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Breakthrough in pervaporation membrane for dehydration of solvent streams

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Hydrothermally stable hybrid

Breakthrough in for dehydration of

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After several years of development, researchers at the Universities of Twente and Amsterdam and the Energy research Centre of the Netherlands have succeeded in obtaining a membrane system which is hydrothermally stable under semi-industrial dehydrating conditions at elevated temperature. This organic-inorganic hybrid membrane system combines the best of both worlds: flexibility and water repelling properties of organics, and thermal and solvent stability of ceramic membranes. Continuous testing over periods of up to almost two years revealed reliable and stable operation of this membrane system for the dehydration of a 95 wt% n-butanol – 5 wt% water mixture via pervaporation at 150°C.

The challenge

Distillation has always been the leading technology to separate liquid mixtures. As distillation is rather energy consuming, energy efficient alternatives such as pervaporation are currently under investigation. With pervaporation (*per*meation and *evaporation*), liquid mixtures are separated by selectively evaporating one component from that mixture through a membrane. This membrane has the ability to sieve on a molecular scale, i.e. small molecules will pass, while larger ones will be rejected, depending on the sub-nanometer pore size of the membrane. Since only the component with the smallest molecular size has to be evaporated - rather than the complete feed as in a distillation process - pervaporation consumes much less energy. The energy savings depend strongly on the specific application and can be as high as 50 or 70%.

However, high temperature pervaporation has not yet made it to the industrial market, due to poor separation performance or the absence of reliable ceramic membrane systems. For low temperature applications and relatively mild chemical conditions, the PVA membranes of e.g. Sulzer Chemtech are applicable, but remain on a moderate scale. For a truly large scale and economically feasible pervaporation process, the process temperature has to be sufficiently high, in line with the temperature of the process stream to avoid heat losses. Moreover, the higher the temperature, the better the pervaporation performance will be. For this purpose, PVA nor pure silica-based microporous ceramic membranes are stable enough to allow prolonged application under the demanding industrial conditions of e.g. 150°C.

The solution

At the Universities of Twente and Amsterdam and the Energy Research Centre of the Netherlands, we have overcome these limitations by developing a revolutionary hydrothermally stable hybrid organic-inorganic membrane system (Castricum, 2008(a), 2008(b)). We started in 2001 by improving microporous silica-based ceramic membranes. At that time it was known that membranes made of this material were prone to attack by water at temperatures of 60°C and higher. Hydrolysis of siloxane (Si-O-Si) bonds in the silica network led to defects in the membrane structure and, as a result, to poor selectivity. Although silica membranes are still applicable for gas separation at high temperatures in an atmosphere without water, they could not be used in dehydration of solvent streams.

Within an STW-funded project, we aimed to replace as many Si-O-Si 'siloxane' bonds by hydrolytically stable Si-C-C-Si silicon-carbon bonds. This proved to have several advantages: Incorporation of organic parts into the inorganic structure led to pores in the structure that were even smaller than the pores in the original microporous silica network, as a result of the smaller silicon-carbon bond lengths as compared to the original siloxane bond length. This small averaged pore size of 0.24 nm is advantageous to separate small molecules such as water and methanol from process streams with high selectivity. The material acts here like a molecular sieve.

membrane systems: best of both worlds

pervaporation membrane solvent streams

A second success is that the material was indeed hydrothermally stable. Even after a test period of more than one year under semi-industrial conditions the separation performance of the membrane did not deteriorate significantly (see “Test results”).
Last but not least, the membranes appeared to be relatively easy to synthesize. Although it is only 200 nm thick, the hybrid selective membrane top layer is sufficiently defect-free and hardly susceptible to cracking, both during synthesis and use.
It is assumed that the organic C-C bridges induce sufficient flexibility into the original inorganic structure. From a materials science point of view, the hybrid system is quite remarkable: it combines the features of two systems that are separately not reliable or stable, into a reliable, stable and easy-to-handle system. From a process technological point of view, the system performs very well.

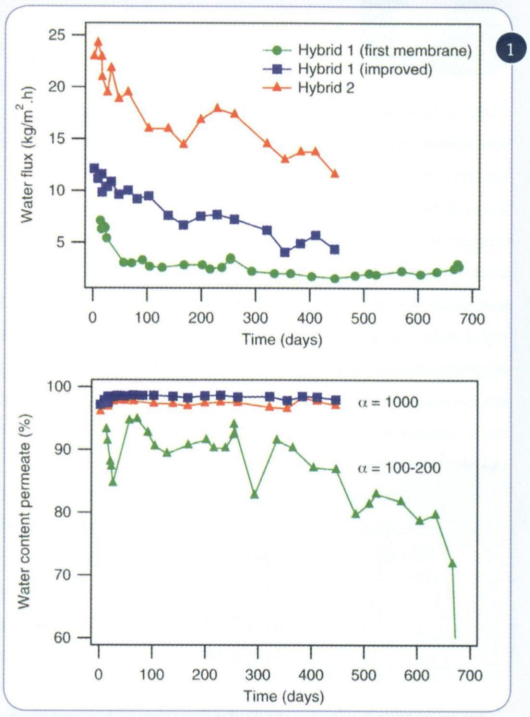
Test results (see figure 1)

As a model system for dehydration of solvents, pervaporation of a 95 wt% n-butanol – 5 wt% water mixture at 150°C was selected. Several membranes were tested, each with approx. 40 cm² of membrane area. The first membrane (Hybrid 1) worked for nearly two years under these conditions before breaking down. An sample of an improved membrane type (Hybrid 1 - improved) has been running for 450 days with a higher flux of 5-10 kg/m².h and separation factor (α) of around 1000. Further improvements in the material lead to membrane Hybrid 2, having fluxes in the range of 15-25 kg/m².h with the same high separation factor of around 1000. This separation factor is well above the minimum value required for practical applications. At the time of writing, these last two membranes are still on stream and show no reduction of selectivity.

Past, present and future

In 2006, the breakthrough performance and the possible opportunities to apply this hybrid membrane system were recognised, and a worldwide patent was filed. Further testing so far supports the potential of the membrane system under real industrial conditions. Applications include the purification of industrial solvent streams by selectively removing water. Currently, we are investigating this membrane type in the dewatering of a number of organic streams, including aggressive, aprotic solvents and several alcohols. Low-cost ways of dewatering alcohols are particularly interesting for the biofuel sector. In addition, gas separation applications in which hydrothermal stability is of importance are considered. A very important future application may be related to the production of hydrogen in a membrane reactor.
The next step will be the scale-up to a pilot plant, and demonstration projects on location under real conditions. For this purpose, a consortium is being put together, in which membrane manufacturers, system integrators, end users and knowledge providers will collaborate to take the first steps towards implementation of this membrane system. ●

References
See *www.npt.nl* at Inhoudsopgaven.



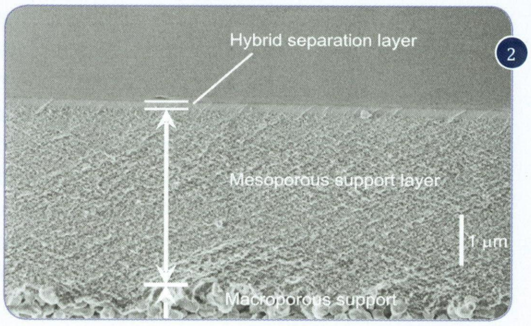


Fig.1 Hybrid membrane pervaporation

Fig.2 Hybrid membrane SEM

Membrane synthesis (see figure 2)

The membrane synthesis is quite simple, and can be scaled-up easily to membrane areas that are needed to perform industrial separations.
Silicon and carbon containing metal-organic precursor compounds are allowed to polymerize in a wet-chemical process to a polymeric sol. This sol is brought in contact with a tubular porous alumina support, and - as a result of the capillary forces induced by the pores of this support - the sol gels to a polymeric network. This supported gel is cured at 300°C in a nitrogen environment, to obtain the desired hybrid membrane system.