Innovative Hollow Fiber Ceramic Membranes

TNO researchers discuss the institute's role on the cutting edge of ceramic hollow fiber membrane technology, including manufacturing, characterisation and utilisation.

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Membranes are finding increased usage for separation processes in the (petro) chemical industry. They can be considered as selective walls or filters through which certain compounds can move with a larger rate than others, hence accomplishing separation.

These separation processes occur generally under relative mild conditions (low temperature and/or pressure), leading to a reduction in use of energy when compared with traditional techniques (e.g. destillation). Most of the membranes are made from polymeric materials.

In cases where high demands are made on thermal stability and lifetime of membranes (e.g. when steam sterilisation is required or when a process is conducted at a high temperature) ceramic membranes are available.

Over the past decade, interest has increased in the application of ceramic membranes in multifunctional membrane reactors, where chemical reactions are carried out in the presence of a membrane (Saracco and Speccia, 1998).

Compared to the usually applied flat and tubular membranes, ceramic hollow fiber membranes, invented and developed by TNO, have the advantage of being compact (e.g. have a surface/volume ratio of > 1000 m^2/m^3). Moreover, the TNO invention has reduced the manufacturing costs of these membranes considerably.

Manufacturing Membranes

The patented process for manufacturing ceramic hollow fiber microfiltration (MF) membranes consists of three stages. These three stages are described here in some detail for the manufacturing of alumina hollow fiber microfiltration membranes.

Ceramic powder is mixed with a polymeric binder system. Alumina powder (CT 3000 SG from Alcoa with average particle size of 0.5 µm) is mixed on a 50:50 vol% base with a polymeric binder system consisting of a number of organic compounds. The mixing process is conducted in a double Z-blade mixer (Werner Pfleiderer, type LUK 5.0K3) at a temperature between 85 and 125°C.

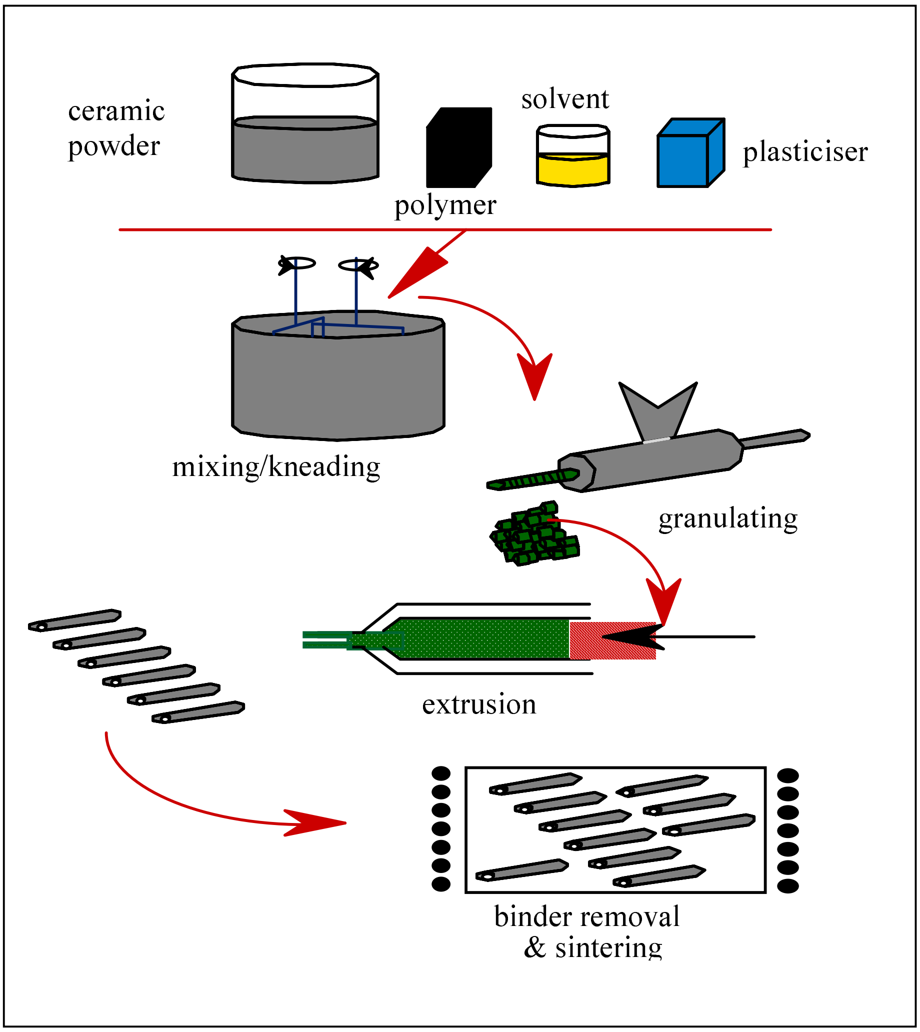
The mixture is cooled down and granulated in a Pallman PS2 granulator. These granules are used as input for the extrusion stage.

This ceramic-polymeric mixture is shaped into a hollow fiber by extrusion. Extrusion equipment consists of an extruder (18 mm Brabender or Extrudex), a spinneret and a collect unit to receive the extruded hollow fiber.

The Brabender has been used for manufacturing most of the ceramic hollow fibers in the past. This extruder is equipped with six different temperature zones, increasing in temperature from 80 to 125°C.

The ceramic/polymer granules are thrown in the hopper at room temperature and the material is transported via a screw through the temperature zones to the last zone (at 125°C) outside the extruder which contains the spinneret. The continuously produced hollow fiber is collected and cut into pieces with a length of ~40 cm.

The organic binder is removed from the



Scheme of the manufacturing process for MF membranes

hollow fibers by subjecting them to a heat treatment in air ≤600°C for 10 hours (Prins furnace). The fibers are then heated further to the desired sintering temperature (between 1150 and 1350°C) for 1-3 hours with a ramp of ~60°C/h.

Due to the sintering process, alumina particles are more closely bonded to each other to give the porous alumina hollow fiber sufficient mechanical strength. The resulting outer diameter of the alumina fiber is smaller than the diameter of the orifice of the spinneret.

Similar experiments to that decribed for alumina membranes have been performed for silicon nitride membranes. Other ceramic materials that are under investigation are silicon carbide, hydroxy apatite, zirconia and perovskites.

Membrane Characteristics

Since these MF membranes are monolithic, their pore size distribution, average pore diameter and porosity are easily determined by mercury intrusion porosimetry. For alumina MF membranes, porosities of ≤50% have been obtained, with average pore diameters of ~0.15-0.18 µm.

The mechanical strengths of these membranes are determined by performing 3-point bending tests (until fracture) to membranes of 12 mm length. The 3-point bending tests have been performed with a large number of test samples for each batch (good statistics) and have reached values of ≤150-170 MPa. Related to this, burst pressures (inside-out) of 220 bars have been measured.

Characterisation of silicon nitride hollow fiber MF membranes have been reported elsewhere (Terpstra, 1997). Using SNE-10 powder of UBE and changing the amount of sintering additive (yttria and alumina, ≤6.1 mass%), the pore size is varied from 0.2-0.6 µm with a porosity between 30-50%.

Liquid/Gas Permeation Data

Clean water fluxes through TNO's alumina hollow fiber MF membranes have been measured, and are currently up to 600 l/m^2.bar.h. This is in the same order of magnitude as what is theoretically expected. A membrane system with expected clean water flux of >1500 l/m^2.bar.h is currently under development.

TNO's clean water flux values are comparable to or better than permeation values of commercially available tubular MF membranes with comparable pore size. In addition, in the case of TNO's hollow fiber ceramic membranes, the surface-over-volume ratio is much larger than for tubular membranes (4000 m^2/m^3 for hollow fiber membranes with outer diameter 0.5 mm, as compared to 200 m^2/m^3 for tubular membranes with typical tube diameter 10 mm).

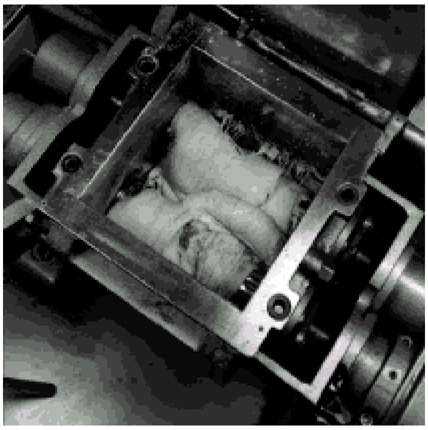
Gas permeation measurements are performed using the dead-end geometry, in which a pure gas enters the membrane at room temperature with a pressure >1 atm (the high pressure side). The gas is forced through the membrane, and the low pressure side of the membrane is at 1 atm.

By normalising the gas flow (in mol/s) for the pressure difference over the membrane and the membrane surface area, the gas permeation value (in Nm^3/hr.bar.m^2 or mol/m^2.s.Pa) is obtained.

Gas permeations of hydrogen, propane and n-butane through a home made α-Al$_2$O$_3$ hollow fiber support have been measured, resulting in values of >100 Nm^3/hr.bar.m^2 for hydrogen and ~30 Nm^3/hr.bar.m^2 for propane and n-butane.

An interesting feature of TNO's ceramic MF membranes is that the permeation through the support (with pores of ~0.15 µm) is mainly determined by Knudsen diffusion, as demonstrated by the fact that the permeation is independent of the average pressure over the small pressure range investigated. In the case of Knudsen diffusion the transport of gases is determined by the square root of the masses of these gases.

Theoretical Knudsen factors for hydrogen/propane and hydrogen/



Mixing of a ceramic/polymer system in a double Z-blade mixer.

n-butane are 4.7 and 5.4. The experimentally-determined permselectivities of hydrogen/propane (3.3) and hydrogen/n-butane (3.5) are approaching the Knudsen factors of these mixtures.

Top Layer Application

Microfiltration membranes manufactured with the aforementioned process can serve as a support for highly selective membranes. Since these supports are rather thin (0.05-0.4 mm) the flow resistance is low. This is an advantage.

A recipe and a coating procedure have been developed for applying a γ-alumina top layer (from a boehmite sol) on hollow fiber α-alumina supports. Coatings can be applied on the inside and the outside of the hollow fibers.

From SEM photographs, and the strong decrease in permeation on application of one or more gamma-layers, it is concluded that homogeneous layers of high quality can be applied on hollow fiber supports.

By means of chemical vapour infiltration (CVI), it is possible to modify the pores of macroporous (d_p = 0.15 µm), uncoated alumina hollow fiber substrates by depositing silica on the internal pore wall. Reducing the average pore size of this membrane system will make it suitable for separating hydrogen selectively from a mixture of gases. Separation factors for hydrogen over nitrogen at 600°C of 1000 and higher have been reported (Morooka, 1995).

The entire membrane manufacturing process is rather simple and, hence, relatively inexpensive. It consists of only two steps (support manufacturing and microporous top 'layer' application) and there is no need to apply additional intermediate layers.

Membrane Applications

The oldest known application of ceramic membranes is the separation of gases for the production of fuel for nuclear reactors. For a long time, uranium isotopes (gaseous UF_6) have been separated from each other by means of porous ceramic membranes, with pores of a few nanometers.

These pores are small enough to pass the lighter isotopes (U^{235}) faster than the heavier ones (U^{238}). After repeating this process for over 1000 times, an enriched mixture of 3% U^{235} becomes available (out of 0.7% U^{235}, occurrence in nature), which is suitable as nuclear fuel.

Typical non-nuclear applications of ceramic membranes are currently in beverage industries (beer/wine clarification, concentration of fruit juices). A large advantage, as compared to polymeric membranes, is that ceramic membranes can be steam sterilised or cleaned with aggressive media. In the food industry, sanitary conditions are very important. In addition, they are inert/neutral as far as taste is concerned.

In the chemical industry, ceramic membranes are applied in the purification of waste streams to facilitate water/oil separation.

An important potential application of ceramic membranes is the use in a combined separation-reaction process in a ceramic membrane reactor (CMR). Saracco and Specchia (1998) define a membrane reactor as "a multifunctional reactor where one or more chemical reactions, generally catalytically promoted, are carried out in the presence of a membrane".

While polymer membranes can only be applied at low temperatures, mostly in biotechnological processes, ceramic membranes open opportunities for applications in the (petro)chemical, fine chemical and pharmaceutical industry - in more harsh environments and at much higher temperatures.

In recent years, with classic ceramic tube membranes, this approach has met with substantial interest both at universities, research institutes and in industry.

Ceramic membrane reactors, implying CMR's with perm- and nonperm-selective catalytically active ceramic membranes and CMR's with catalytically active and/or selective ceramic membranes surrounded by a packed bed or fluidised bed of catalyst particles, have been applied in various processes.

Research has focused on:

- Gas separation, in particular H_2 from CO and CO_2, formed by steam reforming of methane or by a water-gas shift reaction;
- O_2-N_2 gas separation for the production and application of pure oxygen from air;
- Dehydrogenation and dehydration reactions (e.g. dehydrogenation of ethane, propane, cyclohexane and ethylbenzene);
- Catalytic partial oxidation of methane to syngas;
- Partial oxidation reactions (e.g. of ethene).

Concerning dehydrogenation, Saracco and Specchia (1998) wrote that, "perhaps the most interesting latest results are those coming from the use of zeolite membranes in membrane reactors"

The importance of ceramic membranes in membrane reactors has recently been ventilated by the establishment of two large consortia on the conversion of natural gas to transportation-grade liquid fuels and premium chemicals. Air Products

Alumina Hollow Fiber MF Membrane Characteristics

Firing Conditions	Porosity (%)	d_{50} (µm)	3p Strength (MPa)	Weibull Modulus
1150°C, 1 h	47	0.157	29	8
1200°C, 1 h	46	0.165	48	13
1300°C, 1 h	35	0.168	129	12
1350°C, 1 h	32	0.184	147	
1350°C, 3 h	24	0.173	168	

Alumina hollow fiber MF membrane characteristics as function of the firing conditions during manufacturing. (Porosity, average pore diameter, 3-point bending strength and related Weibull modulus) heads one consortium. In the other, Praxair is involved.

The heart of each of these processes is a ceramic membrane that has the ability to separate oxygen from air with 100% selectivity by means of an electrochemical process. Air flows along one side of the membrane. Oxygen that is transported through the membrane reacts with methane of the natural gas that flows along the other side of the membrane.

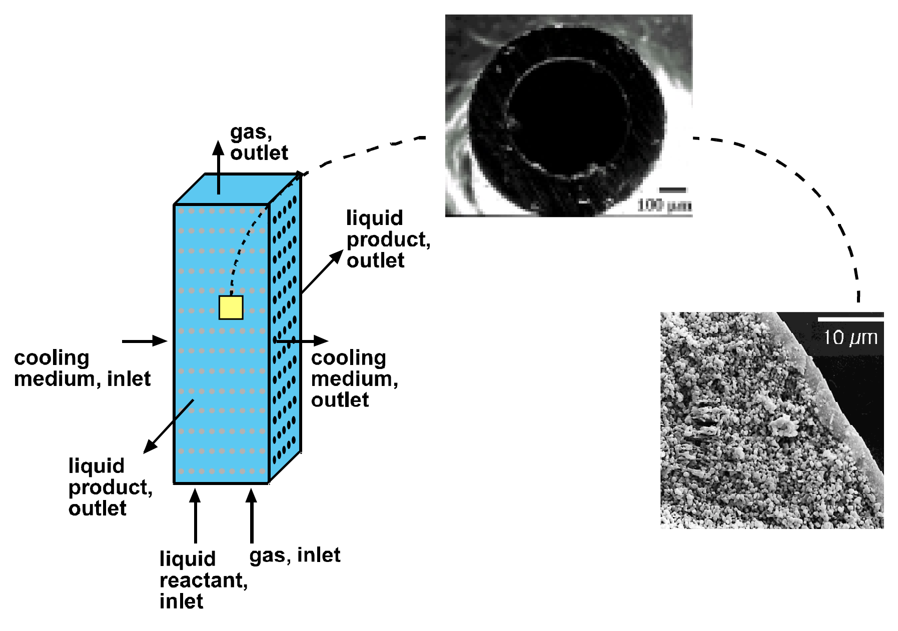
By using a suitable reforming catalyst, syn gas (a 2:1 mixture of hydrogen and carbon monoxide) is the reaction product. In a subsequent step, this syn gas is or can be converted into compounds that can be transported easily (e.g. methanol).

Advantages of the current process are:

- There is no need for a separate oxygen production plant (reducing energy and capital costs);
- There is no need to separate nitrogen at a downstream stage;
- Distant gas resources (e.g. under Alaska) are made economically feasible.

At present, both in the United States and in Europe research activities are going on directed at bringing the potential advantages of CMR's to practical applications. Particular attention is given to improved stability, permeability and/or permselectivity of tailor-made ceramic membrane systems. Cost-reduction is of major importance in bringing these systems to the market.

The innovative hollow fiber ceramic membranes invented by TNO have the potential to meet these goals. TNO has recently succeeded in sealing ceramic hollow fibers in a full ceramic module. This opens the way for further developments to CMR's for practical applications. In this respect, combinations of a catalyst and a hollow fiber CMR are regarded to be of particular interest.



Principle of membrane slurry reactor as under development at TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Apeldoorn, The Netherlands (Klaassen, 1998).

The concept of process-integrated removal and/or recovery of catalyst is currently being tested at TNO, applying a cross-flow membrane slurry reactor.

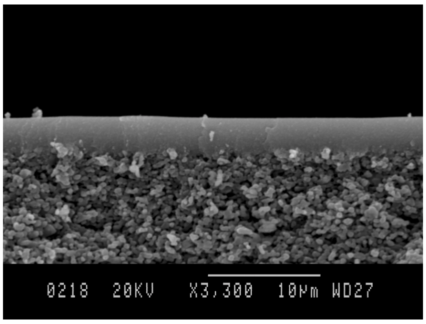
The space between the ceramic hollow fibers contains catalyst particles as a slurry in the liquid reactant. Hydrogenation experiments are performed on a model substrate. The liquid reaction phase is discharged from the reactor through the hollow fibers (Klaassen, 1998).

TNO's Role

Much basic materials research for membrane technology is performed at universities. Pioneering work has been performed by the Inorganic Materials Science group at the University of Twente in The Netherlands, formerly headed by Prof. Anthonie Burggraaf and currently by Prof. Henk Verweij.

TNO's role is to transform the knowledge generated at universities, at TNO itself and at other R&D organisations to industry where it is implemented into practical situations. This transformation role (bridge between university and industry) is very broad and consists of functions including consulting (including design and development) and manufacturing (including optimisation, scaling-up and commercialisation) of hollow fiber membranes.

TNO has made a clear commitment toward the hollow fiber geometry, since it is believed that scaling up is relatively simple by making use of the hollow fibers with their high surface-over-volume ratio. Hollow fiber mem-



Electron microscope photograph of an α-alumina hollow fiber substrate with a thin γ-alumina top layer. The pore size of the substrate is 0.2-µm. Pore size of the 5-µm thin top layer is 4 nm.

Clean Water Permeation Data*

Firing	ε	r_p (µm)	r_{outer} (mm)	r_{inner} (mm)	Clean Water Permeation (l/m^2.bar.h) Calculated	Measured
1300°C, 1 h	0.31	0.11	0.7	0.25	328	480
1300°C, 1 h*	0.3	0.1	0.25	0.2	1512	-

Clean water permeation data of alumina hollow fiber membranes as function of firing conditions, porosity (ε), average pore radius (r_p), membrane outer radius (r_{outer}) and inner radius (r_{inner}).
* Under development

Permeation Results

Gas	Pressure Difference (kPa)	Flow (ml(STP)/min)	Permeation (Nm^3.hr^{-1}.bar^{-1}.m^{-2})	Permeation (mol.s^{-1}.Pa^{-1}.m^{-2})
H_2	4.3	36.2	105	13.0 x 10^{-6}
	6.2	50.5	103	12.8 x 10^{-6}
C_3H_8	4.1	10.2	31.6	3.92 x 10^{-6}
	6.6	16.3	31.3	3.88 x 10^{-6}
	10.2	25.9	31.8	3.94 x 10^{-6}
n-C_4H_{10}	3.2	7.6	29.8	3.69 x 10^{-6}
	6.2	14.4	29.4	3.65 x 10^{-6}
	10.5	24.5	29.5	3.65 x 10^{-6}

Permeation results of hydrogen, propane and n-butane through a home-made α-Al_2O_3 hollow fiber support, fired for 3 h at 1300°C. Permeation is performed at 20°C; membrane surface area (of one hollow fiber) is 4.8x10^{-4} m^2.

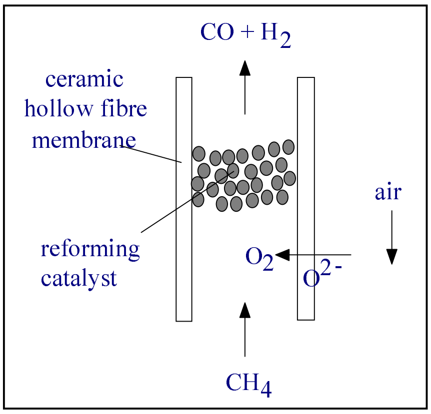
branes are considered third generation mem-branes, a logical successor to the now commonly used second-generation multihole type ceramic membranes.

For further exploration, application and commercialisation of ceramic hollow fiber membrane reactor concepts, TNO is aiming for bi- and multilateral co-operations with parties, in particular industries, that are active in the field of ceramic membrane technology and/or the field of potential applications.

In summary, the following aspects are typical for TNO's role in ceramic membrane technology:

- Low cost processing of hollow fiber MF membranes - ≤10 times cheaper than present generation tubular and multihole type ceramic membranes.
- Membrane surface-over-volume ratio >> 1000 m^2/m^3 - European patent on hollow fibers, extension pending; US and Japanese patent on hollow fibers pending; and European patent on full ceramic hollow fiber module (>500^{o}C) pending.
- Application oriented research is being carried out for optimisation - beverage industry (clarification of wine); chemical industry (membrane slurry reactor); dairy industry; and environmental (waste water).
- Licences and technology transfer offered to potential producers and end-users of ceramic hollow fiber membranes and modules.
- Co-operation is sought or extended with strategic partners on - high selective membrane coating technology; engineering of systems; and setting-up of production plant.

As we begin a new century, TNO is on the cutting edge of ceramic hollow fiber membrane technology and wants to keep this leading position.



Scheme of a membrane system for syn gas production.

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