TECH PAPERS

VITO

NOVEL SOLVENT RESISTANT MEMBRANES AND MEMBRANE-ASSISTED SYNTHESIS CONCEPTS FOR ACHIEVING PROCESS INTENSIFICATION

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Novel solvent resistant membranes and membrane-assisted synthesis concepts for achieving process intensification

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In the quest for achieving process intensification, membrane-based separation technologies can have an important contribution via their integration in new or existing (bio)conversion processes. In this article, an overview of VITO's activities in the development of novel solvent resistant membranes for molecular separation in organic media and membrane-assisted intensification concepts is presented.

1. Introduction

It is not an overestimation to state that membrane-based separation technology has a huge potential in the intensification of (bio)chemical production processes. Its applicability in the direct coupling of molecular separation to batch or continuous reactions makes it an important tool, not only for the downstream processing of product streams but also the improvement of reaction efficiencies or productivities. Moreover, membrane-based separations are low energy-demanding since no (or a very limited) temperature-induced phase transition takes place in the process, and mild operating temperatures can result in higher product quality in case of purification of thermally labile molecules, next to a safer processing. The design of membrane installations is based on a modular principle, making them easy scalable, in function of the reaction batch volume or flow size. A last advantage may be the reduced installation size, when membrane modules with a high surface-to-volume ratio are applied.

This technique enables e.g. purification of target compounds, recovery of expensive homogeneous catalysts, product fractionation, exchange of reaction solvents, as well as in-situ product recovery and the recycle of raw materials, process water and solvents. Consequently, membrane filtration is rapidly becoming a valuable part of the separation specialist's toolbox in the fine chemical, pharmaceutical, food, biotechnology and related industries.

2. Membrane technologies for molecular separation in organic solvent media

In the last years, a growing applicability of membrane technology has been witnessed in the treatment of chemical process streams, parallel to the increasing availability of pH stable and chemical resistant polymeric commercial membranes [1,2,3]. Also the ceramic membranes, with their inherent broad chemical resistance, are now attractive because of their price-competitiveness to the polymeric alternatives.

Since product molecules in chemical processes have low molecular masses in most cases, the applications are typically in the nanofiltration range (200 till 1000 Da molecular weight), where solvent or molecule transport through the microporous structure is driven by a pressure gradient and mainly discriminated by their molecule dimensions. Currently, more or less 18 dedicated polymeric organic solvent nanofiltration (OSN) membranes are commercially available from different vendors, such as Evonik, GMT, AMS technologies and Solsep, whereas several membranes for the treatment of aqueous process streams may show stability in the filtration of water/solvent mixtures. In the field of ceramic alternatives, only Inopor offers membranes sufficiently dense for nanofiltration applications.

Another promising technique is organophilic pervaporation, which can be applied in the recovery of volatile organic components from aqueous process streams. The transport occurs here through a dense membrane via a transmembrane partial vapor pressure difference. The selectivity is obtained by a combination of affinity of migrating components for the membrane material and their diffusion potential through the membrane. Two important vendors of pervaporation membranes are Pervatech and Sulzer.

Whereas both polymeric and ceramic membranes are applicable in downstream processing of solvent streams, only the latter shows an applicability in the direct coupling with chemical process operations at severe reaction conditions, by their combination of chemical, thermal and structural stability. The polymeric types can be applied at milder reactions conditions, for instance in the coupling of organophilic pervaporation with biochemical reactions, typically occurring at lower temperatures.

3. Architecture of ceramic membranes for OSN applications

Ceramic nanofiltration membranes intrinsically show strong hydrophilic properties ascribed to the large amount of surface hydroxyl groups, generated by the (transition) metal oxide framework. In the filtration of solvent streams, this is correlated to a flux performance
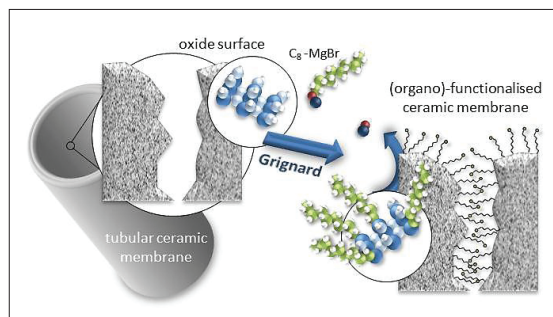
Fig. 1: Illustration of the (organo)functionalization with C8-Grignard reagens on the oxide surface of a tubular ceramic membrane. The surface hydroxyl groups are partially replaced by C8 groups.

in apolar solvents being lower than that of polymeric OSN membranes. However, an increased hydrophobicity can be induced by exchanging the surface hydroxyl groups by more apolar, organic groups in a post-synthesis treatment. Obviously, it remains important that chemical stability and separation properties of the new (organo)ceramic are maintained.

Recently, VITO has developed a unique versatile grafting method, a modification with Grignard reagents, which is capable to create a direct covalent, highly stable bond between the membrane surface and the functional group (Figure 1). This post-treatment is done on commercially available ceramic membranes under very dry conditions and in appropriate solvents. The grafting can be performed with various organic functional groups, like for instance alkyls, phenyls, or amines and opens the path for preparing a wide range of novel membranes with given surface functionalities, called FunMem® [4,5].
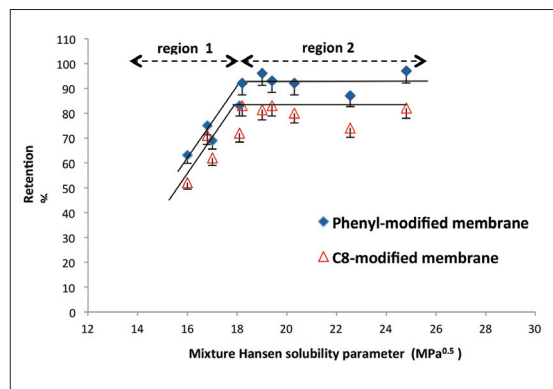

Fig. 2 : Retention of polystyrene (MW = 580 Da) in different solvents for phenyl and octyl functionalised ceramic nanofiltration membranes. The retentions are plotted as function of the total Hansen solubility parameter of the solvents. The lines are a guide for the eyes. This figure was adapted from [9].

Through this strategy, the intrinsic (thermo)chemical stability of ceramic membranes can be combined with good flux performance. Next to this, also the membrane separation properties can be improved via the (organo) functionalization, adding an extra affinity-based selectivity factor in solvent filtration, alongside the solutes' size. Indeed, recent studies [6] have clearly elucidated that OSN is not as straightforward as water filtration: the global separation capacity of a membrane in a solvent-solute mixture is the result of all competitive solute-membrane-solvent interactions. As a consequence, the introduction of functional groups on the membrane surface results in a changed solute or solvent affinity for the membrane, and therefore a changed selectivity. In this philosophy, tailor-made membranes can be made for a given solvent filtration application.

One step Grignard modification with alkyls typically leads to partial replacement of the surface hydroxyl groups, resulting in materials with an amphiphilic character [5, 7]. In a first study, the effect of an functionalization of Inopor's 1 nm TiO_2 nanofiltration membrane on water and organic solvent flux performances was demonstrated [7]. In Table 1, the water contact angles show that the C_1, C_5 and C_8 modified membranes have an increased hydrophobic character, relative to the unmodified sample. The hydrophobicity attained was comparable or higher than for the benchmark polymeric Duramem 300 and Starmem 240 membranes of Evonik MET. The overall water flux performance remained similar after the modification, whereas the non-polar solvent fluxes increased significantly to economically viable levels. The combined high flux performance for both polar and apolar solvents is a consequence of the amphiphilic character of the membranes. At the same time, the membranes showed a similar separation capacity for polystyrene (MW 580 Da) in acetone as the polymeric membranes. Improvement compared to the unmodified membrane is clear, and can be attributed to a higher solvent-membrane affinity. As a consequence, the new membranes can be considered as a ceramic, non-swelling, alternative for the mentioned polymeric membranes.

Further investigations determined the retentions of octyl and phenyl Grignard functionalized nanofiltration membranes in a wide range of solvents, ranging from the very polar water, to the very apolar cyclohexane [8,9]. As solutes we chose three PEG molecules (PEG-600, partially methyl capped PEG and fully methyl capped PEG) and polystyrene, all with almost the same size but different polarities. The retention results for all solutes showed in general a very different behaviour in different ranges of solvent polarity (Figure 2).

Membrane	Contact angle (°)	Permeability (l/m².h.bar)*				Retention PS580
		water	THF	toluene	hexane	in acetone (%)**
1 nm TiO$_2$	19	32	6,6	4,8	1,5	40
C$_1$-1 nm TiO$_2$	70	20	10	8	9,6	84
C$_5$-1 nm TiO$_2$	79	22	44	35	61	80
C$_8$-1 nm TiO$_2$	83	43	59	64	143	84
Duramem 300	45		-			87
Starmem 240	73		-			87
* measured at 2 m/s cross-flow velocity and room temperature						

Tab. 1: Water contact angle, water and solvent permeability and polystyrene PS580 retention for the (un) modified 1 nm TiO2 ceramic and polymeric Duramem and Starmem membranes.
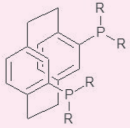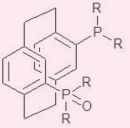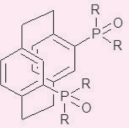
At low solvent polarity, retentions are relatively low, varying with pressure and decreasing with decreasing solvent polarity; at high solvent polarity, retentions are relatively high, independent of pressure and solvent polarity, and similar as the size exclusion value of solute in water. Similar changes of retentions were noticed during solvent exchange from one solvent to another via diafiltration.

The Spiegler-Kedem theory, taking into account both diffusion and convection transport mechanisms, was used as a basis for a fundamental explanation of all the results [9]. Using this theory, region 2 naturally corresponds to a region with high solvent flux (high solvent-membrane affinity), and thus dominating convection. In this region the retentions are mainly determined by size exclusion and equal to the reflection coefficient σ. Region 1 naturally corresponds to a region with low solvent flux (low solvent-membrane affinity), and thus non-negligible influence of diffusion in the solute transport. In this region, also a strong influence of the solute polarity is observed: the solute with the highest solute-membrane affinity, shows the lowest retentions. The relative simplicity of this interpretation is most probably due to the absence of swelling in the ceramic membranes used for this study. The results demonstrate again the importance of all solvent-membrane-solute interactions in the OSN transport, but also show how they can be manipulated to enhance the membrane performance.

To clarify the potential of using the solute-affinity effects in real separations, filtration of a realistic mixture of the metal ligand (S)-3,5-xylyl phanephos (well-known ligand in organometallic catalysis) in isopropanol was performed. The mixture used was contaminated with the mono and dioxide forms of the phosphine in significant quantities. The results show that, even if the three solutes have similar size, they can be separated on the basis of their polarity difference, using a functionalized membrane (Table 2) [8].

This functionalization has also been successfully scaled up to commercial membrane size, and the long term stability of the FunMem® membranes has been demon-

Reference memmbranes	Permeability (l/hm²bar)	Retention (%)		
		A	B	C
0.9 nm TiO$_2$	0.21	30.6	- 8.6	- 56.6
Modified membranes				
C$_8$-1 nm TiO$_2$	0.22	99.3	89.5	- 161.7

Solution: Isopropanol — Solvent. phosphine — Solute.

R =

Tab. 2 : Retention in mixture of isopropanol/phophine for modified and unmodified membranes.
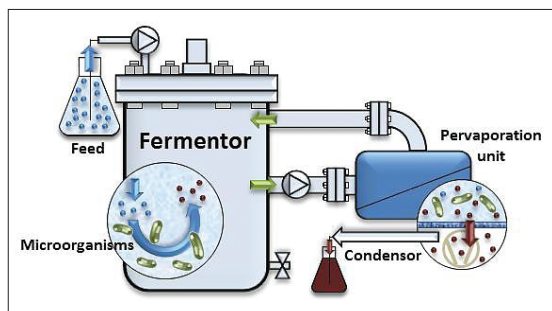
Fig 3: Concept of an integrated fermentor-pervaporation unit. The produced ABE products are toxic for the microorganism. Continuous vacuum driven removal with a dense pervaporation membrane allows to increase productivities.

strated in filtrations at pilot scale, for over 2 months [10]. Moreover, a wide variety of FunMem® with many more functional groups, including different amines, acids and even chiral groups, has been realized [10].

4. Membrane-assisted intensification of (bio)chemical processes

Organic solvent membrane technologies offer several opportunities for combining batch reactions with continuous membrane processing. This coupling can occur via integration of the membrane into the reactor, creating a membrane reactor with limited degrees of freedom for an optimal use of the membrane (process) properties. For instance, membrane surface area and scalability are restricted, the reactor would be dedicated to one or a narrow range of reactions, the membrane cannot be cleaned, etc. … These disadvantages are not present in concepts where the reaction mixture is continuously circulated from the reactor through the separation unit and sent back to the reactor vessel. This tends towards a continuous work-up without negatively affecting the reaction progress. Overall, a more efficient conversion of raw materials to product, a higher productivity, an increased energy efficiency and the closure of solvent and material loops is targeted by retaining or removing given molecules from the reaction mixture. This is exemplified in the following cases.

4.1 Organophilic Pervaporation for in-situ Product Recovery

In general, in-situ product recovery (ISPR) technologies remove inhibitory or unstable (side) products during (bio)chemical conversion processes, and lead to significantly increased productivities and decreased process flows. VITO recently demonstrated the advantage of this concept for the recovery of acetone-butanol-ethanol (ABE) from a continuous fermentation,

via organophilic pervaporation [11] (Figure 3). The metabolism of the producing microorganisms is severely inhibited by these solvents, resulting in relatively low final product concentrations.

The demonstrator consisted of a continuous two-stage fermentation (acidogenic-solventogenic) using freely suspended cells of Clostridium acetobutylicum ATCC 824 [12]. A pervaporation unit with a commercial PDMS composite membrane was directly coupled to the second fermentor for the continuous removal of acetone, butanol and ethanol. This operation easily enabled an increase of the sugar feed concentration from 60 g/l, which is the maximum when no ISPR is applied [13,14], to 120 g/l, resulting in a productivity increase from 0.45 to 0.88 g/l.h. A further augmentation to 150 g/l led to a maximal productivity of 1.13 g/l.h. This operation could be maintained for 200 h, producing a permeate flow, at an average flux rate of 0.62 kg m^2.h and a total solvent concentration of 202 g/kg in the condensate. Sufficiently high solvent titers in the second fermentor were essential for the performance of the pervaporation unit leading to higher fluxes and total solvent concentrations in the permeate. In a more recent study, similar positive effects of ISPR with organophilic pervaporation were obtained using a simulated lignocellulosic hydrolysate as feed [15]. Glucose was completely consumed, next to 61% of the xylose, leading to an overall solvent productivity of 0.65 g/l.h and a high concentration of 185 g/kg solvents in the pervaporation permeate. Stable operation was shown during 192 hours. Based on these experimental results, an integrated process was conceptually designed and compared with a base case. Simulations indicate an energy reduction of ~50% when integrating organophilic pervaporation. This is due to the improved overall water balances and mainly linked to a strong reduction in steam requirement in the downstream processing train. Calculations learn that this will also lead to a decrease of the produced biobutanol price by more than 10%.

4.2 OSN filtration for continuous recovery of homogeneous catalyst

The downstream processing of homogeneous catalyzed reactions is problematic, i.e. the catalyst separation from reaction products, which is currently achieved via distillation, chromatography, extraction or a combination of these techniques. In the case of OSN filtration, very high catalyst rejections and a long-term catalyst stability are absolutely necessary in order to be economically viable. The catalyst can be recovered in consecutive batch filtration-reaction cycles or via
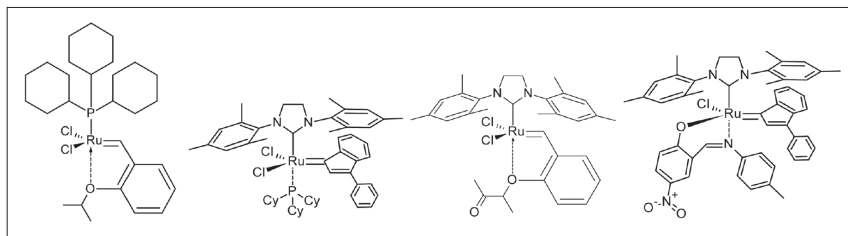
Fig. 4: Homogeneous catalysts used: (from left to right) Hoveyda–Grubbs 1st generation, Umicore M2, M51 and M41.
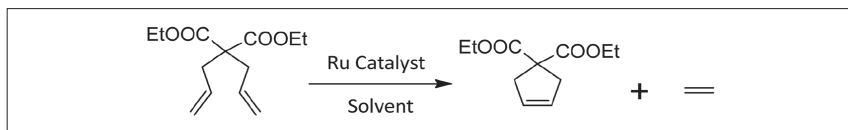

Fig. 5: Model reaction, ring closing metathesis of diethyldiallyl malonate (dedam).

continuous work-up, if the membrane is sufficiently resistant to the reaction pressure and temperature conditions. For example, Evonik demonstrated the possibility of integrating an OSN membrane installation in its hydroformylation unit to separate and recycle the homogeneous rhodium (Rh) catalyst, which resulted in a significant cost reduction, given the high catalyst price [16,17].

VITO evaluated the potential of OSN membranes for catalyst recycle from metathesis reaction mixtures, where metal contaminations of ring closing reaction products are to be reduced [18]. The readily available commercial Hoveyda–Grubbs and Umicore M series homogeneous catalysts were used (Figure 4). The efficiency of catalyst recovery was evaluated in a model reaction: the ring closing metathesis of diethyldiallyl malonate (dedam) (Figure 5).

The experiments showed that catalyst rejections were in general > 90 % but also significant dedam and product rejections were measured for some membranes. As an example, Table 3 compares the results for a FunMem membrane and a commercial polymeric OSN membrane. Also, as mentioned before, retention profiles changed when the solvent was changed in the solute-membrane-solvent matrix. Based on the rejection results, a simulation of the continuous process for the different membrane – catalyst systems was performed. The simulations using the retentions of Table 3 show that with the Funmem membrane the product is rapidly washed through the membrane into the permeate, while approximately 80% of the catalyst remains in the reten-

tate. For the polymeric OSN membrane, however, the catalyst recovery in the retentate is successful, but no good product – catalyst separation is possible.

Recently we extended this work to the recovery of Pd-complexes with the same N-heterocyclic carbene backbone but differing ancillary ligands This class of stable well defined pre-catalysts are used in numerous cross-coupling reactions [19]. High rejection of the organometallic species and low rejection of the reaction product can again be achieved with ceramic nanofiltration membranes, and this in three different membrane-assisted processing modes. While off-line processing proved to be highly performant from a reaction as well as a filtration point of view, with in-line processing the stability of the catalyst and reaction concentration played a central role in attaining high reaction yield. The results also demonstrate the importance of the metal complexes ancillary ligands, an aspect that is often overlooked. With both unmodified and functionalized ceramic membranes high rejection of Pd species and consequently ultra low Pd contamination of reaction products (< 10 ppm) is possible. The FunMem membranes however, proved to be more resistant to fouling than the unmodified ones. To achieve the high rejection of the organometallic compounds originating from the Pd complexes used in this study the formation of clusters or nanoparticles is required. One advantage of this membrane assisted method to separate reaction products from organometallic compounds over more conventional use of adsorbents is losses of product on the adsorbents is minimized.

Membrane	Permeability	Catalyst retention	Product retention
1 nm TiO$_2$ C$_8$	5 l/hm^{2}bar	87 %	35 %
Polymeric OSN	0.8 l/hm^{2}bar	91 %	97 %

Tab. 3: Rejections and permeability for the M2 Ru catalyst in acetone on 2 membranes.
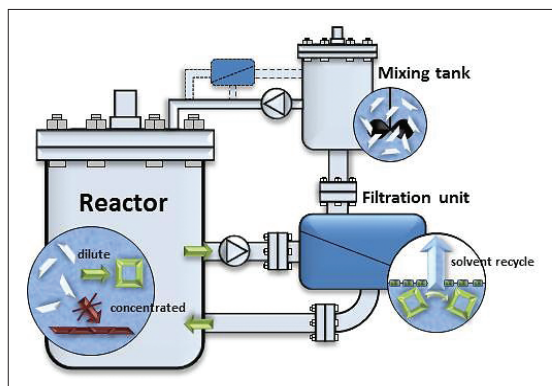
Fig. 6: Concept of a coupled reaction-continuous solvent recycle with controlled (membrane-assisted) reagent addition to the reaction medium. This setup simulates a diluted reaction environment for concentration-sensitive reactions, resulting in high yields with low solvent use.

4.3 Volume Intensified Dilution (VID)

VITO developed a membrane-assisted reaction concept, which is based on a continuous solvent recycling, making it possible to simulate diluted reaction conditions, combined with a reduced solvent use [20]. This is very relevant since many pharmaceutical reactions are to be performed in such conditions, in order to achieve an acceptable selectivity and product yield. These operations require large solvent and reactor volumes, while a small amount of product is obtained. For example, the production of macrocyclic molecules (as active pharmaceutical ingredients) is becoming more common, although it is a very expensive and problematic process, since macrocyclisation takes place in highly diluted media to avoid undesired side reactions.

This Volume Intensified Dilution (VID) concept is also applicable for other reactions profiting from high dilution e.g. reactions suffering from substrate inhibition or precipitation and is not limited to OSN applications.

The coupling can also be performed with aqueous process membranes, ranging from ultrafiltration to reverse osmosis applications, depending on the properties of the reaction mixture and the reactive species. An additional advantage of this strategy is that some chemical reactions, which were considered as unproductive before, are becoming worthwhile now.

In essence, the reaction mixture is continuously circulated through a membrane separation unit during reaction. The substrate and product are retained by the membrane, and sent back to the reaction vessel, while solvent is recycled to the substrate mixture tank (Figure 6). From here a controlled, either membrane assisted or not, substrate supply to the reaction vessel occurs. By combining the controlled dosed feed of reagents and substrate with the continuous in-line solvent recycle, a small volume of the "ideal" diluted reaction conditions are created, reacted and continuously regenerated while minimizing solvent use. Both processing modes are highly flexible, by which they can be easily connected to standard reactors in the chemical industry, on lab and production scale.

The benefit of this novel reaction concept was demonstrated for a representative macrocyclization reaction, i.e. a Mitsunobu reaction to form a 13-membered ring [21], in two typical reaction solvents, dichloromethane (DCM) and tetrahydrofuran (THF). Both ceramic and polymeric OSN membranes were used and reaction performances compared to a state-of-the-art batch operation, performed at the same reaction concentrations and conditions. Whereas at least similar yields were obtained, independent of the reaction concentration, a significant decrease of solvent use could be achieved with Process Mass Intensity (PMI) [22] reductions of more than 40 % in a non-fully optimized system.

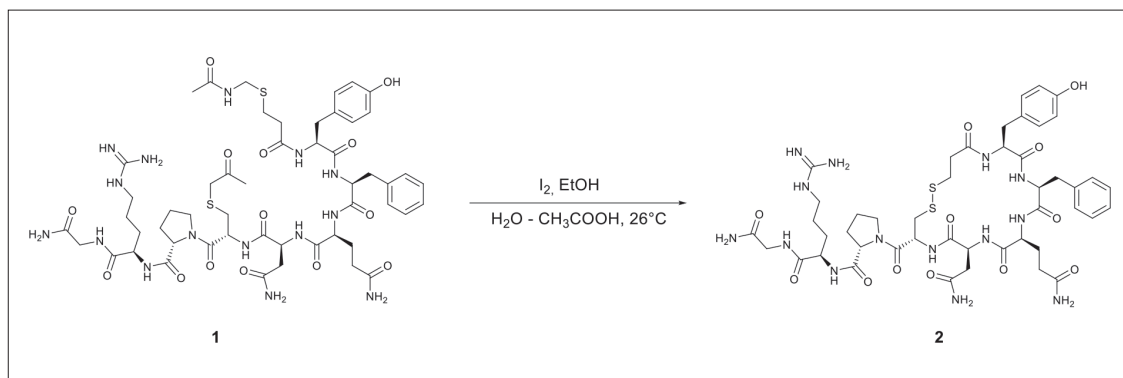More recently, in collaboration with an industrial partner from the pharmaceutical industry, the potential of

Fig. 7: Oxidative disulfide bridge formation to form the cylic peptide Desmopressing (2), evaluated in OSN-assisted Volume Intensified Dilution process.
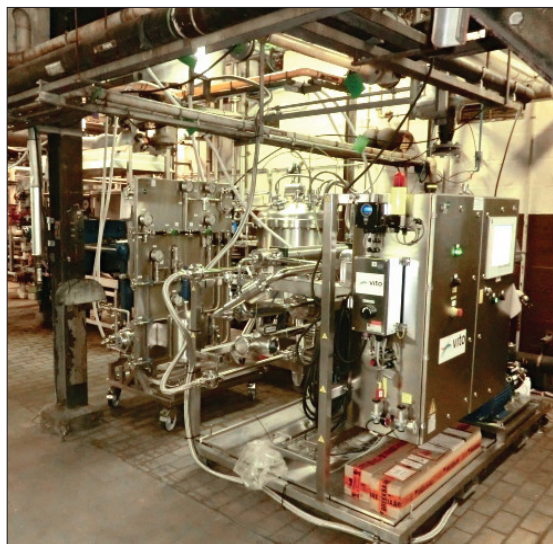
Fig. 8 : the OSN pilot installation of VITO at the location of DSM-Sitech in Venlo.

this methodology has been demonstrated in the preparation of the cyclic peptide, Desmopressin (Figure 5) [23]. As in this reaction, the product can further react with the reagents used, the configuration of the membrane-assisted process was slightly adapted. The results underlined the strength of the VID process : a PMI decrease of even 85 % has been achieved, while at the same time a more efficient reaction was obtained as well. Indeed in this case, an improved product purity has been acquired, alongside an significant increase in conversion (from 84 % to 100%), and product yield (from 71% to 95%). As the same amount of product can now be obtained in a substantially smaller system, this way of processing offers also an obvious decrease in time to market.

During the last Achema fair (2015) at Frankfurt, VITO was nominated for the Achema Innovation Award for this technology.

4.4 Organic solvent nanofiltration at pilot scale

Recently, VITO has designed and acquired a large-scale mobile pilot installation for OSN, to facilitate the transfer of this new promising technology for process intensification to industry. The installation, suitable for all requirements ranging from proof of principle testing to pilot scale production, is mobile and can be equipped both with ceramic (3 x 19 channel elements of 120 cm ~ 0.75 m^2) and polymeric membranes (1x4 inch module ~ 5 m^2). The pilot is full Atex, meets the regulatory requirements of pharmaceutical and fine chemical manufacturing (GMP: good manufacturing practice) and is available to customers on a rental basis [21].

For a project at Sitech-DSM, the VITO pilot was operated on-site in Venlo for the recovery of a valuable API from a methanol-based distillation residue [24]. A lab-scale screening at DSM decided for the optimal membrane, and the optimal process and process parameters were determined using a small-scale spiral-wound membrane module. The batch-wise processing of the existing quantity of distillation residue was performed at pilot-scale, using the GMP-compliant pilot equipment of VITO (Figure 6). In total 52 batches containing each 250 kg of valuable API were successfully processed over a period of 6 months. During this period the pilot ran continuously 24h a day, 7 days a week, with minimal man-power, and without any serious problem. The project allowed Sitech-DSM to recuperate > 10 tons of the valuable API, making the innovative OSN process very cost-effective.

5. Conclusion

In this overview, the development and evaluation of process-integrated membrane systems at VITO was summarized. The different concepts clearly demonstrated the potential of in-line molecular separation for achieving high efficiency and productivity in (bio) catalyzed and delicate synthesis routes, for the production of high added value and high volume chemicals. At the same time, VITO's development of novel solvent resistant membranes for the direct coupling with conversion processes was described: (organo)ceramic nanofiltration membranes combining high chemical and thermal resistance with enhanced flux performance in both water and solvent filtration, ascribed to their amphiphilic character, and tailor-made separation characteristics.

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