the introduction of a chitosan layer on top of SPEEK and an increasing chitosan layer thickness makes the composite membrane more selective towards water vapor. The additional chitosan layer decreases the CO_2 permeability. In

addition, we hypothesize that chitosan slightly penetrates into the SPEEK layer, resulting in a mixed SPEEK/chitosan layer.

Effect of counter ions on the permeation behavior in SPEEK

In order to use SPEEK in water vapor selective catalytic membrane reactors, a membrane material with a high thermal resistance is required because of the required membrane reactor conditions. Koziara et al. [13] proved that exchanging the opposing cation (usually a H^+) of the negatively charged $-\text{SO}_3^-$ moiety in SPEEK for a Na^+ , results in a significant increase of the thermal stability of SPEEK. This work further elaborated on this and showed that in general the thermal stability of SPEEK improves significantly (450-500 °C) when replacing H^+ for another mono- (Li^+ , Na^+ , K^+), di- (Ca^{2+}) or trivalent (Al^{3+}) cation. The nature of the cation in SPEEK also affects the water vapor permeability (Figure 4a) and CO_2 permeability (Figure 4b). Both the water vapor permeability and CO_2 permeability show a strong decreasing correlation

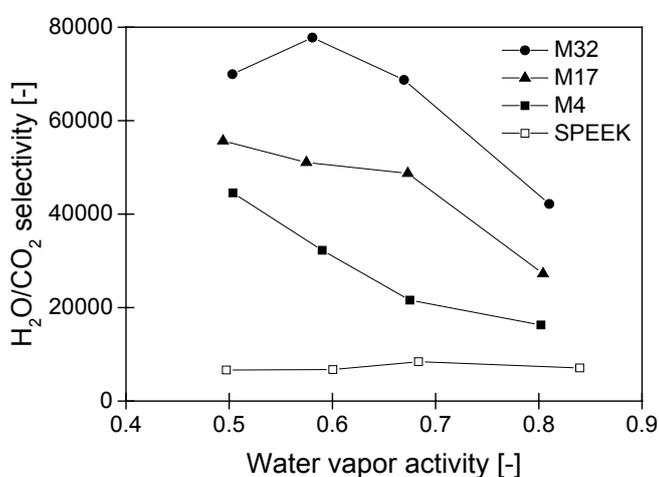


Figure 3: $\text{H}_2\text{O}/\text{CO}_2$ selectivity as function of the water vapor activity for SPEEK/chitosan membranes with increasing chitosan layer thickness (thickness SPEEK layer: 39 μm ; thickness: chitosan layer: 4, 17 or 32 μm).

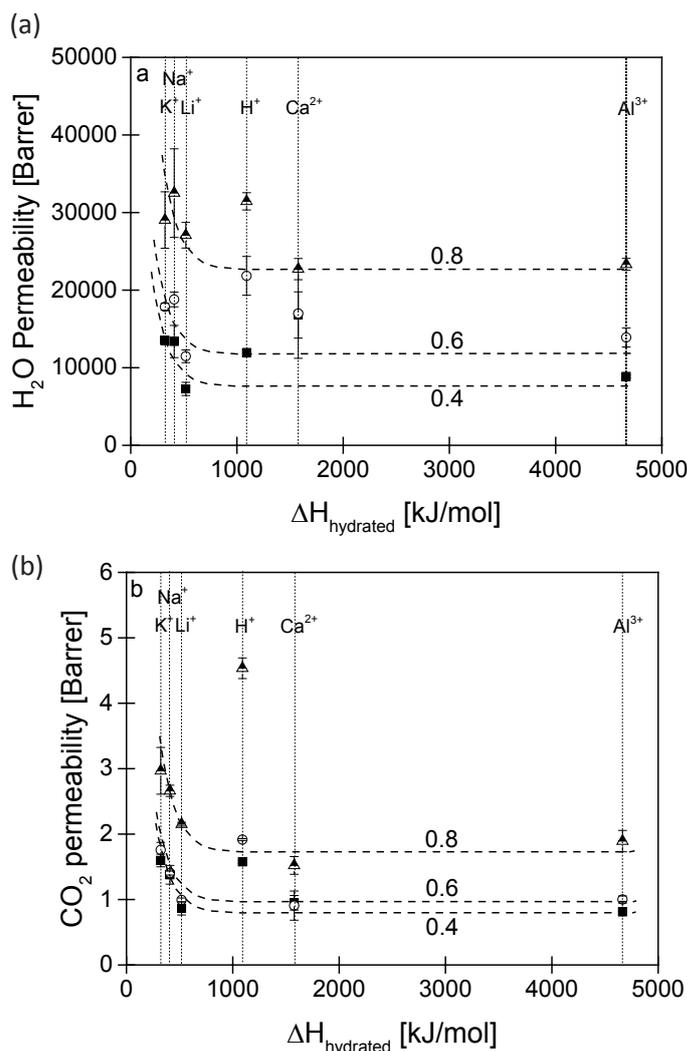


Figure 4: Water vapor permeability (a) and CO_2 permeability (b) as function of the water vapor hydration enthalpy for water vapor activities of 0.4, 0.6 and 0.8.

with increasing cation hydration enthalpy. We hypothesize that this is caused by the formation of bigger cation-water clusters that hinder the permeation of water vapor and CO₂ and the stronger water-cation and CO₂-cation interactions, resulting in a worse desorption. Both phenomena decrease the permeability of both components. However, also other parameters do play a role such as cation-anion interactions and the formation of ionic crosslinks between the -SO₃⁻ group of SPEEK and di- or trivalent charged cations.

Membrane reactors for the production of DMC

Finally also the economic feasibility of the use of water vapor selective catalytic membrane reactors for the direct conversion of CO₂ and methanol to DMC was investigated. The aim of this part of the work was to provide a valuable insight and a better understanding of the process limitations. Therefore a process simulation was performed that considered the full membrane reactor process to convert the components into DMC and also involves the subsequent separation and purification steps to obtain DMC according to specs such that it can be used industrially. Especially also the challenging azeotropic separations (i.e. DMC-methanol and DMC-water) are taken into account.

Figure 5 gives a schematic overview of the process. CO₂ and methanol are converted to DMC in a membrane reactor that selectively removes 98% of all water to prevent equilibrium establishes. Leaving the membrane reactor, gaseous components (CO₂) are removed in a flash drum and the stream is pre-distilled (DIST-01) to increase DMC concentration. Then the DMC in the product stream (#4) is extracted with an extractant in an extractive distillation column (DIST-02) to break the DMC-methanol azeotrope. Finally the product stream (#5) is distilled to separate the extractant from the DMC and to obtain industrial grade DMC (> 99 wt%). The flaw of this process is that, even with the continuous removal of water vapor and the use of an excess of methanol, the conversion in the membrane reactor is too low and the DMC concentration in the reactor effluent is less than 1.5 mol%. Purification of this diluted stream to the desired concentrations requires large size equipment and a substantial amount of energy (13.61 kWh/kg DMC) resulting in high investment and utility costs, thus making this process not profitable. The focus for new membrane reactors should

be on the instant removal of DMC (instead of water) from the reaction area to allow for a more concentrated DMC stream.

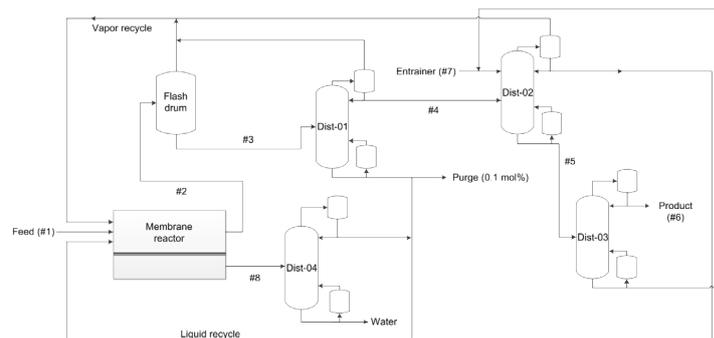


Figure 5: Schematic overview of the process design for the direct conversion of CO₂ to DMC.

Acknowledgement

This research leading to these results has received funding from the European Union Seventh Framework FP7-NMP-2010-Large-4 under Grant Agreement n° 263007 (acronym CARENA).

References

- [1] World Energy Outlook 2011, International Energy Agency.
- [2] Centi, G. and S. Perathoner, Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catalysis Today*, 2009. 148(3–4): p. 191-205.
- [3] Jiang, Z., T. Xiao, V.L. Kuznetsov, and P.P. Edwards, Turning carbon dioxide into fuel. *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences*, 2010. 368(1923): p. 3343-3364.
- [4] Sakakura, T., J.C. Choi, and H. Yasuda, Transformation of carbon dioxide. *Chemical Reviews*, 2007. 107(6): p. 2365-2387.
- [5] Delledonne, D., F. Rivetti, and U. Romano, Developments in the production and application of dimethyl carbonate. *Applied Catalysis a-General*, 2001. 221(1-2): p. 241-251.
- [6] Keller, N., G. Rebmann, and V. Keller, Catalysts, mechanisms and industrial processes for the dimethyl carbonate synthesis. *Journal of Molecular Catalysis a-Chemical*, 2010. 317(1-2): p. 1-18.
- [7] Pacheco, M.A. and C.L. Marshall, Review of dimethyl carbonate (DMC) manufacture and its characteristics as a fuel additive. *Energy & Fuels*, 1997. 11(1): p. 2-29.
- [8] Ono, Y., Catalysis in the production and reactions of dimethyl carbonate, an environmentally benign building block. *Applied Catalysis a-General*, 1997. 155(2): p. 133-166.
- [9] Santos, B.A.V., V.M.T.M. Silva, J.M. Loureiro, and A.E. Rodrigues, Review for the Direct Synthesis of Dimethyl Carbonate. *ChemBioEng Reviews*, 2014. 1(5): p. 214-229.
- [10] Mengers, H., N.E. Benes, and K. Nijmeijer, Multi-component mass transfer behavior in catalytic membrane reactors. *Chemical Engineering Science*, 2014. 117: p. 45-54.
- [11] Sijbesma, H., et al., Flue gas dehydration using polymer membranes. *Journal of Membrane Science*, 2008. 313(1-2): p. 263-276.
- [12] Zhong, S.L., X.J. Cui, T.Z. Fu, and H. Na, Modification of sulfonated poly(ether ether ketone) proton exchange membrane for reducing methanol crossover. *Journal of Power Sources*, 2008. 180(1): p. 23-28.
- [13] Koziara, B., et al., Thermal stability of sulfonated poly(ether ether ketone): on the role of protodesulfonation not published yet.

University of the Netherlands



Kitty Nijmeijer presents 5 lectures on membranes at Online University

Prof. Kitty Nijmeijer recently joined the online scientific program broadcast by the University of the Netherlands (De Universiteit van Nederland) where she presented 5 lectures on membrane science and technology accessible for a broad audience. The University of the Netherlands is an online platform on which 'the best professors in the Netherlands present their research'. The lecture series of Kitty consists of 5 independent lectures with english subtitles.



UvN-Membrane lecture 1

Which essential part of your body is the size of a football pitch?

In this lecture, Kitty Nijmeijer provides an introduction to the world of membranes. She tells us about the membranes in our bodies (which form an ingenious system), the history of membrane science and the search for the most efficient synthetic membranes. In conclusion, Professor Nijmeijer demonstrates how to make a membrane.

Lecture with English subtitles available at:

<https://www.youtube.com/watch?v=GMRltxn3sMA>

UvN-Membrane lecture 2

How can you purify blood using a pig's gut and a bomber?

A total of 6500 people in The Netherlands alone suffer from serious kidney disease. Three times a week, these people need to go to a hospital for dialysis. Kidney transplantation is their only hope. In this lecture, Nijmeijer demonstrates how, thanks to membranes, the 6500 people in NL suffering from kidney disease now have the chance of a better life.

Lecture with English subtitles available at:

<https://www.youtube.com/watch?v=qKdy98yUsrI>

UvN-Membrane lecture 3

Why is tap water cleaner than water bought from a supermarket?

In this lecture, Nijmeijer explains how membranes can be used for solving one of the biggest problems of our era, namely the availability of clean water for everyone!

Lecture with English subtitles available at:

<https://www.youtube.com/watch?v=nYbmC2G7jsU>

UvN-Membrane lecture 4

How can I change factory smoke into drinking water?

In this lecture, Professor Nijmeijer demonstrates how membrane researchers are able to convert the filthy emissions from factories into clean drinking water using membranes. This makes it possible to convert factories into water suppliers, all thanks to membranes.

Lecture with English subtitles available at:

<https://www.youtube.com/watch?v=YI0E-hvGW3E>

UvN-Membrane lecture 5

How can the Afsluitdijk (Enclosure Dyke) generate energy?

In this lecture, Professor Nijmeijer goes one step further. She demonstrates how, with the help of membranes, the Afsluitdijk (a major dyke in The Netherlands) can be used for generating electricity. This 'Blue Energy' technology is successfully implemented at the Afsluitdijk recently.

Lecture with English subtitles available at:

<https://www.youtube.com/watch?v=mDK3K1C9EyY>

The website of the University of the Netherlands can be found at: www.universiteitvannederland.nl (in Dutch). For more information, please contact Prof. Kitty Nijmeijer (E-mail: d.c.nijmeijer@utwente.nl; Phone: +31 53 489 4185).



Flow field flow fractionation (Flow-FFF)

Introduction

Pressure driven membrane processes like MF, UF, NF and RO are widely used for water treatment purposes. Components in natural water sources separated by MF or UF include a.o. natural organic matter NOM (fulvic and humic acids, humin, polysaccharides, some proteins), and nanoparticles. Both NOM as well as nanoparticles are known to foul membranes. For this reason it is important to analyze and characterize the components present in the feed water on their size (distribution) and interactions. In this way, fouling phenomena can be understood better. One technique to do so is flow field flow fractionation, a chromatography-like technique available at the Membrane Science and Technology Group. This overview briefly discusses the measurement principles, the equipment available and an example of the use of this powerful technique.

Principle

Field flow fractionation (FFF) is a family of chromatography-like separation technologies first described in 1966 by Calvin Giddings [1]. In FFF, a force field is applied to a very thin channel in which a particle containing fluid is flowing. The force is applied perpendicular to the fluid flow direction, causing the particles to separate. This separation is dependent on the mobility of the particles in the applied force field. The force field can be of different origins, like thermal, electrical, magnetic, gravitational, centrifugal, or a flow field. The most widely applied variant in FFF is flow-FFF, where the separation is caused by hydrodynamic force acting on a fluid in a very thin flow channel. Two variants are most applied: Hollow-Fiber Flow-FFF (HF5) and Asymmetric Flow-FFF (AF4). The equipment at the MST group is based on the latter principle, AF4.

Figure 1 [2] shows schematically how AF4 is working. Flow and sample are confined in a flat channel made out of two plates. The upper plate is impermeable; the lower plate is a semipermeable, low MWCO ultrafiltration membrane. Phase (a) is the so called focus phase, where the sample is injected towards the membrane and molecules and particles are focused in a narrow band. Confusingly, unlike in membrane filtration, this flow perpendicular to the membrane is called a cross flow field. As a result of this cross flow field, the sample

is transported towards the membrane. At the same time, due to Brownian diffusion the sample redistributes itself. Smaller particles have higher diffusion coefficients and consequently will move to a higher position up in the channel than larger particles. When equilibrium is reached, the particles have redistributed themselves and the elution phase (b) starts.

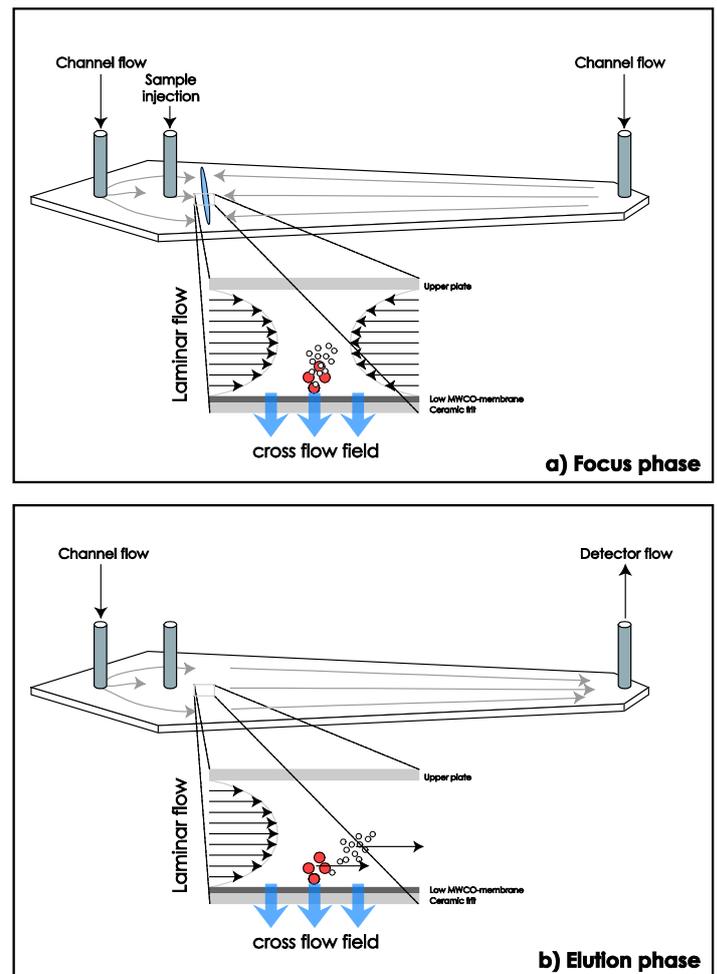


Figure 1: The principle of flow-FFF in an asymmetric flow channel. Phase (a): the focus phase ; phase (b): elution phase [2].

In the channel a parabolic velocity profile is present. This velocity difference in the channel separates the particles based on their size. The smaller particles present higher up in the channel will leave the channel much faster than the bigger particles closer to the membrane. The cross flow can be remained during the elution phase, but can also be changed while eluting or even decrease with time (gradient elution).

Analysis

The flow cell is only a small part of the AF4 setup (Figure 2). Once the particles are separated and have left the separation channel, analysis can take place. For this, our AF4 setup is equipped with a differential RI (dRI) detector, a multi-angle light scattering (MALS) detector which is connected to a dynamic light scattering (DLS) apparatus, and a UV-VIS detector. Concentrations of particle fractions are measured using the dRI detector and/or by UV-VIS. By analyzing the angle dependency of intensity of the scattered light (the Rayleigh scattering), MALS can determine the absolute molecular mass and size (rg, radius of gyration or 'root-mean square' radius) of macromolecules. For certain classes of particles, via classical light scattering MALS can provide information their size, shape and structure. Because of Brownian motion, particles or molecules in suspension scatter light at different intensities. DLS measures these fluctuations and calculates the particle size (hydrodynamic radius) of macromolecules and particles using the Stokes-Einstein relation.

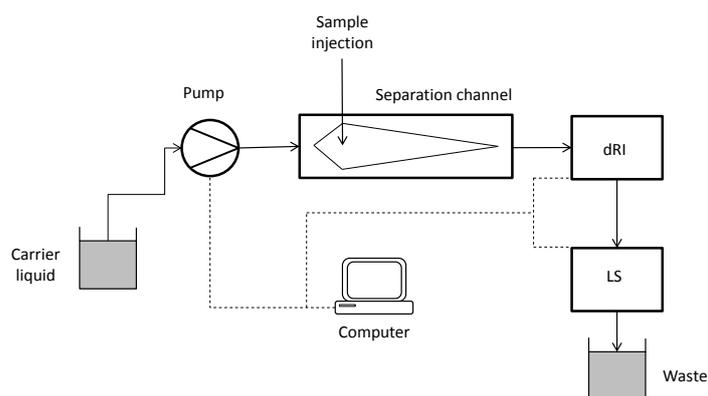


Figure 2: Schematic representation of the AF4 setup and subsequent characterization at MST. dRI = differential refractive index; LS = light scattering (drawing by Krzysztof Trzaskus).

Equipment and specifications

The AF4 equipment at MST is obtained from Wyatt Technology Europe GmbH, Germany (Figure 3). An Eclipse 2 AF4 system is connected to an Agilent 1100 HPLC isocratic pump and micro-vacuum degasser system. Fractionation of the sample takes place in the flow cell (Figure 4), after which the fractions were analyzed by a variable wavelength UV detector (Agilent 1100 series). Subsequently, the sample enters the Optilab rEX dRI detector (Wyatt). Finally, the sample is analyzed by a Dawn Helios-8 MALS detector (Wyatt) placed at an angle of 108°, which is connected to DLS (Nanostar, Wyatt) via a glass fiber cord.



Figure 3: AF4 equipment at MST. From left to right: PC for data logging and calculations, flow cell (Wyatt), manual injector/dRI/MALS+DLS (all Wyatt), and autosampler/UV-VIS/HPLC pump (all Agilent).

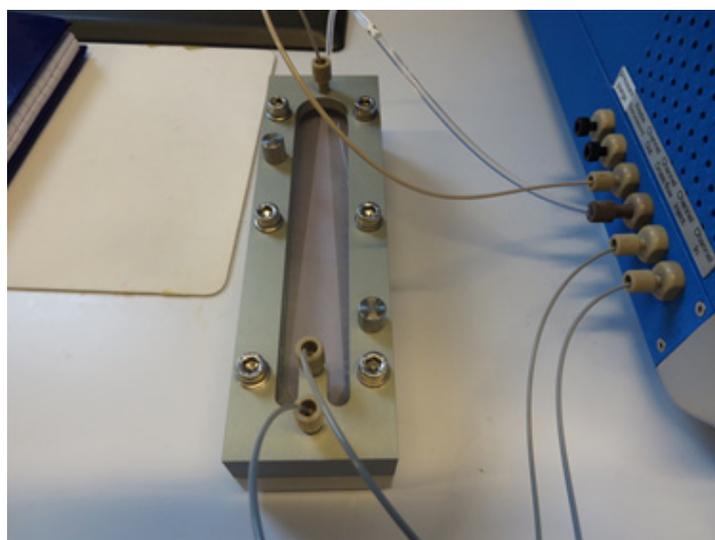


Figure 4: Flow cell used, equipped with a 5 kDa regenerated cellulose acetate membrane.

AF4 is a technology suitable for the broad analysis of soluble and colloidal components, covering the full size ranges of natural colloids and natural and manufactured nanoparticles. Its measurement range goes from a few nanometers up to a few micrometers, but in AF4 literature sizes even up to 100 μm are reported. Analysis is quick, typically in the order of 10 to 30 minutes per sample. Other advantages include the continuous and non-destructive separation of particles at a high resolution, and the possibility to couple a wide range of detectors to the AF4. In principle, the fractions can be collected after on-line detections and analyzed off-line with e.g. AFM, TEM, and ICP-MS. This offers the user the possibility to determine a wide range of particle properties. Disadvantages of AF4 include, a.o., material losses, particle-membrane interactions and possible contamination with

particles from previous experiments when the membrane used in the channel is too old [3].

At the MST group, the AF4 'disadvantage' of particle-membrane interactions was used by van de Ven et al. to investigate the behavior of alginate molecules under filtration conditions [2]. Firstly, the flat membrane in the AF4 flow cell was chosen such concerning membrane material and cut-off that it was similar to the membrane used in the actual hollow fiber filtration process. Furthermore, filtration conditions in the flow channel were comparable to those in the hollow fiber UF module. In this way, by using AF4 not only the confirmation of the polymer in different solutions, but also the interaction of the polymer with the membrane material could be investigated in detail. Solutions of sodium alginate in different ionic environments were used as easy to make and reproducible model feed water. By exploring the distinctly different elution profiles when electrolytes were added to the alginate, information on interaction between alginates and membrane material could be extracted (Figure 5). Increasing skewness of the peak when adding electrolyte indicated enhanced interaction of the alginate with the membrane material. Conformation plots revealed that by the addition of NaNO_3 the alginate structure changed from a stretched conformation to a random coil structure. Currently, Krzysztof Trzaskus (NanoNextNL PhD at MST) uses AF4 to investigate the fouling behavior of nanoparticles in the presence of polymeric stabilizers during membrane microfiltration. Summarizing, our work shows the power of AF4 as tool to investigate the influence of a changing feed water matrix on filtration and fouling behavior of feed solutions in membrane processes.

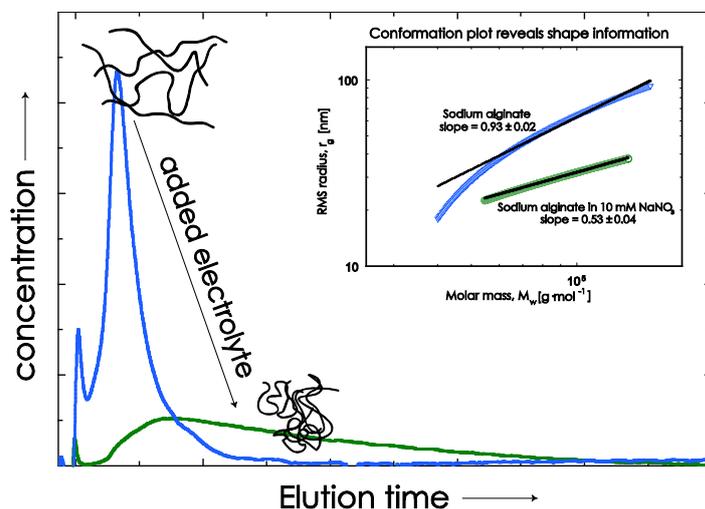


Figure 5: Influence of added electrolyte (10 mM NaNO_3) on AF4 elution profile of sodium alginate using a PES membrane in the AF4 flow cell [4].

For more information on flow field flow fractionation, please contact Dr.ir. Antoine Kemperman (phone: +31-53-489-2956 or email a.j.b.kemperman@utwente.nl).

References

- [1] J. Calvin Giddings, A New Separation Concept Based on a Coupling of Concentration and Flow Nonuniformities, *Separation Science and Technology*, 1 (1966), 123-125.
- [2] Wilbert van de Ven, Ineke Pünt, Antoine Kemperman, Matthias Wessling, Unraveling ultrafiltration of polysaccharides with flow field flow fractionation, *Journal of Membrane Science*, 38 (2009), 67-74, DOI 10.1016/j.memsci.2009.04.008.
- [3] M. Baalousha, B. Stolpe, J.R. Read, Review- Flow field-flow fractionation for the analysis and characterization of natural colloids and manufactured nanoparticles in environmental systems: A critical review, *Journal of Chromatography A*, 1218 (2011), 4078-4103.
- [4] W. van de Ven, I. Pünt, A. Kemperman, M. Wessling, Unraveling dead-end ultrafiltration with Flow Field-Flow fractionation, poster presentation 12th NMG/BMG Poster day 2008, Antwerp, Belgium.

PhD defence Joris de Grooth

On Wednesday February 4, 2015, Joris de Grooth defended his PhD thesis entitled 'A tale of two charges: Zwitterionic Polyelectrolyte Multilayer Membranes'. In his thesis, Joris investigated the build-up of polyelectrolyte multilayers on both model surfaces and on porous membranes. On porous membranes multilayer, coating led to the formation of novel nanofiltration membranes. Further incorporation of zwitterionic moieties led to a great degree of control over the membranes separation properties. The work was supported by Pentair/ X-Flow.

For more information, please contact Dr.ir. Wiebe de Vos (w.m.devos@utwente.nl; phone: +31 (0)53 489 4495).



Thin sulfonated poly(ether ether ketone) films for the dehydration of compressed carbon dioxide

(Defence date: October 9, 2015)



Beata Koziara

The dehydration of compressed carbon dioxide is needed to recover this fluid after its use to extract water from food products. The removal of water from food aids to extend the shelf life of food. Currently, the dehydration of compressed carbon dioxide is performed via adsorption of the water on zeolite adsorbents, as shown in Figure 1a. Membrane technology has been considered a competitive alternative for zeolites [2] (Figure 1b). The need to replace zeolites with another technology comes from the fact that the full recovery of the adsorption capacity of zeolites requires heating to 600 °C, which causes high operating costs. Membrane technology is known to be energy efficient [3].

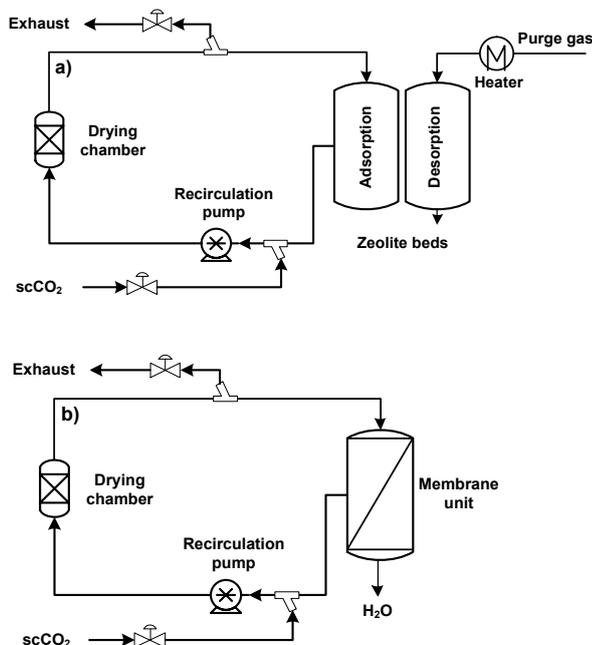


Figure 1: Food drying process using pressurized carbon dioxide with (a) zeolite beds [1] and (b) an alternative for zeolites - a membrane unit, as dehydration units.

Scope of the PhD project

In this PhD project, the potential of composite hollow fiber membranes in the dehydration of pressurized carbon dioxide is assessed with respect to membrane material science and

process design.

Hydrophilic sulfonated poly(ether ether ketone) (SPEEK) (Figure 2) is a potential membrane material for the process. SPEEK membranes possess high selectivity for water over nitrogen and carbon dioxide [4-6]. The degree of sulfonation, DS (%), is defined as the percentage of repeating units of poly(ether ether ketone) that has been sulfonated. Not only a good performance of SPEEK membranes in molecular separation is essential, but the membrane stability in the process conditions as well. High water activity in compressed carbon dioxide can be detrimental for highly sulfonated SPEEK because of excessive swelling. Therefore, we investigated the properties and swelling behavior in liquid water of thin films derived from SPEEK of DS=84 % within the context of their application as thin selective layers in composite hollow fibers.

For a process design, a method is needed to remove water from the permeate side to maintain the driving force for water permeation. By performing process simulations in Aspen Plus® and economic evaluation based on the simulation results, we evaluated the usage of low pressure carbon dioxide as sweep gas. High pressure sweep is not practical because the solubility of water in a pressurized gas is much lower than at low pressure. The feed carbon dioxide in the simulations was assumed to be in a supercritical state (scCO₂) at 50 °C and 100 bar. A schematic representation of the process design is shown in Figure 3. To avoid high CO₂ emissions, permeate has to be recirculated and regenerated.

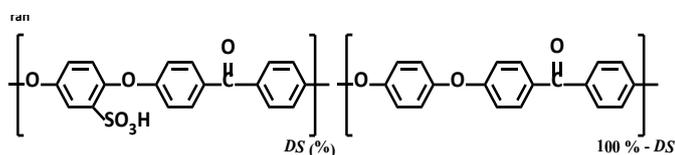


Figure 2: Structure of sulfonated poly(ether ether ketone) (SPEEK) with a given DS (%), randomly sulfonated.

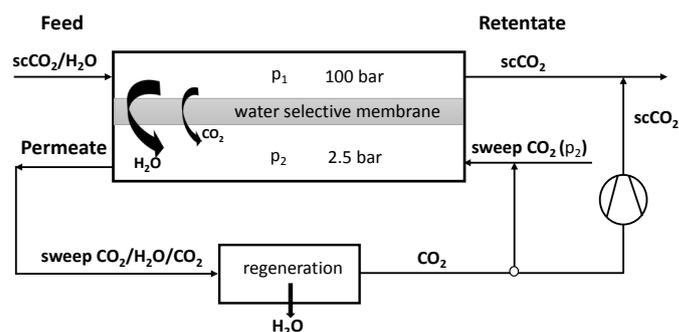


Figure 3: Scheme of a dehydration process of scCO₂ using a hollow fiber membrane module.

Material properties of thin SPEEK films and the effect on water-induced swelling

We investigated properties of thin SPEEK films using spectroscopic ellipsometry. Spectroscopic ellipsometry is an optical method that is used to determine thickness and refractive indices of a film coated a substrate in ambient atmosphere, or upon exposure to liquids or gases [7]. We found that SPEEK possess different refractive indices parallel (n_{xy}) and perpendicular (n_z) to the surface of the film. Thus, the films are optically anisotropic. The difference between two refractive indices is called optical anisotropy, Δn ($\Delta n = n_{xy} - n_z$). Thin polymer films often exhibit anisotropy as the effect of stresses applied on film during film formation. Our experiments aimed to find relations between the stresses in the thin SPEEK films and the formation method and conditions. The thin films were formed via spin-coating and solution deposition, by using highly volatile alcohols or the non-volatile N-methylpyrrolidinone (NMP). These two methods and the rate of solvent evaporation imply different forces imposed on the polymer chains during film formation. Films were conditioned in vacuum at 30 or 140 °C after formation. The measurements showed that the SPEEK films are always anisotropic, and the refractive index n_{xy} is always

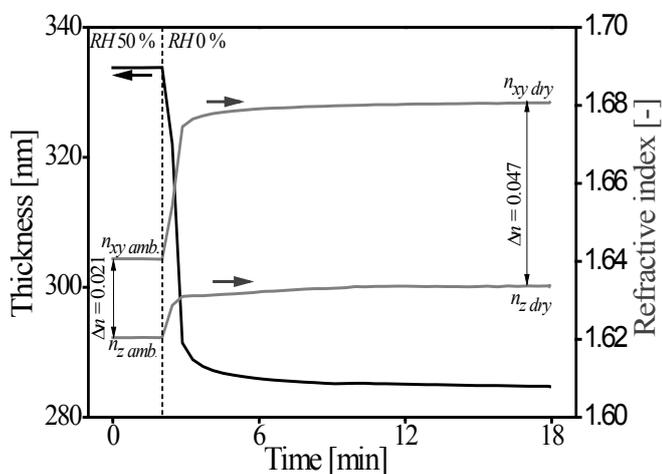


Figure 4: Thickness, refractive indices and optical anisotropy changes of a SPEEK film containing water vapour absorbed from the ambient (at relative humidity degree RH of 50 %) upon drying [8].

higher than n_z . This is independent on formation procedures or solvent used. The results indicate that internal stresses are inherent to membranes from this polymer. The stresses can be reversible relieved via plasticization by sorbents such as water vapor from the ambient or residual organic solvents. The relief of stresses is manifested by a reduction in value of the optical anisotropy. Upon removal of the plasticizer the anisotropy increases, as shown in Figure 4 on a representative

SPEEK film (~330 nm). More details can be found in [8].

We assessed the impact of optical anisotropy in thin SPEEK films on swelling in liquid water [9]. Experiments revealed that the water-induced swelling of SPEEK films with an equal DS (coated in a humid atmosphere) at the particular temperature can be dissimilar. This discrepancy was found to be dependent on the anisotropy in the material. Films with higher initial optical anisotropy prior to swelling swell more than films with lower initial anisotropy. This behaviour is shown in Figure 5, which represents thin film swelling at

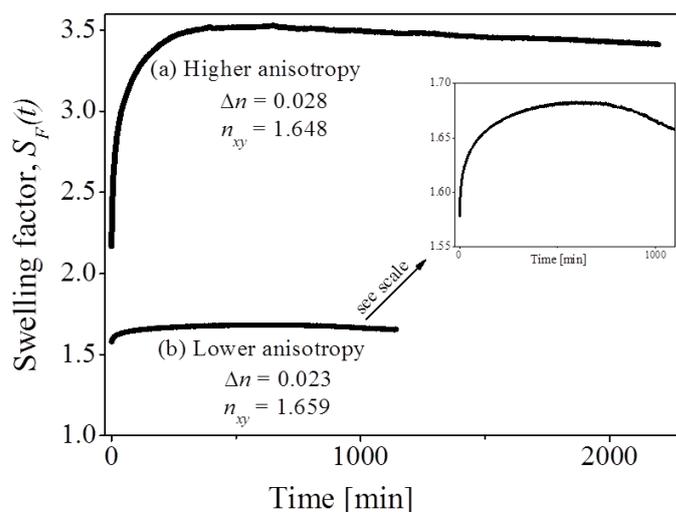


Figure 5: Time-dependent water-induced swelling at 40 °C of ~300 nm SPEEK films with a DS of 84 % and (a) relatively high optical anisotropy ($\Delta n=0.028$), and (b) relatively low optical anisotropy ($\Delta n=0.023$) [9].

40 °C water. The film that has the higher initial anisotropy, $\Delta n=0.028$, shows a maximum swelling factor value of ~3.5 followed by a continuous relaxation-induced decrease in film thickness. For the film with the lower initial optical anisotropy, $\Delta n=0.023$, the maximum swelling factor is only ~1.7. For the film with the initial Δn of 0.043, the swelling factor was found to be ~5 (meaning the film swells 5 times its dry thickness) after first 5 minutes of swelling (not shown in the graph) [9].

We ascribe this correlation to two phenomena. Firstly, the optical anisotropy in a film is directly dependent on the ambient relative humidity degree, and therefore, on the water vapor absorbed from the ambient by this film. The higher initial concentration of water vapor in the film prior to swelling causes a pre-saturation of this film with water molecules. Therefore, a subsequent swelling upon contact with liquid water is less apparent for such film. Secondly, the optical anisotropy corresponds to internal stresses in the film

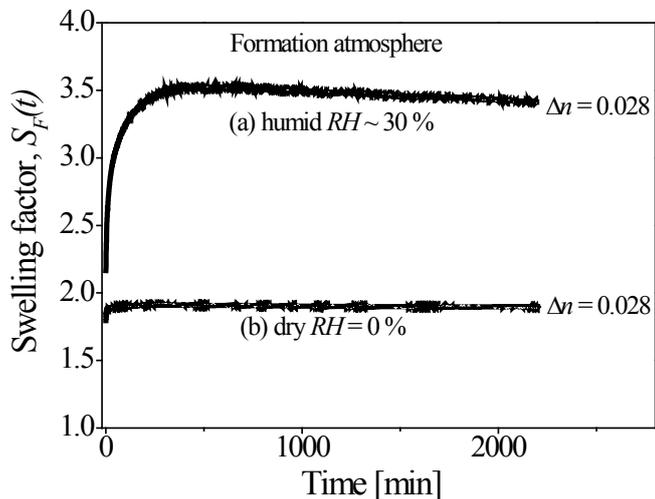


Figure 6: Water-induced swelling at 40 °C of ~300 nm SPEEK films with a DS of 84 %, formed under (a) humid, $RH \sim 30\%$ and (b) dry, $RH = 0\%$ atmosphere [9].

that affect the free energy of the film, and hence its potential to swell. A higher optical anisotropy corresponds to more residual stresses, and thus a higher free energy status, which results in more pronounced swelling. Combined, both effects cause that films with higher initial values of the anisotropy exhibit a higher propensity to swell [9]. We observed a particular swelling behaviour for films that were formed without access of water ($RH = 0\%$). Hydration of the polymer during membrane formation affects the internal molecular structure of SPEEK membranes and their morphology, which in turn has impact on swelling [9]. Figure 6 shows the swelling of films formed with and without the presence of water. The swelling of the 'dry' film is significantly reduced as compared to the 'humid' film, despite the equal DS, Δn and water temperature.

Process design

We compared the hybrid process design shown in Figure 3 with the simple design, in which the permeate is released to the atmosphere. In both designs, a refill stream is implemented such that the losses of CO_2 in the retentate are compensated for. In the hybrid design, the regeneration stage of the permeate is applied. The regeneration occurs by removal of water, which permeates through the membrane, via condensation (due to compression to 55 bar and cooling to 25 °C), and via an additional membrane unit. This regenerated and compressed permeate is further split into two streams: (1) first stream is further compressed to 100 bar and combined with the retentate; (2) second stream is depressurized to 2.5 bar (there a turbine is implemented to generate electricity) and combined with the sweep gas. The membrane permeance and selectivity were varied.

It is not straight forward which system type is superior. We considered the economic viability of the designs based on the duration of the dehydration process and the size of the feed. For hybrid design, the recirculation and regeneration of the permeate requires high investment and operating costs for compressors. On the other hand, simple design can be considered environmentally unfriendly and have high operating costs caused by the high CO_2 emissions. This can be seen in Figure 7 for a representative calculation of annual operating (OPEX) and capital (CAPEX) expenditures for a feed stream of 2,000 kg/h. In this simulation, a very high water

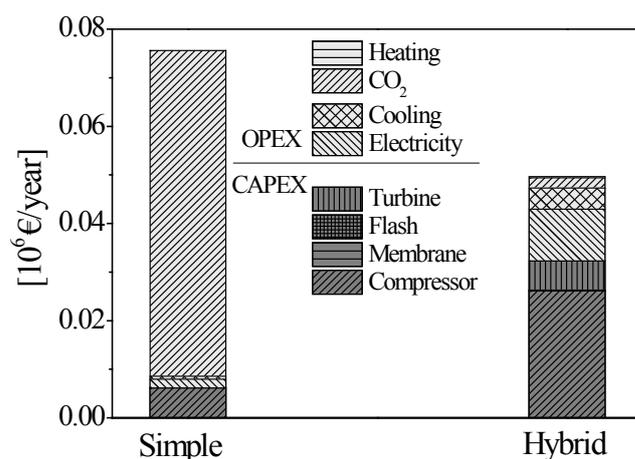


Figure 7: Annual costs for the low feed, simple and hybrid designs for a period of 8 years.

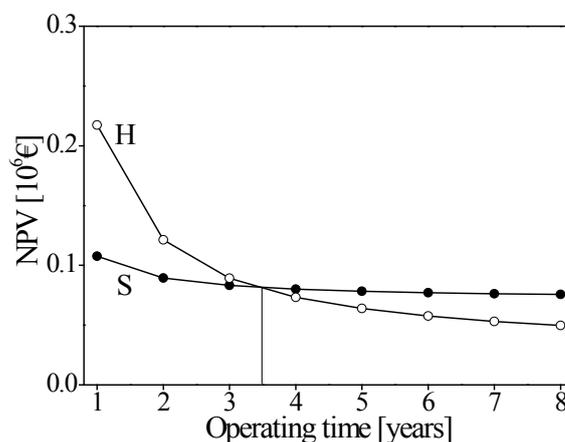


Figure 8: NPV of the low feed, simple (S) and hybrid (H) design. The usage of H is more beneficial compared to S assuming operating times longer than 3.5 years.

permeance of 250,000 GPU was assumed (therefore there are very minor capital costs for a membrane unit because the required membrane surface area to dehydrate the feed is very small). Additionally, the selectivity of 5,000 was assumed, which is a representative value for SPEEK membranes in highly swollen state. As visible in the graph, the investment costs for a flash vessel, in which water condensation from the

permeate stream occurs due to decreased temperature, are also minor. In the case presented in Figure 7, the investments in recirculation are not beneficial up to 3.5 years of operation. This is represented in Figure 8 by comparing the net present value (NPV) of both designs. In the up-scaled process (feed stream of 100,000 kg/h), the investments in recirculation is feasible when the process will take longer than 1 year. Due to the upscale, the losses of CO₂ are so high that the application of compressors and the rest of equipment pays off after 1 year. The actual water permeance through highly hydrophilic polymers was reported to be around 5,000 GPU, which increases the membrane surface area needed to perform dehydration and consequently, the investments costs in membrane unit.

Overall conclusions

Membrane technology is a promising alternative to perform the dehydration of compressed carbon dioxide. In terms of SPEEK membrane material (and likely other sulfonated polymers) we showed that the internal structure and morphology directly depends on the hydration of the polymer during and after formation, which has direct impact on membrane performance. Further, it is sensible to use membrane with reduced predisposition to swell in order to avoid excessive swelling that might lead to ruptures. This can be achieved, for instance, as we showed by membrane formation at RH=0 %. Additionally, in this project we chemically modified the thin SPEEK films using ethylene glycol and glycerol, according to the procedure described in [10] in order to reduce and control thin film swelling. Other methods for strengthening of membranes derived from sulfonated polymers can be found in [11]. The investigation of alternative methods to remove water from the permeate side or to regenerate the sweep gas would further contribute to

the development of the dehydration process of compressed carbon dioxide.

Acknowledgement

This work was performed in the TTIW-cooperation framework of Wetsus, European centre of excellence for sustainable water technology (www.wetsus.nl). Wetsus is funded by the Dutch Ministry of Economic Affairs, the European Union Regional Development Fund, the Province of Fryslân, the City of Leeuwarden and the EZ/Kompas program of the 'Samenwerkingsverband Noord-Nederland'. Beata Koziara would like to thank the members of Wetsus research theme 'dehydration' for the fruitful discussions and their financial support.

References

- [1] Almeida-Rivera, C.P., S. Khalloufi, and P. Bongers, Prediction of supercritical carbon dioxide drying of food products in packed beds. *Drying Technology*, 2010. 28(10): p. 1157-1163.
- [2] Lohaus, T., et al., Drying of supercritical carbon dioxide with membrane processes. *The Journal of Supercritical Fluids*, 2015. 98: p. 137-146.
- [3] Baker, R.W., *Membrane Technology and Applications*. 2nd ed. 2004, California: John Wiley & Sons, Ltd.
- [4] Jia, L., et al., Sulfonation of polyetheretherketone and its effects on permeation behavior to nitrogen and water vapor. *Journal of Applied Polymer Science*, 1996. 60(8): p. 1231-1237.
- [5] Sijbesma, H., et al., Flue gas dehydration using polymer membranes. *Journal of Membrane Science*, 2008. 313(1-2): p. 263-276.
- [6] Potreck, J., *Membranes for flue gas treatment. Transport behavior of water and gas in hydrophilic polymer membranes*. PhD Thesis 2009, University of Twente.
- [7] Fujiwara, H., *Principles of Spectroscopic Ellipsometry*, in *Spectroscopic Ellipsometry*. 2007, John Wiley & Sons, Ltd. p. 81-146.
- [8] Koziara, B.T., K. Nijmeijer, and N.E. Benes, Optical anisotropy, molecular orientations, and internal stresses in thin sulfonated poly(ether ether ketone) films. *Journal of Materials Science*, 2015. 50(8): p. 3031-3040.
- [9] Koziara, B.T., Akkilic, N., Nijmeijer, K., Benes, N.E., The effects of water on the morphology and the swelling behaviour of sulfonated poly(ether ether ketone) films. Submitted to *Soft Matter* 2015.
- [10] Mikhailenko, S.D., et al., Properties of PEMs based on cross-linked sulfonated poly(ether ether ketone). *Journal of Membrane Science*, 2006. 285(1-2): p. 306-316.
- [11] Hou, H., M.L. Di Vona, and P. Knauth, Building bridges: Crosslinking of sulfonated aromatic polymers—A review. *Journal of Membrane Science*, 2012. 423-424: p. 113-127.

PhD defense Salman Shahid

On Thursday February 5, 2014, Salman Shahid defended his PhD thesis entitled 'Polymer-Metal Organic Framework (MOF) mixed matrix membranes for gas separation applications'. In his thesis, Salman investigated the use of Molecular Organic Frameworks (MOFs) to enhance the high-pressure gas separation performance of polymeric membranes and the effects of the presence of MOFs on plasticization in CO₂/CH₄ separations.

For more information, please contact Prof. dr. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl; phone: +31 (0)53 489 4185).



New people

Gel membranes for (waste) water treatment

Kanwal Shahid obtained her Bachelor degree in Natural Science (Chemistry) at the Lahore College for Women University, in Lahore, Pakistan. The topic of her Bachelor thesis work was the “Removal of heavy metals from waste water using waste material”. She completed her Master studies in Chemistry (specialized in Biochemistry) at the same university. For her Master thesis work, she joined the Separation and Conversion Technology group (SCT) at VITO, Belgium, as a guest researcher. At VITO, she worked on the “Downstream processing of biosurfactants especially applying membrane technology”. The

objective of her research work was extraction and purification of biosurfactants from a fermentation broth by applying different polymeric and ceramic nanofiltration membranes.

In March 2015, she joined the Membrane Science and Technology group at the University of Twente as a PhD candidate. Her PhD project focuses on developing dynamic gel-layer membranes of biopolymers present in waste water for waste water treatment. This gel layer acts as the actual separation layer for small (colloid sized) particles, so it might serve as a cheap alternative for MF membranes. The project involves the design and development, characterization and application of this new type of gel layer membranes. Due to (biological) degradation, fouling, compaction or other mechanisms the performance of the gel-layer will deteriorate with time. To address this aspect, also long term stability, and efficient gel layer removal and replacement mechanisms will be investigated. Later on, for more NF or even RO related applications, it will be investigated whether it is possible to embed specific constituents in the gel layers that selectively remove e.g. organic micropollutants or specific ions. Additionally, to evaluate membrane performance under real conditions, larger scale experiments with real waste waters will be performed.

The research is conducted at the Wetsus research centre in Leeuwarden, under the supervision of the research groups Environmental Technology of Wageningen University and Membrane Science and Technology of the University of Twente.

Name: Kanwal Shahid

Origin: Pakistan

Contact

+31 (0)58 2843163

k.shahid@utwente.nl



Researcher

Bob Siemerink went to the laboratory school ROC-ON in Hengelo and he received his Bachelor in chemistry at ‘Saxion Hogescholen’ in Enschede. After his study he worked one year at van Heek textiles as a laboratory worker. Subsequently he worked for 4 years at Quadrant EPP in Almelo as an R&D technician. His main task at Quadrant was the development of improvements and new compositions for cast nylon 6 products.

Music making is his biggest hobby. He plays the drums in 3 different music groups: a orchestra, a pop brass band and a party band. Most of his leisure time you can find him behind a drum-kit, timpani or snare drum. Bob also like to travel. Camping in Europe, or a road-trip through the USA. San Francisco is one of his favorite cities.

Within the Membrane Science and Technology group, Bob is the new technician. His background in chemistry is of high value for the development of the next generation polymer membranes. In addition he has a strong background in analytical techniques for polymer and membrane characterization.

Name: Bob Siemerink

Origin: Dutch

Contact

+31 (0)53 4895526

B.J.Siemerink@utwente.nl



It all started in Twente

What is your name?

Geert-Henk Koops

What are your date of birth and your place of birth?

Really, why would that be interesting? I was born in Ommen, Overijssel, The Netherlands on 23 December 1964.

What is your marital status and do you have children?

I'm happily married with my wife Shinobu and we have no kids.



Where are you currently employed and what is your position?

I'm currently working at GE Water & Process Technologies in Oakville Canada as Global Technology Leader for UF/MBR. My team develops, validates and implements new products and processes for water and wastewater treatment. The products include membranes, modules and cassettes as well as biological reactors removing ammonia, recalcitrant components and heavy metals, like selenium.

Where is your company located and where do you live?

The company is located in Oakville, Canada. This is roughly a 30 min drive west of Toronto at Lake Ontario. We live in the same city in the older part of the town.

When did you start your PhD and when did you receive your PhD degree?

This is a long time ago. I started in April 1988 and graduated in June 1992. I was one of the last students of Prof. Cees Smolders before he retired.

On which topic did you do your PhD?

In those days Pervaporation was a hot topic. It was a new and upcoming membrane process that was going to replace the classical distillation processes; no doubt. Well, we all know how



that ended :(. My topic was on dehydration of acetic acid with a focus on material aspects and membrane development.

Do you still have contacts with your former PhD students from that time?

Yes... Oh, you want to know with whom? Matthias Wessling, one of my old roomies is the one I still see and talk to on a regular basis. Antoine Kemperman I see mostly when I pay a visit to Enschede and we go out for a drink or at a conference. Other people from those days I sometimes see at conferences or shows/exhibitions are Petrus Cuperus, Ingo Blume or Erik Roesink.

Then there were Cees Smolder's "Boerenkool" parties, which he organized every 5 years since his retirement and invited all his graduated PhD students. There I met many more. Great event. I wonder if Cees still does this.



What was your first job after your PhD?

I'm not sure if you can call it a job, but after my PhD I received a scholarship to work for 2 years at a research institute in Japan, a kind of post-doc position. Best decision ever. The pay was great. The country is fantastic. I met many great

people from all over the world I'm still in contact with. We traveled a lot to see the country and had parties every single week. This is also the place I met Shinobu and got married... in a Shinto Shrine, the traditional way. Only great memories.

How did your career develop?

After my Japan adventure I returned back to the University of Twente and started working at the EMI Twente as R&D manager. Did that for 11 years with a lot of pleasure and a fantastic team. I then decided to move to the industry. Membrane development was my passion and I was looking for an R&D management position in a membrane company. I heard that Zenon Environmental Inc. was looking for a Director R&D, which was exactly what I wanted. I got the job and moved to Canada. A year later Zenon was acquired by General Electric and that is where I still am. About 6 years ago I moved from Director R&D and being responsible for membrane development into my current role as Global Technology Leader for UF/MBR, the former Zenon business. I lead a team of 60 engineers and technicians in Canada and Hungary and I'm involved in various projects being executed by local teams in China and Singapore.



How do you relate your career to the experience you gained during your PhD?

I owe my whole career to my PhD. All my life I have been working in R&D and in the field of membrane technology. The passion for both was developed during my PhD.

How did you experience your time in Twente?

It was in one word awesome and therefore not a difficult decision to come back and spent another 11 years in Twente working for the EMI. For me it is important to have fun, a

group of smart people around me, and challenging projects to work on. That is what I found in Twente.

What important things did you learn during your PhD?

Many things. First of all, my English language skills improved quite rapidly together with my "klaverjassen" skills. Then I learned how to design and execute experiments, how to interpret results and make decisions based on those results, how to spin hollow fibers and the basics of membrane development, how to present my work, and how to write scientific papers. I developed a broad understanding of membrane technology by interacting and learning from my colleagues. As I said before, it formed the basis for my whole career and today I still use many of the skills I learned back in those days.

What was the biggest challenge during your PhD?

The biggest challenge was to finish within 4 years and be satisfied with my accomplishments.

Do you maybe remember an anecdote or a specific moment of that time?

In my first year, a few months after I started I got to attend a conference in Nancy, France. It was one of those Pervaporation conferences organized by the Bakish family, with about 90-100 attendees. Remember, these were the early days when the membrane community was still relatively small. Anyways, I was listening to many interesting papers and everything was cool. Then it was my roommate, Herry Nijhuis' turn. He presented about his work on volatile organic compound removal from water. He was talking about solubility coefficients and correlations between certain materials and organic solvents or something like that. After Herry was done a German professor stood up and started a tirade against the proper use of the solubility theory and Herry's approach of using solubility coefficients. Basically, he told Herry he did not know what he was talking about. At that moment, torn between anger and fear I thought only one thing; I WILL NOT SPEAK AT A CONFERENCE, EVER. Later, when I got to know that professor and attended more conferences I learned that this was quite an exception, thank God. As a matter of fact I have never experienced something like that ever again.

What was the best moment of your PhD?

Finishing my thesis and mailing it out to the committee. And yes, we used envelopes in those days.

What would you have done differently if you could do your PhD again?

Interesting question. I would have subcontracted my attempted modeling part to a really smart person or simply have left it out.

Which advice do you have for the current generation PhD students?

Embrace the opportunity that has been given to you. A PhD title can take you to places, although you are in control of your destination.

Finish your thesis before you start your next adventure. I have seen too many people not finish because they start a job right away and believe they can do the writing in the evenings and weekends. Trust me, does not work.

For the Dutch students take a post-doc position in a foreign country. A few years abroad will enrich your life forever.

What is your precious memory of the group?

There are many. Being part of the membrane family, playing cards during lunch, indoor soccer, Batavieren race, the BBQ and X'mas parties, John Heeks, playing competitive Bridge

with Marcel as a partner and boy did I make a lot of mistakes... in the eyes of Marcel, the many bets for a box of beer (mainly with Marcel), the Friday afternoon and evening "borrels", the bicycle tours through beautiful Twente, the group excursions to Germany and France, fooling around with colleagues, making fun of Jean Marc's French accent when he spoke Dutch or English. Actually he is one of the few that learned the Dutch language very quickly and very well, not counting our German friends. And of course all the lovely people that were there from 1988 – 1992.

What could be different in our research group?

It has been a while since I was there, but I hope that the relaxed, fun and truly family like atmosphere is still there. It was always a pleasure to come to work and do things together, also after hours. If that is gone, I would change it back.

What did you miss while working in the group?

I missed my mother... no, kidding. I did not miss anything. We could do whatever we thought was necessary to do good research.

Do you maybe want to add something else? Feel free.

Just a question: When is the next reunion?

Science on national TV in 'De Wereld Draait Door'

On March 18, 2015, Prof. Kitty Nijmeijer was on the Dutch national television in the program 'De Wereld Draait Door'. The program 'De Wereld Draait Door' is a daily program on the Dutch television, broadcast at prime time.

One century ago, in 1915, Albert Einstein developed his famous theory of general relativity. To celebrate the 'Einstein Year' four scientists were invited to explain their favorite equation. Over 1.5 million people saw Kitty explaining the ideal gas law and thermodynamics.



The item can be found at: <http://dewerelddraaitdoor.vara.nl/media/336350>

Vacancies

Within the research group Membrane Science and Technology of the University of Twente, we have two vacancy for Ph.D. positions.

2 Ph.D. positions: “Next Generation Aquaporin embedded Forward Osmosis Membranes”

The development of more selective and highly permeable water filtration membranes is crucial for the next generation water purification membranes. The cell membranes of many living organisms are unique in this respect as these have exceptionally high fluxes and corresponding selectivities. Such cell membranes use proteins, so-called aquaporins that serve as small water channels, which allow fast transport of only water molecules and retain all contaminants. The Danish company Aquaporin is world leader in mimicking such proteins and in the development of biomimetic membranes using nature’s technology in synthetic water purification membranes. Although the first generation aquaporin membranes have extraordinary high fluxes, much is unclear and undeveloped yet. The goal of the present project is the development of the next generation aquaporin embedded membranes together with the Danish company Aquaporin.

In this project, two Ph.D. students will work together on the development of the next generation aquaporin membranes. The first Ph.D. project will focus on the design and development of a highly porous support membrane optimized for FO processes, while the second Ph.D. project is dedicated to the development of the semi-permeable aquaporin layer. At the interface of both projects, the Ph.D. students will closely collaborate. A stay of 1 year at the company Aquaporin in Denmark is part of the program of

both Ph.D. students.

The research will be conducted at the Membrane Science and Technology group, faculty of Science and Technology of the University of Twente (www.utwente.nl/tnw/mtg).

We are looking for highly motivated and enthusiastic researchers with an MSc degree. For the PhD position on support development, we look for candidates with a background in (polymer) chemistry, chemical engineering or a related topic. For the second Ph.D. project we look for candidates with a biological or chemistry background. Expertise in membrane development is preferred. Both projects require a profound physical chemistry or chemistry background and a scientific attitude. Candidates should have excellent experimental and theoretical skills.

We prefer candidates with a good team spirit, who like to work in an internationally oriented environment. Fluency in English is a requirement. An interview and a scientific presentation will be part of the selection procedure.

We offer you a PhD position for 4 years. Your starting salary will be € 2083, - gross per month in the first year and up to € 2664, - gross per month in the last year.

Interested candidates are invited to send, by email, a motivation letter, curriculum vitae (including references) and a list of BSc and MSc courses and grades to Prof. dr. ir. Erik Roesink (h.d.w.roesink@utwente.nl); phone: +31653317991) for the position on membrane support development and to Prof. Dr. Ir. Kitty Nijmeijer (d.c.nijmeijer@utwente.nl); phone: +31 53 489 4185) for the position on the development of the semi-permeable aquaporin layer.

Upcoming Ph.D. defenses

Beata Koziara

Thin sulfonated poly(ether ether ketone)films for the dehydration of compressed carbon dioxide.

October 9, 2015; 12.45 h, University of Twente

Harro Mengers

Membrane reactors for the direct conversion of CO₂ to dimethyl carbonate.

October 22, 2015; 16.45 h, University of Twente

Seminar

Membranes in food processing

Kamer van Koophandel, Kennispark and the European Membrane Institute organize a seminar about membranes in food processing applications. The seminar is very interesting for SMEs active in the food industry as well as for equipment manufacturers. Next to a short introduction from the organizers there are three invited speakers:

Lex van Dijk (Blue-Tec)

- Concentration by Forward Osmosis and Reverse Osmosis.

Albert van der Padt (WUR and Friesland Campina)

– Fractionating and cold sterilization of dairy products.

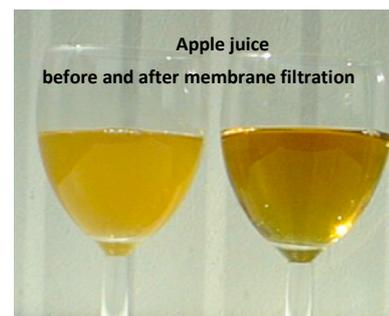
Jens Potreck and André Mepschen (Pentair/X-Flow)

– Food wastewater treatment and wine/beer filtration.

The meeting closes with a reception that allows an informal and more in-depth discussion with the speakers.

Date: October 1, 2015; 14:30 – 17:00hr. Location: Kennispark Twente, Enschede, The Netherlands.

More information: Dr. Zandrie Borneman (z.borneman@utwente.nl)



EMS

Antoine Kemperman elected board member EMS

In January 2015, dr. Antoine Kemperman joined the board of the European Membrane Society (EMS) for the next 4 years. As elected board member, Antoine is in charge of the visibility of the society. The EMS aims at promoting membranes and membrane activities all over Europe and to foster collaborations with the other membrane societies in the US, China and Asia. The most important activity of the EMS is among others, Euromembrane. Furthermore the society organizes multiple actions to stimulate and enhance the participation of especially younger researchers in the field of membranes: The EMS provides lecture and poster prizes, a best paper award and a significant amount of travel awards for international membrane conferences is provided to early stage researchers.



Antione Kemperman

Publications

- de Grooth, J., Haakmeester, B., Wever, C., Potreck, J., de Vos, W.M., Nijmeijer, K., Long term physical and chemical stability of polyelectrolyte multilayer membranes, (2015) Journal of Membrane Science, 489, pp. 153-159.
- Shahid, S. Nijmeijer, K. Nehache, S., Vankelecom, I., Deratani, A., Quemener, D., MOF-mixed matrix membranes: precise dispersion of MOF particles with better compatibility via a particle fusion approach for enhanced gas separation properties, (2015), Accepted for publication in Journal of Membrane Science.
- Ilyas, S., de Grooth, J., Nijmeijer, K., De Vos, W.M., Multifunctional polyelectrolyte multilayers as nanofiltration membranes and as sacrificial layers for easy membrane cleaning, (2015) Journal of Colloid and Interface Science, 446, pp. 365-372.
- Koziara, B., Nijmeijer, K., Benes, N., Optical Anisotropy, Molecular Orientations, and Internal Stresses in Thin Sulfonated Poly(ether ether ketone) Films, (2015), Journal of Materials Science, 50, pp. 3031-3040.
- Shang, R., Vuong, F., Hu, J., Li, S., Kemperman, A. J. B., Nijmeijer, K., Cornelissen, E. R., Heijman, S. G. J., Rietveld, L. C., Hydraulically irreversible fouling on ceramic MF/UF membranes: Comparison of fouling indices, foulant composition and irreversible pore narrowing, (2015), Separation and Purification Technology, 147, pp. 303-310.
- Wibisono, Y., Yandi, W., Golabi, M., Nugraha, R., Cornelissen, E.R., Kemperman, A.J.B., Ederth, T., Nijmeijer, K., Hydrogel-coated feed spacers in two-phase flow cleaning in spiral wound membrane elements: A novel platform for eco-friendly

-
- biofouling mitigation, (2015) *Water Research*, 71, pp. 171-186.
- Wibisono, Y., El Obied, K.E., Cornelissen, E.R., Kemperman, A.J.B., Nijmeijer, K., Biofouling removal in spiral-wound nanofiltration elements using two-phase flow cleaning, (2015) *Journal of Membrane Science*, 475, pp. 131-146.
 - de Grooth, J., Oborný, R., Potreck, J., Nijmeijer, K., de Vos, W.M., The role of ionic strength and odd-even effects on the properties of polyelectrolyte multilayer nanofiltration membranes, (2015) *Journal of Membrane Science*, 475, pp. 311-319.
 - IJzer, A.C., Vriezokolk, E., Rolevink, E., Nijmeijer, K., Performance analysis of aromatic adsorptive resins for the effective removal of furan derivatives from glucose, (2015) *Journal of Chemical Technology and Biotechnology*, 90 (1), pp. 101-109.
 - Spruijt, E.; Biesheuvel, P. M.; de Vos, W. M., Adsorption of charged and neutral polymer chains on silica surfaces: The role of electrostatics, volume exclusion, and hydrogen bonding, (2015) *Physical Review E*, 91 (1), pp. 012601.
 - Mears, L. L. E.; de Vos, W. M.; Prescott, S. W.; Magro, G.; Rogers, S.; Skoda, M. W. A.; Watkins, E. B.; Zimmermann, H.; Richardson, R. M., The adsorption of fluorinated dopants at the surface of 5CB: a neutron reflection study, (2015) *Liquid Crystals*, pp. 1-9.
 - Yip, N.Y., Vermaas, D.A., Nijmeijer, K., Elimelech, M., Thermodynamic, energy efficiency, and power density analysis of reverse electrodialysis power generation with natural salinity gradients, (2014) *Environmental Science and Technology*, 48 (9), pp. 4925-4936.
 - Vermaas, D.A., Kunteng, D., Veerman, J., Saakes, M., Nijmeijer, K., Periodic feedwater reversal and air sparging as antifouling strategies in reverse electrodialysis, (2014) *Environmental Science and Technology*, 48 (5), pp. 3065-3073.
 - Vermaas, D.A., Veerman, J., Saakes, M., Nijmeijer, K., Influence of multivalent ions on renewable energy generation in reverse electrodialysis, (2014) *Energy and Environmental Science*, 7 (4), pp. 1434-1445.
 - De Grooth, J., Reurink, D.M., Ploegmakers, J., De Vos, W.M., Nijmeijer, K., Charged micropollutant removal with hollow fiber nanofiltration membranes based on polycation/polyzwitterion/polyanion multilayers, (2014) *ACS Applied Materials and Interfaces*, 6 (19), pp. 17009-17017.
 - Vriezokolk, E.J., De Weerd, E., De Vos, W.M., Nijmeijer, K., Control of pore size and pore uniformity in films based on self-assembling block copolymers, (2014) *Journal of Polymer Science, Part B: Polymer Physics*, 52 (23), pp. 1568-1579.
 - de Vos, W. M.; Cattoz, B.; Avery, M. P.; Cosgrove, T.; Prescott, S. W., Adsorption and Surfactant-Mediated Desorption of Poly(vinylpyrrolidone) on Plasma- and Piranha-Cleaned Silica Surfaces, (2014) *Langmuir : the ACS journal of surfaces and colloids*, 30 (28), pp. 8425-8431.
 - Abbott, S. B.; de Vos, W. M.; Mears, L. L. E.; Barker, R.; Richardson, R. M.; Prescott, S. W., Hydration of Odd–Even Terminated Polyelectrolyte Multilayers under Mechanical Confinement, (2014) *Macromolecules*, 47(10), pp. 3263-3273.
 - Lee, K.P., Zheng, J., Bargeman, G., Kemperman, A.J.B., Benes, N.E., pH stable thin film composite polyamine nanofiltration membranes by interfacial polymerization, (2015) *Journal of Membrane Science*, 478, pp. 75-84.
 - Cattoz, B., de Vos, W. M., Cosgrove, T., Crossman, M., Espidel, Y., Prescott, S. W., Interpolymer Complexation: Comparisons of Bulk and Interfacial Structures, (2015) *Langmuir : the ACS journal of surfaces and colloids*, 31 (14), pp. 4151-4159.
 - Abbott, S. B., de Vos, W. M., Mears, L. L. E., Cattoz, B., Skoda, M. W. A., Barker, R., Richardson, R. M., Prescott, S. W., Is Osmotic Pressure Relevant in the Mechanical Confinement of a Polymer Brush?, (2015) *Macromolecules*, 48 (7), pp. 2224-2234.

Follow MST on Twitter!



The Membrane Science and Technology group has its own Twitter account!
Follow @MST_UTwente for the latest news of the MST group in a nutshell!

Membrane Science and Technology

Vision

The research group Membrane Science and Technology of the University of Twente, headed by Prof. Kitty Nijmeijer, focuses on the multidisciplinary topic of polymer membranes to control mass transfer through interfaces.

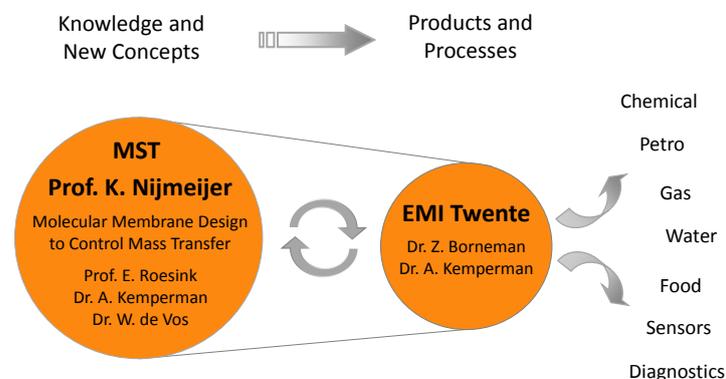


Figure 1: Organizational structure research group.

The group consists of two separate entities (Figure 1): the academic research group Membrane Science and Technology (MST) and the European Membrane Institute Twente (EMI), which performs confidential research directly with the industry.

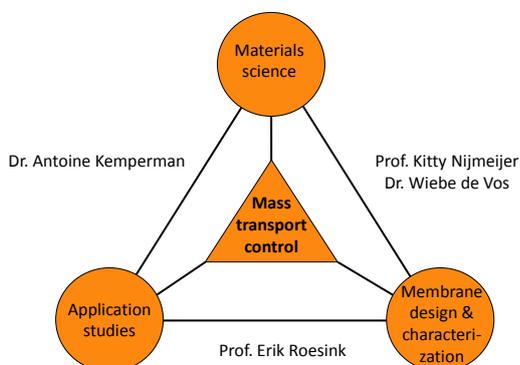


Figure 2: Membrane Science & Technology.

Research within the group is dedicated to the design, development, characterization and application of polymer membranes for Energy, Water and Life Sciences. We aim at tailoring membrane design, morphology and characteristics on a molecular level to control mass transport in applications (Figure 2). More specifically, our research focuses on the separation of molecular mixtures and achieving selective mass transport. We consider our expertise as a multidisciplinary knowledge chain ranging from molecular design towards process applications.

Most of our research is dedicated towards specific applications. We distinguish three main application clusters, i.e. Energy, Water and Life Sciences (Figure 3).

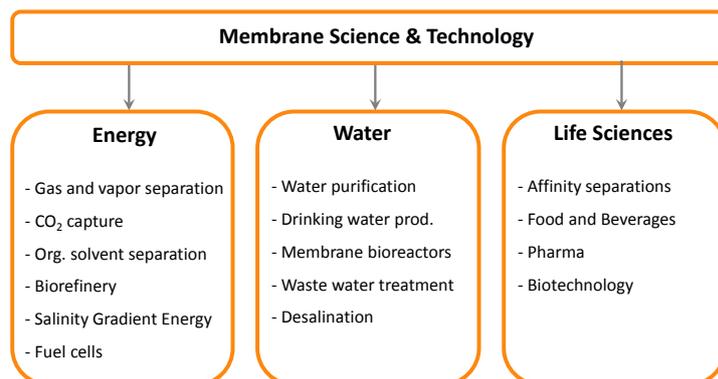


Figure 3: Major application clusters Membrane Science & Technology.

Energy

The research cluster Energy is dedicated to the molecular design and synthesis of polymer membranes for e.g. gas and vapor separations (CO₂ capture, olefin/paraffin separation,



water vapor removal), biorefinery applications, fuel cells and the generation of energy from the mixing of salt and fresh water ('salinity gradient energy' or Blue

Energy). Relevant research aspects are control of structure-properties relationships, ultimate selectivity, molecular recognition, and separation of complex, multi-component mixtures.

Water

Within the application cluster Water, research addresses the development of membranes and the application of membrane technology for water treatment, e.g. water purification, desalination, membrane bioreactors and waste water treatment. In particular it investigates the relation between membrane design, morphology and membrane properties in relation to performance, selectivity and causes, consequences and control of fouling.

Life sciences

The cluster Life Sciences focuses on the design of porous membranes to separate complex multicomponent mixtures in pharmaceutical, food, beverage and biotech applications. Important subjects are the tuning of the material properties and structure (e.g. pore morphology and porosity), the

development of functional materials (e.g. affinity separations of biomolecules) and the creation of improved processes. In addition, aspects related to process design and industrial implementation, such as scale-up of novel membrane fabrication methods, are investigated. The research group consists of 30-35 people among which approximately 15-20 Ph.D. students, three permanent researchers, five B.Sc. and M.Sc. students and five academic staff members. Next to the head of the group, Prof. Kitty Nijmeijer, the staff consists of Prof. Erik Roesink, Dr. Wiebe de Vos, Dr. Antoine Kemperman and Dr. Zandrie Borneman, who is responsible for the EMI Twente. Next to extensive, general knowledge on polymer membrane science and technology, each of the staff members has his/her own specific field of dedicated expertise (Table 1).

Table 1: Specific expertise of the staff members of MST.

Name	Specific expertise
Prof. Kitty Nijmeijer	Membrane design and characterization, molecular selectivity, molecular recognition, dense membranes, Energy and Water
Prof. Erik Roesink	Membrane formation, porous systems, phase inversion, solvent-free membranes, biomimetic membranes, Water and Life Sciences
Dr. Antoine Kemperman	Causes, consequences, cleaning and control of membrane fouling, interactions at the interface, Water European Membrane Institute (EMI) Twente: Confidential contract research directly with the industry
Dr. Wiebe de Vos	Membrane surface science, surface modification, multilayers, polymer brushes, Water and Energy.
Dr. Zandrie Borneman	European Membrane Institute (EMI) Twente: Confidential contract research directly with the industry

Knowledge valorization

Our group has decided to establish a significant effort in the valorization of its knowledge. The European Membrane Institute Twente (EMI Twente) was established in 1995 and performs confidential contract research directly with the

industry and public organizations. Research is governed by questions from stakeholders. To guarantee confidentiality, we work with highly skilled researchers with long standing experience in membrane technology

in our group. Students are not involved. EMI Twente creates, transfers and translates (fundamental) scientific knowledge into products, processes and applications. Projects can last from only a few days up to three years and can involve membrane development and synthesis, membrane characterization, and/or membrane application studies. The EMI Twente acts as the interface between the academic research and the industrial needs.

Services

The EMI Twente provides the following services:

- Membrane development
- Membrane characterization
- Membrane application studies
- Desktop studies
- Consultancy
- Selling of equipment (e.g. cells for gas separation, UF and MF, casting knives, cloud point meters, hollow fiber spinning lines, spinnerets)



For more information, please contact:

Prof. Dr. Kitty Nijmeijer
d.c.nijmeijer@utwente.nl
www.utwente.nl/tnw/mtg

Dr. Zandrie Borneman (EMI Twente)
z.borneman@utwente.nl
www.utwente.nl/tnw/emi

MNT- Information

Membrane News Twente is published two times per year and aims to inform the membrane community about the activities of the Membrane Technology Group of the University of Twente (membrane@utwente.nl www.utwente.nl/tnw/mtg).

Editors
Kitty Nijmeijer
Shazia Ilyas