About us

Welcome to the Energy research Centre of the Netherlands, the largest research centre in the Netherlands in the field of energy. At this moment ECN employs about 900 people. ECN is situated in the dunes near Petten, a village in the north-western part of Holland. ECN carries out research in the field of energy. In search for sustainable energy supply and consumption, the researchers move between fundamental research at universities and appliance of knowledge and technologies in practice. The technology developed at ECN has a large impact on daily life. For example, solar systems are placed on roofs of houses and modern wind mills are spinning in the field by means of technology developed by ECN. With this the institute exerts an important function for the society of today and tomorrow. The main goal of the program Energy Efficiency in the Industry (EEI) is to develop innovative solutions for the reduction of energy and raw-materials use in industry together with our industrial partners.

Since 1998, ECN has been developing nanoporous membranes for gas separation, pervaporation and nanofiltration applications. Over the years, the group has developed an outstanding reputation and has developed a solid intellectual property position. The group has been focused on the scaling up the sol-gel membrane technology. It was among the first to show the productivity of silica and silica based membranes on one meter long tubes.

For more information on the membrane activities of ECN please visit the home page of the Membrane Technology group; www.ecn.nl. More information on ECN's hydrogen separation membrane technology can also be found on; www.hysep.com.

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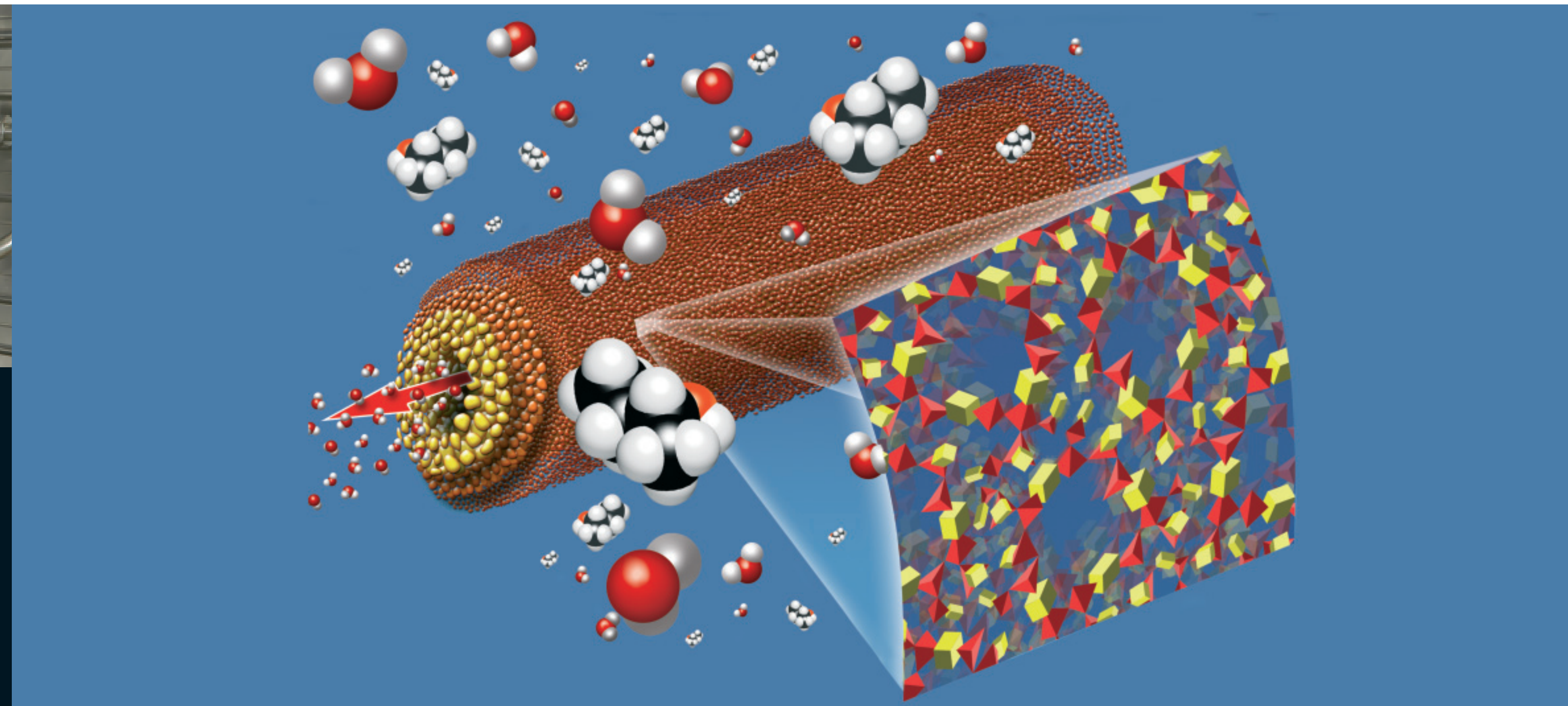
ECN

Energy research Centre of the Netherlands

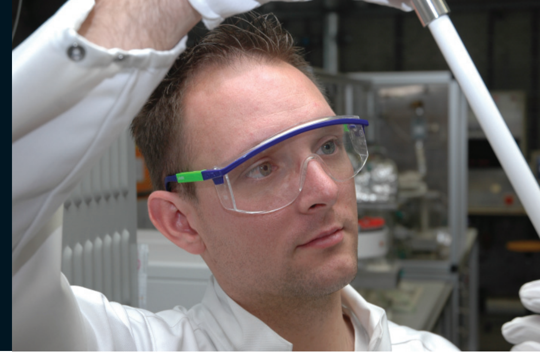
HybSi®

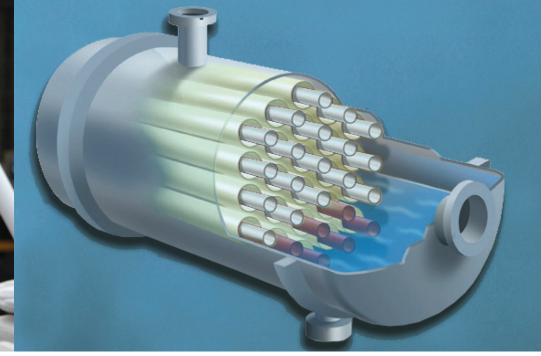
Pervaporation Membranes



Introduction

HybSi® is the trade name of a recently developed nanoporous membrane system with an unprecedented high stability under both hydrothermal and acidic conditions. Typical applications of HybSi® membranes are pervaporation and vapor permeation. Characteristic of the membrane material is that it combines organic and ceramic units that are connected on an atomic level. By doing so the best of both worlds are combined in this true hybrid material.





Technology

What is pervaporation?

Pervaporation is the selective evaporation of one of the components of a liquid mixture using a membrane. The word pervaporation itself is a combination of the words permeation, the transport through a membrane, and evaporation, the phase transition from the liquid to the vapor phase. It is not a pressure driven process such as several filtration processes and reverse osmosis. Instead, the driving force is due to the fact that on the feed side the chemical potential is higher than on the permeate side, similar to what is found in gas separation membranes. The gradient in chemical potential is maximized by using high feed temperatures and low pressures on the permeate side. Alternatively to pervaporation, membranes can often be used in vapor permeation mode as well. In this case the feed is fully vaporized. Often a detailed analysis of the full process is required to determine which option offers the highest benefits to the end user. These kinds of membrane processes are beneficial for the separation of e.g. azeotropes. In distillation the complete liquid feed is evaporated leading to high energy demands. By replacing distillation by the pervaporation membranes or combining the two processes large energy savings are possible.

Membrane stability

A fair number of pervaporation membranes are available on the market today. These polymeric and ceramic membranes all have their advantages and disadvantages, and a careful selection has to be made based on detailed knowledge of the process. The HybSi® team has been working over the years to overcome common disadvantages and offer membranes for a wider application window.
This has been achieved by enhancing the stability towards

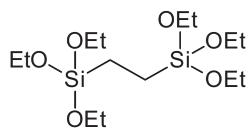
- hydrothermal attack,
- the presence of acids,
- the presence of aggressive organic solvents

All of this results in a membrane system that is applicable in a wide range of solvents and is stable in the presence of water and acids at high temperatures.

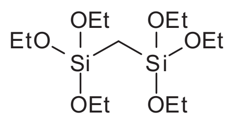
Details of the HybSi® material

HybSi® is an organic-inorganic hybrid silica-based amorphous material. The hybrid nature of this material lies in the fact that each silicon atom is not only connected to oxygen atoms as in pure silica, but also to an organic fragment.

The special feature of HybSi® is that the organic fragments are acting as integral bridging fragments of the structure, and not just as end standing groups as in methylated silica. The result is a true hybrid silica pore network in which organic and inorganic fragments cooperate. It is prepared by a sol-gel process from so-called bis-silyl precursors, such as BTESE ($(EtO)_3Si–CH_2CH_2–Si(OEt)_3$) and BTESM ($(EtO)_3Si–CH_2–Si(OEt)_3$).



BTESE



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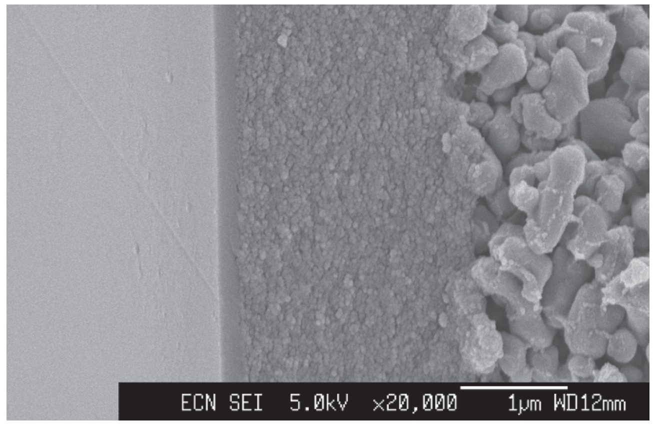


Cross-sectional SEM micrograph of the layered structure of a hybrid membrane, showing the supporting layers and the ~150 nm thick selective HybSi® top layer.

Explanations

Several explanations have been proposed for the remarkable stability of the HybSi®. These include

- More stable bonds: the hydrothermally instable Si-O-Si bonds are replaced by Si-$(CH_2)_n$-Si bonds
- Higher crack propagation energy resulting in more ductile material in which initiated nano-cracks do not easily grow to a defect.
- Increased connectivity number of the basic building block from four to six siloxane bridges, resulting in a lower surface diffusion coefficient
- Lower solubility, the larger bis-silyl units are expected to have a much lower solubility leading to suppressed mobility of silica fragments.

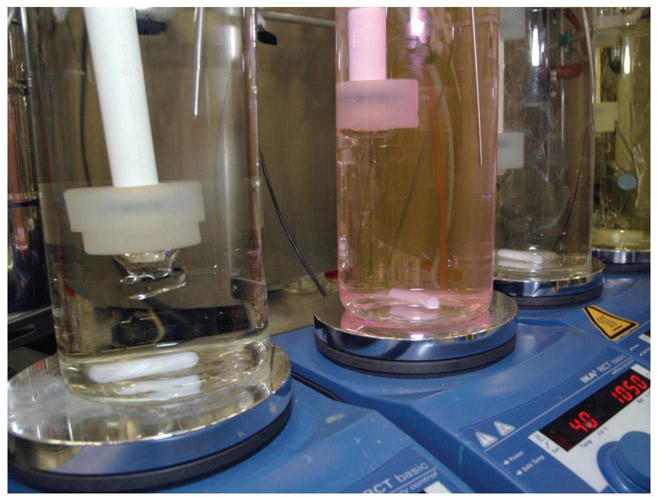
Specific applications

Examples of water and methanol azeotropes that can be separated with the HybSi® membrane system include:

Permeating species	Retained species	Azeotrope wt% of retained species
Water	Acetonitrile	83.7
Water	Ethanol	95.5
Water	*n*-Propanol	71.7
Water	*t*-Butanol	88.3
Water	Methyl acetate	95.0
Water	Methyl ethylketone	89.0
Water	Tetrahydrofuran	95.0
Methanol	Toluene	31.0
Methanol	Methyl acetate	81.3
Methanol	Tetrahydrofuran	69.0

Other dewatering examples for which HybSi® can be used include complex distillations and processes like:

- Acetone/phenol in e.g. the oxidation of. cumene
- Acrylates
- Bisphenol A
- Carbonates
- Diols
- EDC/VCM/PVC
- Isocyanates
- Propylene oxide
- Terephthalate compounds and terephthalic acid



Products & Services

Licenses and patents

The HybSi® membrane and the necessary sealing and module technology are covered by a number of ECN patents. ECN is looking for interested parties to take a license on its technology and broad patent portfolio. Potentially interested parties include companies that are interested in membrane fabrication, or that are interested in marketing full separation equipment that contain HybSi® membrane technology, or that are interested in the final utilization of it. We can provide a detailed technology transfer and aim for a joined effort in the further scale-up and market development of HybSi® membranes.

Membranes and modules

ECN provides to selected end users two different single tube modules with HybSi® membrane, with a membrane surface area of ~40cm² and ~400cm² respectively. These ECN steel modules, including membrane and metal housing seal, are delivered with Swagelock connections to feed, retentate, and permeate. They are certified to function at T_{max} = 200°C and P_{max} = 15 bar.

Laboratory measurements

ECN offers to perform pervaporation measurements for interested end users on their industrial mixtures. The emphasis is on water and methanol separation from organic solvents. To this end ECN has more than ten glass pervaporation set ups available. For more demanding conditions a further 5 stainless steel autoclaves are available that can run up to 30 bars pressure and 200°C in a batch experiment set-up. These installations can run 24/7 including fresh feed addition. They are normally operated with one membrane of ~15 cm length and typically use 1-2 liter of feed liquid. For larger scale measurements with continuous flow feed conditions a set up with a feed capacity of ~35 liters is available. This set up can be run with six membranes in series with pressures up to 25 bars and temperature up to 150°C.

On site pilot testing

A further service that ECN offers is on site testing with a total membrane surface area of 1 m². To this end a skid mounted test installation is available, that has passed a number of HAZOP analyses and is explosive proof. This unit can run batchwise as stand alone equipment using a 1000 liter feed vessel, or in line using a continuous feed.