

# Implementing membrane technology in the process industry: problems and opportunities

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## Abstract

Although membrane filtration is an accepted technology in water treatment and in the dairy, food and beverage industries, membrane-based separations are relatively new for the chemical industry. Therefore, for a major part of these techniques, there is still a long way to go to make them truly attractive as an alternative to distillation, absorption and adsorption or extraction. However, the improvement potential in large-scale processes is enormous. In this paper, we present four different successful implementations of membrane-based separations in our chemical company, ranging from upgrading of a process gas stream in a bulk chemical process to recovery of enzymes in a fine-chemical process. The technical–economical aspects of these projects are discussed.

The approach for implementation strongly differs depending on the existing situation in the plant. Replacement of existing separation units by more efficient membrane units quite often appears economically unattractive, whereas in new installations or debottlenecking situations, membrane separations have a better chance of success. Reliability and durability are key criteria in the process industry. Therefore, it should be strongly recommended that a large-scale data base be created, e.g. by proper demonstration projects. Some general conclusions are presented concerning recommended directions in the future development of membrane technology.

*Keywords:* Industrial installations; Gas separation; Ultrafiltration; Pervaporation/vapour permeation

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## 1. Introduction

In the past years, membrane research focused mainly on material development and fundamental aspects of membrane properties as a function of membrane (micro-)structure. Various concepts of membrane separations were developed, with pores ranging from the sub-nanometer scale up to the micrometer scale, and have found more or less established places in membrane science and technology. However, not much attention was paid to the process technology aspects.

Membrane separation technology has not really gained a foothold in the chemical industry, partly because until recently no suitable membranes were available and partly because generally the process industry is conservative. However, there is an advantage to be gained from letting membrane technology join the family of large-scale molecular separations as it offers some unique chances not achievable with other separation processes. Furthermore, it can compete, either as a stand-alone unit or as a hybrid unit, with established separations in terms of investment and operating costs. Although membrane separations are accepted unit operations in the dairy, food and beverage

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industries, membranes are relatively new as a unit operation for the chemical industry. Uncertainties are the long-term stability of the flux and the chemical stability of the membranes. The introduction of membranes in this industry depends on the economics, reliability and durability.

In this paper, we discuss our experiences in implementing membrane technology.

## 2. Gas separation

### 2.1. Hydrogen gas separation in ammonia production and hydrogenation

Currently, three methods are in large-scale use for separating hydrogen gas from different feedstocks: cryogenic recovery, pressure swing adsorption and membrane permeation.

#### *Cryogenic recovery*

Cryogenic recovery is based on differences in relative volatility of gases at very low temperatures. It is the oldest technique and is normally used on a very large scale of operation ( $> 10\,000\text{ Nm}^3/\text{h}$ ). Byproducts can be recovered, for example ammonia plant purge gas can yield argon, nitrogen and methane.

Cryogenic recovery is based on partial condensation and consists of two parts: pretreatment and separation in the so-called cold box [1]. Purge gas is fed to the cryogenic unit at a pressure of about 76 bar. In the pretreatment section, ammonia is removed from the purge feed gas by absorption in water. In the cold box, the gases are partially condensed and hydrogen remains in the vapour phase. The boiling point of helium is lower than that of hydrogen, so helium is also present in the hydrogen-rich phase. The product gas pressure is about 70 bar.

#### *Pressure swing adsorption (PSA)*

Pressure swing adsorption is based on selective adsorption of one or more components of a gas or liquid stream at the surface of a microporous adsorbent material. Since the adsorption forces are relatively weak, the adsorbate can be desorbed by either increasing the temperature or reducing partial pressure of the adsorbate. Each adsorber runs through the same cycle, characterized by adsorption at a high pressure and

regeneration at a low pressure (pressure swing). The optimum adsorption pressure is between 20 and 30 bar. Several adsorber vessels are combined in such a way that feed gas, product gas and tail gas streams are continuous flows [2].

For hydrogen separations, the commonly used adsorbent materials are zeolites and activated carbon. Hydrogen and helium are very weakly adsorbed while methane and carbon dioxide are more strongly adsorbed. Argon and nitrogen are moderately adsorbed [3].

The maximum hydrogen recovery efficiency depends on the number of adsorbers and on the composition of the feed gas. If nitrogen is present, the recovery yield is low, since nitrogen is relatively weakly adsorbed. For example, in the presence of about 25% nitrogen in the feed, the maximum hydrogen recovery yield is only 68%. In the presence of 25% methane, the recovery yield can be much higher, 85 to 89%, depending on the number of adsorbers.

#### *Membranes*

Membranes used for gas separations are predominantly based on polymers such as cellulosic derivatives, polysulfone, polyamide and polyimide. Membranes for gas separation are non-porous and separation is based on the differences in solubility and diffusivity through a membrane between the gas components. Generally, the solubility of a component increases and the diffusivity decreases with increasing molecular weight.

The purity of the product gas is dependent on the separation factor, the pressure ratio and the composition of the feed gas. The pressure difference over the membrane determines the membrane area required.

The selection of a separation process depends on several factors, e.g. composition of the feed stream, by-product requirements, temperature, pressure and the desired purity and recovery yield for the product. The associated considerations are illustrated in the description of the following cases.

### 2.2. Case 1. Hydrogen recovery in ammonia production [4]

In 1983 DSM decided to build a hydrogen recovery unit for one of its ammonia plants. The purge gas of the ammonia reactor ( $\sim 10\,000\text{ Nm}^3/\text{h}$ ) was normally used as fuel gas and valuable hydrogen was wasted.

Table 1  
Comparison of the expected performance of the two optional hydrogen recovery units, IJmuiden site, DSM

	Cryogenic unit	Membrane unit
Purity (%)	83.2	87.8
Recovery yield (%)	88.4	93.0
Hydrogen pressure (bar)	70	70 (60% of product stream) 25 (40% of product stream)

The gas stream contained 50 to 75% H<sub>2</sub> and 20 to 25% N<sub>2</sub> at a pressure of 135 to 140 bar.

Since no argon production was required on the site, two options were considered: cryogenic recovery and membrane separation. If argon was to be produced, cryogenic recovery would have been the only feasible option; argon and nitrogen are not separable by membranes. PSA was not taken into consideration, as the optimum pressure for PSA is too low and a large amount of nitrogen is present.

The comparison between both options is summarized in Table 1.

As can be seen from this table, the membrane unit produces a higher-quality hydrogen with a higher recovery yield. The unit delivers the product gas at two pressure levels, 70 and 25 bar, because the membrane unit consists of two stages in series. This offsets somewhat the advantages of a higher purity and recovery yield. The operating costs are about equal for both units.

Since both the investment costs and the expected maintenance costs were lower for the membrane unit than for the cryogenic unit, the first one was chosen. Other considerations were the more simple operation and the shorter delivery time of the membrane unit.

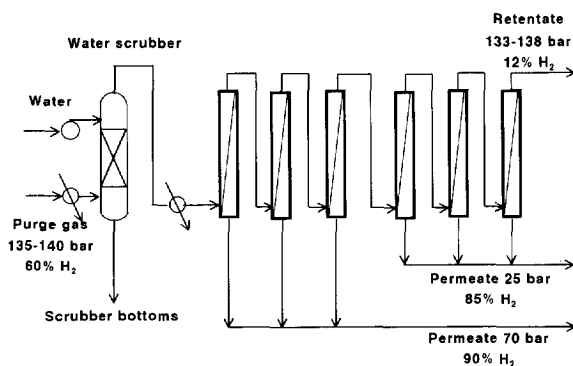


Fig. 1. Hydrogen recovery by membrane permeation.

Indeed, maintenance of the membrane unit has been minimal and the unit operates very smoothly.

The unit was installed in 1983 (Fig. 1). The performance decreased slightly over the years, probably due to aging of the membranes. In 1983 the average overall purity was 87.8% hydrogen with a recovery yield of 93%. The overall purity increased to 89%, but the recovery yield decreased to 78%.

The unit was successfully in operation until 1993, when the ammonia plant was shut down due to economic reasons.

### 2.3. Case 2. Hydrogen purification [5]

For a hydrogenation process at DSM's Geleen site, The Netherlands, a hydrogen gas with a high purity was required in order to minimize purge losses (the hydrogenation takes place at 80 to 100 bar) and to achieve optimum conversion and selectivity. Because of the high purity required (at least 98% H<sub>2</sub>) only two commercially available hydrogen separation processes were considered feasible: PSA and membrane permeation.

### 2.4. Feed gas source selection

At DSM's production site in Geleen, several hydrogen-containing feedstocks are available: naphtha cracker gas (90% hydrogen), synthesis gas for ammonia production (74% hydrogen) and product gas from a cryogenic recovery unit fed with ammonia purge gas (92% hydrogen). Of these feed gases, only naphtha cracker gas and product gas from the cryogenic recovery unit were considered suitable. The synthesis gas would only be used if the other two feed gases were not available, for example, due to a higher priority for other uses. Given this situation, there were four options: recovery by PSA or by membranes, using hydrogen gas from either the naphtha cracker or the cryogenic unit as feed.

### 2.5. Product purity

By means of PSA, it is possible to produce from naphtha cracker gas a hydrogen gas with a purity of 99.9%, with a recovery yield of 84 to 89%, depending on the number of adsorbers. With cryogenic product gas as feed, the maximum purity of the product is 99.6%

hydrogen, because helium is also present (0.3%). In addition, the hydrogen recovery yield is lower, 80%, due to the presence of 6.2% nitrogen. This means a larger volume of tail gas is produced, which can only be used as a fuel gas (1.3 bar pressure). It is possible to increase the recovery yield by lowering the product purity. However, the recovery yield is raised to only 81%, when the product purity is decreased to 98% hydrogen. Therefore, this option does not lead to lower costs.

By means of membranes, it is possible to produce from both feed sources a hydrogen gas with a purity of 98 to 99%, with recovery yields varying from 64 to 95%. In all cases tail gas will be used as a fuel.

## 2.6. Feed gas pressure

The naphtha cracker gas has a pressure of about 20 bar and a temperature of about 30°C. These are perfect feed conditions for PSA.

For a membrane unit, this feed gas can be used at the available pressure or it can be compressed. At a compression to 50 bar, a higher recovery yield can be achieved and a smaller quantity of feed gas is needed. With membrane permeation, a higher recovery yield leads to a lower purity. At a higher pressure drop, a permeate with the same purity can be produced at a higher recovery yield.

If precompression is used, and a larger pressure difference over the membrane is generated, the membrane units can be smaller. Of course, the costs of the pre-compressors have to be taken into account. The sum of the equipment costs is comparable to the cases without precompression.

Cryogenic product gas is available at a pressure of 70 bar and a temperature of 33°C. With PSA the feed pressure has to be reduced to 20–30 bar, as this is the most efficient pressure for PSA. The product gas then has to be recompressed to 100 bar. The cryogenic product gas is, however, directly usable for a membrane unit.

## 2.7. Product gas pressure

The purified gas from the PSA unit is available at 19 bar and 35°C. The tail gas has a pressure of 1.3 bar and can only be used as a fuel.

With naphtha cracker gas as feed at 20 bar pressure, the membrane permeate pressure of the product gas must be low (9 bar) to produce a purity of 99%. For a product gas with 98% hydrogen, the permeate pressure is 10 bar. The permeate pressure for the unit yielding the higher purity product is lower, so the unit can be smaller. However, a larger compressor is required in order to compensate for the lower pressure. The investment costs for both options are comparable. The variable costs are higher for the unit producing a higher purity, because of a lower recovery yield.

With cryogenic product gas as feed for the membrane unit, the permeate pressure can be higher: 32 bar, and a relatively small membrane area is needed.

## 2.8. Summary

Table 2 shows that with naphtha cracker gas as feed, membrane permeation with precompression to 50 bar and a hydrogen purity of 98% leads to the lowest costs.

With cryogenic product gas as feed, membrane permeation producing a hydrogen gas with a purity of 98.2% is the best choice. The retentate gas remains at a high pressure and is recycled to the ammonia process compressor. In this way, no synthesis gas is degraded to fuel gas. The overall recovery yield of hydrogen is 100% in this case (Fig. 2). The variable costs are lower than for any of the other options. A hydrogen gas with

Table 2  
Comparison of the alternative hydrogen purification processes, Case 2, product capacity 2000 Nm<sup>3</sup>/h

	$P_{\text{feed}}$ (bar)	$P_{\text{product}}$ (bar)	Purity (%)	Recovery (%)	Normalized costs		
					Fix.	Var.	Total
Feed: naphtha cracker feed gas (90% H <sub>2</sub> , 10% CH <sub>4</sub> ), $P = 20$ bar							
PSA	20	19	99.9	84	0.49	1.03	1.52
Membranes	20	10	98.1	82	0.43	1.06	1.49
Membranes	20	9	99.0	64	0.42	1.31	1.73
Membranes	50	20	98.3	95	0.43	0.94	1.37
Membranes	50	20	99.0	77	0.44	1.13	1.57
Feed: cryogenic product gas (92% H <sub>2</sub> , 6% N <sub>2</sub> ), $P = 70$ bar							
PSA	20	19	99.6	80	0.56	0.84	1.40
Membranes	70	32	98.2	93	0.27	0.73	1
Membranes	70	32	99.0	69	0.33	0.99	1.29

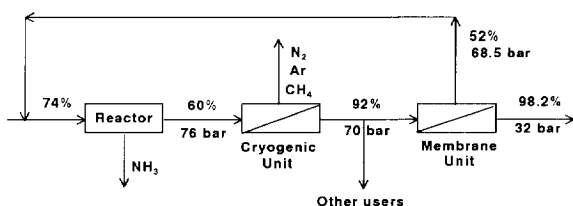


Fig. 2. Hydrogen purification by membrane permeation.

a purity of 99% is also achievable, but is more expensive.

The membrane process for a product gas with 98.2% hydrogen with cryogenic product gas as feed has been selected for reasons of lowest costs, better feed availability and, although not discussed here, location of the hydrogenation plant (shorter supply lines).

In practice, it is often necessary to develop several process options in parallel. In the course of the project, described in Case 2, there was an option for a different hydrogenation process for the same product. This alternative hydrogenation process required a higher hydrogen pressure, about 200 bar. In the latter case, PSA with naphtha cracker gas as feed would have been the best choice. Because of the high purity of the hydrogen produced by PSA (99.9%), an exit gas stream could have been recycled to the reactor, saving feed gas.

### 3. Separation/recovery of enzymes

#### 3.1. Case 1. Enzyme separation

At one of our sites, a fine chemical is being produced by a series of reactions, of which one step is catalyzed by enzymes. The enzyme solution contains the enzyme itself, cells, cell debris and several cell contents. The biocatalyst must be removed from the process solution, because it interferes with downstream processing and because it contaminates the product. In principle, two separation processes can be used: filtration and ultrafiltration. As the biocatalyst tends to clog the filter cloth, thereby reducing the filtration rate, filtration can only be used with a filter-aid. Ultrafiltration seemed an interesting alternative, as no additives were necessary. The enzyme itself is cheap enough for a once-through use and the remaining enzyme activity at the completion of the reaction is too low for re-use.

In Table 3, the economics of the UF unit are compared to two alternative filtration units. Filter 1 is a

Table 3

Enzyme separation, Case 1, capacity: 5 m<sup>3</sup>/(8 h)

	Filter 1	Filter 2	UF unit
Investment, Dfl	370 000	250 000	300 000
Operating costs/year			
Capital costs, Dfl	148 000	100 000	120 000
Electricity, Dfl 0.10/kWh	4 000	6 000	12 000
Detergent, Dfl 5.30/kg			11 000
Membranes, Dfl 300/m <sup>2</sup>			10 000
Filter aid, Dfl 2.00/kg	50 000	75 000	
Disposal costs, Dfl 150/ton	4 000	6 000	
Total costs, Dfl/year	206 000	187 000	153 000

continuous pressure filter and Filter 2 is a plate pressure filter.

The fine chemical is produced in batches, the assumed batch volume is 5 m<sup>3</sup> and it has to be filtered in 8 h.

In the calculations, it is assumed that the membranes will have to be cleaned every day with a special detergent. As membrane life time is assumed to be one year, the membranes will have to be replaced every year.

The figures show that ultrafiltration is the best choice if a new separation process must be installed.

After some preliminary laboratory-scale experiments, an ultrafiltration unit was installed at a pilot plant site. The experiments were very successful. The permeate was outstandingly clear and the operators found the unit easy to operate and maintain. Therefore, it was decided to install a pilot plant at a multi-purpose production facility.

Due to a process alteration at a later date, neither an UF unit nor a filtration unit were required. The negative effects of the presence of enzymes and cell debris in the product solution were compensated by using carbon adsorption, which was already installed for the purification of the product. Of course, the carbon adsorption unit had to be enlarged in order to separate the enzymes and cell debris, next to other impurities, from the product. The additional costs for the enlarged carbon adsorption are approximately Dfl 100 000 per year, which is less expensive than either ultrafiltration or filtration.

#### 3.2. Case 2. Enzyme recovery

For another fine-chemical process, where one of the reaction steps is an enzymatic conversion, the expen-

sive enzyme must be recovered. If filtration is used to separate the biocatalyst, the filter aid must be recycled too, as separation of the biocatalyst from the filter-aid is not possible. With ultrafiltration, the biocatalyst could be recycled without any additional compounds. Also, the ultrafiltration gives an enzyme retention of more than 99%, much higher than filtration (about 50%). An ultrafiltration unit was installed in 1988. The membranes must be replaced every six months, whereas the membrane manufacturers claim a much longer life time, one to two years. This appears to be due more to the current cleaning procedures than to anything else, therefore, the cleaning procedure needs to be optimized.

## 4. Purification of alcohols

### 4.1. Industrial experience

Distillation, pervaporation (PV) and vapour permeation (VP) are used for the separation of water from alcohols. Distillation is still the most common unit operation. Pervaporation plants have been operating since 1982, mostly for the separation of water/ethanol and of water/iso-propanol. The first industrial vapour permeation plant has been operating for water/ethanol since 1989 [6]. Flat sheet modules are currently in use for both PV and VP. Spiral wound modules for PV and VP have recently entered the market. To our knowledge there is no industrial experience yet with hollow fibre membranes for pervaporation or vapour permeation.

### 4.2. Case 1. Iso-butanol recovery

The capacity of a resin plant had to be increased. During an etherification reaction, water is formed and must continuously be removed from the reaction mixture in order to enhance the reaction. However, iso-butanol forms an azeotrope with water. After condensation of the butanol/water vapour, a phase separation occurs and the butanol-rich phase (85% iso-butanol) is recycled to the reactor. If, however, the iso-butanol content in the recycle stream can be increased to at least 98% butanol, a reduction of about 50% in etherification time can be achieved. The capacity of the existing reactor can then be increased without installing an expensive new vessel.

In Fig. 3 and Fig. 4, flow sheets of processes with PV and VP as separation process are shown.

### 4.3. Cost comparison

To be able to decide which option for the separation is most economically feasible, the costs of the separation methods must be compared. The figures for the investment and utility costs of VP and PV with flat sheet modules were made available by the vendors of the equipment. The costs of the hollow fibre units and of the distillation are our own estimates. In Table 4, the estimated costs of the separation methods are summarized.

From Table 4, it is apparent that VP or PV with hollow fibre modules is by far the most economically feasible option. Distillation is the most expensive

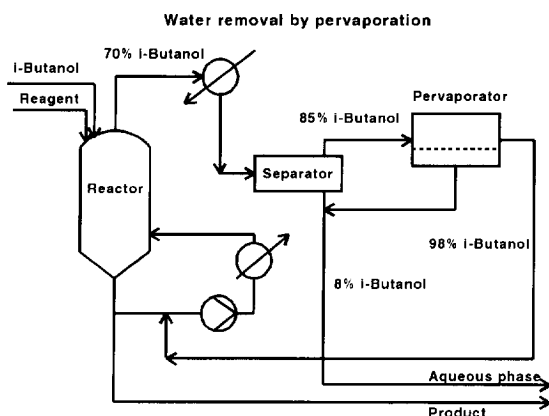


Fig. 3. Water removal using pervaporation.

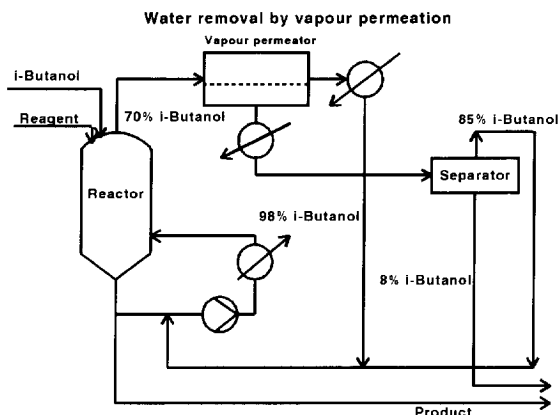


Fig. 4. Water removal using vapour permeation.

Table 4  
Normalized costs of separation of water from iso-butanol

Separation	VP/PV hollow fibre	VP flat sheet	PV 1 flat sheet	PV 2 flat sheet	Distillation
Variable costs	0.07	0.13	0.18	0.17	0.27
Fixed costs	0.93	1.86	1.86	2.13	2.19
Total costs	1.00	1.99	2.04	2.30	2.46

option, in terms of investment costs and variable costs.

The commercially available VP and PV plants are equipped with flat sheet membranes. Since the production costs of both the hollow fibre membranes themselves and the hollow fibre modules are much lower than those of flat sheet membranes, the equipment and the membrane replacement costs will be the lowest.

All processes considered (distillation, vapour permeation and pervaporation) are economically feasible for the removal of water from the butanol/water stream, the payback time being 0.5 to 1.25 years.

Distillation is the safest option and requires little or no research, but it is the most expensive.

Vapour permeation is in principle simpler than pervaporation, but there is not as much industrial experience as there is for pervaporation.

Using commercially available flat sheet membranes is a relatively safe option. Using hollow fibre membranes for vapour permeation or pervaporation involves the greatest risks, as the modules and the process must be developed for this application. However, the profit potential is the highest.

At this moment, none of the solutions mentioned above are considered, since the capacity increase will be realised by product re-allocation. In this way, no investments in equipment for the purification of iso-butanol are necessary.

#### 4.4. Case 2. Iso-propanol recovery

One of the reaction steps in a fine-chemical process is an esterification reaction with iso-propanol. During this reaction, water is formed and must be removed. The composition of the vapour is 94% alcohol and 6% water. For reuse of the alcohol, it is sufficient to lower the water content to 1%. If water cannot be removed, the effluent vapour of the reactor has to be condensed and incinerated. There were several alternatives considered for the recovery of the alcohol. Since the waste stream is relatively small, pervaporation proved to be

the optimal solution. The unit was installed in April 1993. The payback time of the PV installation was approximately nine months.

## 5. General conclusions

In the process industry the final choice of a separation process is always the result of a complex balance between the economics, the desired purity and the recovery yield of the product and depends on various constraints and conditions, such as, the possibility of integration with other processes, the capacity desired and the composition of the feed.

Membrane processes have a future as stand-alone units, as well as in combination with other processes such as distillation.

For gas separations, both PSA and membranes have limitations in the combination of feed pressure, product pressure, purity, etc. It is expected that a properly designed hybrid system will outweigh the disadvantages of the specific techniques and favourably combine their advantages.

Since membrane technology for process applications in the chemical industry is relatively unknown, extensive research and economic evaluations are still necessary in order to convince potential large-scale users.

Also, psychological barriers play an important role, which should not be overlooked when trying to implement a novel technology.

In the cases discussed, a new separation unit had to be built. To replace an existing unit with membranes, the hurdles are even more difficult to overcome. Reliability and durability are key criteria in the process industry. For R&D it is essential to focus on developing robust membrane units. Otherwise, it will remain difficult to achieve sufficient acceptance for implementation. To enhance this, it should be strongly recommended that a large-scale data base be created, e.g. by proper demonstration projects.

From our point of view, as regards large-scale units, it is preferable that existing membrane technologies be improved rather than introducing completely novel and exotic concepts, which will require many years of development before they can be applied to large-scale units.

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