

MEMBRANES FOR VAPOR/GAS SEPARATION

Richard W. Baker

Membrane Technology and Research, Inc.

1360 Willow Road, Suite 103, Menlo Park, CA 94025

Email: info@mtrinc.com

Keywords: Membranes, vapor/gas separation, membrane system process design, polyolefin plant resin degassing, gasoline vapor recovery systems, monomer recovery systems.

ABSTRACT

The first small membrane units for separating organic vapors from air were installed in the late 1980s. By the mid-1990s, MTR was selling million-dollar systems to petrochemical plants to recover olefins from polyolefin manufacture. About the same time, licensees of GKSS technology in Europe began installing large systems to capture gasoline vapors from tank farms and fuel terminals. The market for vapor separation systems is now at least \$20-30 million per year. More than 100 large systems, with a value of \$1-5 million each, have been installed. In addition, at least 500 small systems, with a value of \$10,000-\$100,000 each, are operating to capture vapor emissions from retail gasoline stations, industrial refrigerator units and petrochemical process vents.⁽¹⁻⁴⁾

This chapter covers the development of vapor/gas separation technology and its emergence as a recognized sector of the membrane separation business. Separations of organic mixtures, such as light hydrocarbon streams, and of organic/water mixtures, present different technical challenges and are not discussed here.

MEMBRANES AND MODULES

Gas transport through dense polymer membranes is governed by the expression:

$$j_i = \frac{D_i K_i (p_{i_o} - p_{i_i})}{\ell} \quad (1)$$

where j_i is the volume (molar) flux expressed as $[\text{cm}^3(\text{STP}) \text{ of component } i]/\text{cm}^2 \cdot \text{s}$; ℓ is the membrane thickness, P_{i_o} is the partial pressure of component i on the feed side, and P_{i_i} is the partial pressure of component i on the permeate side. The diffusion coefficient, D_i , reflects the mobility of the individual molecules in the membrane material; the gas sorption coefficient, K_i , with units $[\text{cm}^3(\text{STP}) \text{ of component } i/\text{cm}^3 \text{ of polymer}] \cdot \text{pressure}$, reflects the number of molecules dissolved in the membrane material. The product $D_i K_i$ can be written as \mathcal{P}_i , which is called the membrane permeability, and is a measure of the membrane's ability to permeate gas.

The best measure of the ability of a membrane to separate two gases, i and j , is the ratio of their permeabilities, $\alpha_{i/j}$, called the membrane selectivity, which can be written as

$$\alpha_{i/j} = \frac{\mathcal{P}_i}{\mathcal{P}_j} = \left[\frac{D_i}{D_j} \right] \left[\frac{K_i}{K_j} \right] \quad (2)$$

The ratio D_i/D_j is the ratio of the diffusion coefficients of the two gases and can be viewed as the mobility selectivity, reflecting the different sizes of the two molecules. The ratio K_i/K_j is the ratio of the sorption coefficients and can be viewed as the sorption or solubility selectivity, reflecting the relative solubility of the two gases. In polymer materials, the diffusion coefficient decreases with increasing molecular size, because large molecules interact with more segments of the polymer chain than do small molecules. Hence, the mobility selectivity, D_i/D_j , always favors the permeation of small molecules over large ones. The sorption coefficient of gases and vapors is a measure of the energy required for the gas to be sorbed by the polymer, and increases with increasing condensability of the permeant. This dependence on condensability means that the sorption coefficient usually increases with molecular size, because large molecules are normally more condensable than smaller ones. Hence the sorption selectivity, K_i/K_j , favors the permeation of larger, more condensable molecules, such as hydrocarbon vapors, over permanent gases, such as oxygen and nitrogen. It follows that the effects of permeant molecular size on the mobility and sorption selectivities are opposed.

Because of the competing effects of the mobility selectivity term and the sorption selectivity term in Equation (2), the selectivity of gas pairs is different in glassy and rubbery polymers. This difference is illustrated by the data in Figure 1.

- In glassy polymers, such as polyetherimide, the rigid nature of the polymer chains means the mobility selectivity term in Equation (2) is dominant. Permeability falls with increasing permeant size, and small molecules permeate preferentially. When used to separate an organic vapor from nitrogen, amorphous glassy membranes preferentially permeate nitrogen.

- In rubbery polymers, such as polyisoprene, the sorption selectivity term is dominant. Permeability increases with increasing permeate size, and large molecules permeate preferentially. When used to separate an organic vapor from nitrogen, rubbery membranes preferentially permeate the organic vapor.

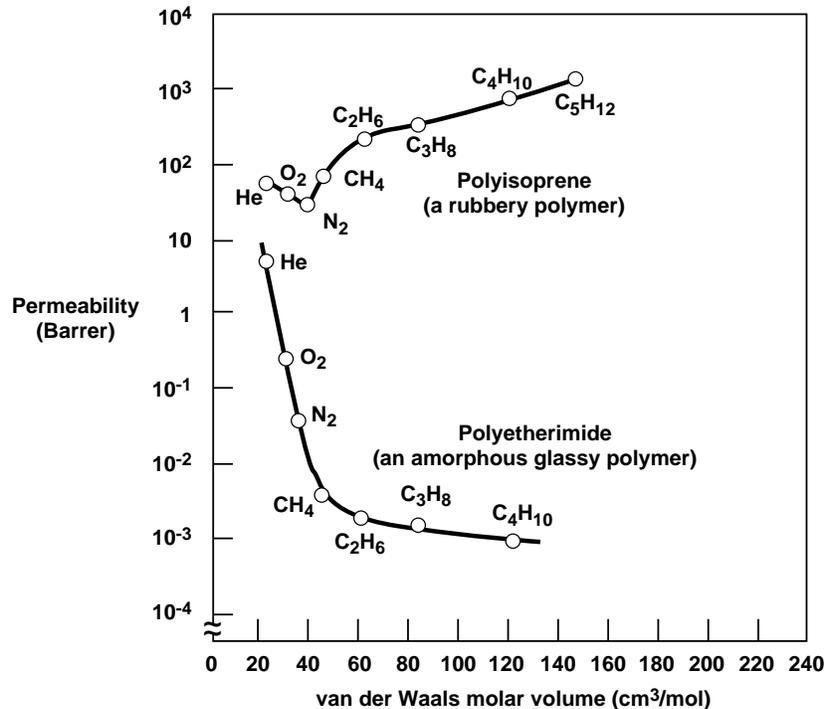


Figure 1. Permeability as a function of molar volume for a rubbery and a glassy polymer, illustrating the different balance between sorption and diffusion in these polymer types.

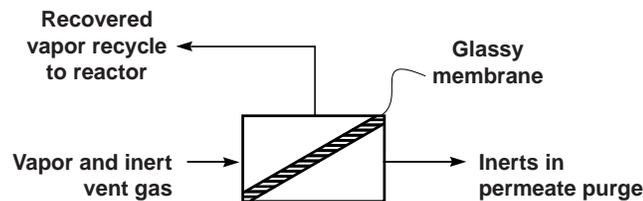
From the discussion above, it appears that vapor/permanent gas separations can be performed with either rubbery vapor-selective membranes or glassy gas-selective membranes. In practice, almost all commercial plants use rubbery membranes, predominantly membranes made from silicone rubber (polydimethyl siloxane) [PDMS]. Rubbery membranes are preferred for several reasons:

1. Rubbery polymers tend to have much higher permeability than glassy polymers. (As Figure 1 shows, polyisoprene is over 100 times more permeable than polyetherimide to oxygen.) The higher the permeability, the smaller is the membrane area required to permeate a given volume flow of gas. Therefore, in system design, higher permeability translates to fewer membrane modules, and lower capital cost.
2. The vapor/permanent gas selectivity of most glassy polymers is very dependent on organic vapor partial pressure. At low vapor concentrations (or partial pressures), the selectivity of the membrane approaches the selectivity predicted by the ratio of pure gases. However, as the organic vapor concentration (partial pressure) increases, the amount of vapor sorbed in the polymer also increases. The vapor plasticizes the polymer, which becomes rubbery. In the plasticized material, the nitrogen permeability increases, but the organic vapor

permeability increases even more. The membrane then switches from being a glassy, permanent-gas-selective membrane to being a rubbery, organic vapor-selective membrane. Examples of the few exceptions to this behavior are the perfluoro polymers Teflon[®] AF (DuPont) and Hyflon[™] AD (Solvay Solexis).⁽⁶⁾ These polymers, because of the inert nature of their perfluoro chemistry, have exceptionally low sorptions for most organic vapors and so retain their glassy nature, even in the presence of high concentrations of organic vapors. Membranes made from these polymers have found a limited use in separating air from gasoline vapor vent streams at retail gas stations.

3. Rubbery membranes provide better selective purge capability. The final reason that rubbery, vapor-permeable membranes are usually preferred is illustrated in Figure 2, which shows flow schemes for two types of membrane systems used to recover the vapor component from a vapor/inert gas vent gas stream. The objective of this very common type of process is to produce an inert vent gas purge stripped of as much of the organic vapor component as possible. In the first design shown in Figure 2(a), a glassy polymer membrane is used to treat the vent gas. The inert gases permeate the membrane, and the vapor-enriched residue gas is recycled to the process. The advantage of this design is that the pressure of the recovered vapor-containing residue gas is only slightly below the pressure of the feed gas. This allows the residue gas to be recycled to the process with minimal recompression. However, the membrane must be very selective to prevent excessive amounts of vapor passing through the membrane. Few glassy polymer membranes are sufficiently selective to make this design practical.

(a) Vapors retained by a glassy membrane



(b) Vapor permeated by a rubbery membrane

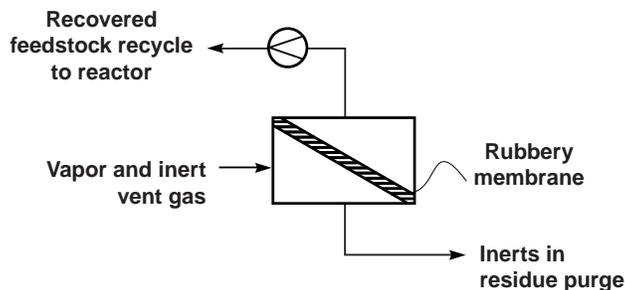


Figure 2. The two principal designs for membrane vent-gas systems.

In the design shown in Figure 2(b), a rubbery membrane is used. The vapor to be recovered permeates the membrane, leaving a residue stream enriched in the inert components. The advantage of this design is that even modestly selective membranes can produce an inert vent gas stream almost completely depleted of vapor. All of the organic vapor component is recycled back to the process. The disadvantage of this design is that the vapor-rich permeate to be recycled to the reactor is at low pressure and must be recompressed.

Silicone rubber composite membranes have been used in almost all of the vapor separation systems installed to date. Silicone rubber is extremely permeable and has adequate vapor/inert gas selectivities for most applications. Polyoctylmethylsiloxane (POMS), closely related to silicone rubber (polydimethylsiloxane), has been suggested as a material with slightly better selectivity but has not been widely used.⁽⁷⁾ For a few years, there was also a good deal of interest in the polyacetylene polymers poly(1-trimethylsilyl-1-propyne) (PTMSP), poly(p-tert-butyl diphenylacetylene)PptBDPA and poly(4-methyl-2-pentyne) (PMP).^(8,9) These glassy polymers, because of the rigidity of their polymer backbones, have extraordinarily high free volumes and very unusual gas permeation properties. In particular, the polymers are even more permeable and more selective to condensable vapors than silicone rubber, the industry benchmark polymer. Unfortunately, the high cost of the polymers and their poor chemical and physical stability have prohibited commercial use, and most researchers have now abandoned work with these materials.

Silicone rubber is soft and elastic. For this reason, silicone rubber membranes are made as composite structures of the type shown in Figure 3. A non-woven support paper provides mechanical strength. The pores of this paper are too large to be coated directly with the silicone rubber selective layer, which is usually less than $5 \mu\text{m}$, and sometimes less than $1 \mu\text{m}$, thick. Instead, the paper is first coated with a finely microporous ultrafiltration support membrane. This membrane provides a smooth surface on which the very thin silicone rubber layer can be coated. The permeance of the support membrane is usually 10- to 1,000-fold higher than that of the selective silicone rubber layer, so the overall resistance to flow is predominantly in the silicone rubber layer.

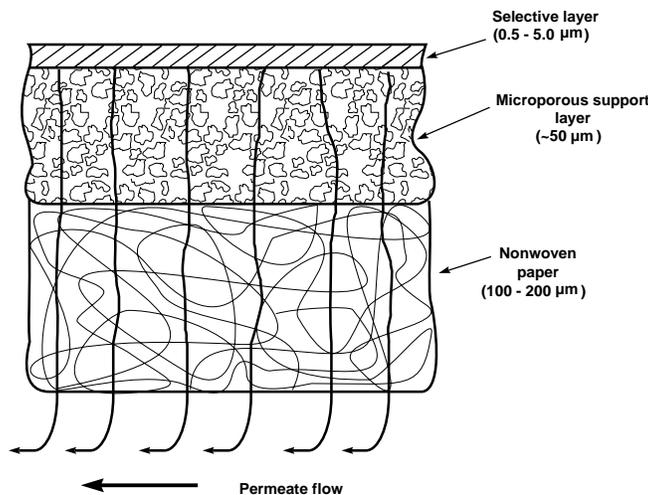


Figure 3. Schematic illustration of a composite membrane.

Composite membranes are made in sheets or rolls and fabricated into large-membrane-area membrane modules for use in industrial systems. GKSS, the main European supplier of vapor-gas separation units, packages their membranes into plate-and-frame modules. MTR, the main U.S. producer, uses spiral-wound modules.

PROCESS DESIGN

One-Stage Selective Purge Systems

In a number of processes, the goal of the membrane system is to recover and recycle vapor components previously lost with an inert gas purge.⁽¹⁰⁾ Figure 4 shows the design of a typical reactor purge unit, for a reactor that achieves incomplete conversion of feedstock. Typically, the reagents enter the reactor vessel, heat and pressure are applied, and the desired reaction occurs in the presence of a catalyst. The products of reaction then move to a separator and are cooled or scrubbed to remove the product as a liquid. Unreacted components are released as a gas, which is recycled to the reactor.

A common problem with this type of process is the buildup of inert impurities in the reactor-separator-recycle loop. Inert components occupy reactor capacity and progressively diminish the process efficiency. These components can be gases such as carbon dioxide generated by a side reaction in the reactor. More commonly, they enter the reactor with the feedstock. Oxygen is often contaminated with 0.5 to 1.0% argon; propylene is contaminated with 0.5 to 5% propane; ethylene with ethane; hydrogen with traces of methane and so on. To control contaminant build-up, a portion of the recycle gas is purged from the reactor recycle loop. However, the concentration of inerts in the purge may be only a few percent, so for every mole of purged argon or propane, many moles of valuable feedstock may be lost. The opportunity for membranes in such a process is to recover these valuable components.

A simple one-stage membrane system fitted with silicone rubber membranes that preferentially permeate the valuable feedstock vapor and reject the inert gas contaminants is shown in Figure 4. The permeate gas, enriched in the vapor components, is compressed and sent back to the reactor; the residue gas, containing only the inert components, is purged. Feedstock losses can be essentially eliminated with such a design.

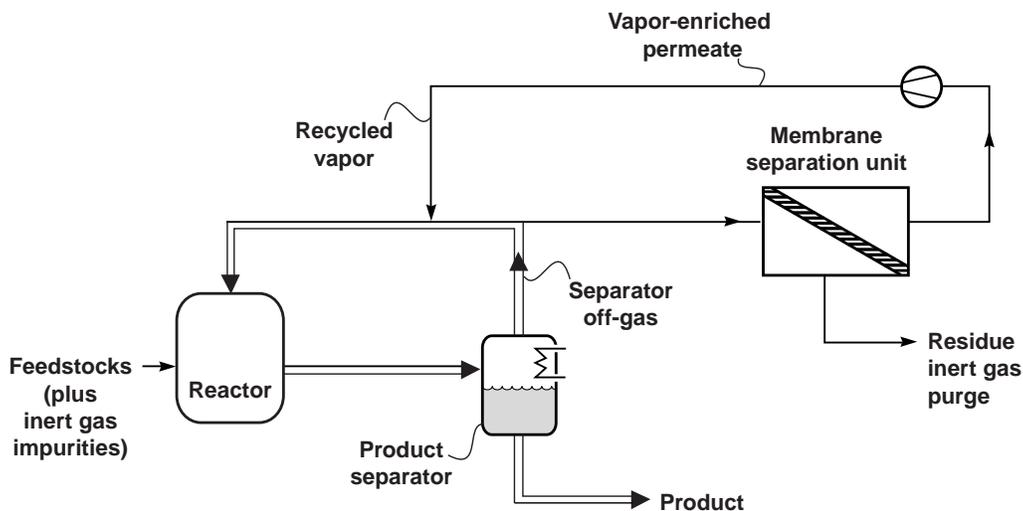


Figure 4. Membrane separation system used to recover organic vapor from a reactor vent stream containing vapor components to be recovered and inert gas components to be released.

Multi-step and Multi-stage System Designs

The objective of one-stage membrane systems as shown in Figure 4 is to produce an inert gas purge stream stripped of the vapor component. This can be done with great success, but, because the membrane selectivity is modest, the vapor recycle stream recirculated to the reactor is only modestly enriched, perhaps two- or three-fold, in the vapor component. In some applications, this is acceptable; in others, a more complete separation is required. The solution is to use two membrane units in series.

One-stage, two-stage and two-step membrane flow schemes for treating the same feed stream are illustrated in Figure 5.* The three designs shown are all based on the same vapor-permeable membranes with a vapor/nitrogen selectivity of 10 and an inert gas permeance, also commonly referred to as pressure-normalized flux, or simply called P/l [based on Equation (1)] of 100 gpu ($1 \text{ gpu} = 1 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$). All these schemes purge the same amount of the inert gas (54.4 scfm). Because the concentration of the hydrocarbon vapors in the permeate gas recycled to the reactor varies, the initial volume of feed gas to the membrane unit (90% inerts, 10% hydrocarbon vapors) is different for each system.

* A system contains a second membrane *stage* when the second membrane unit is placed on the *permeate* gas from the first membrane unit. The system contains a second membrane *step* when the second membrane unit is placed on the *residue* gas from the first membrane unit.

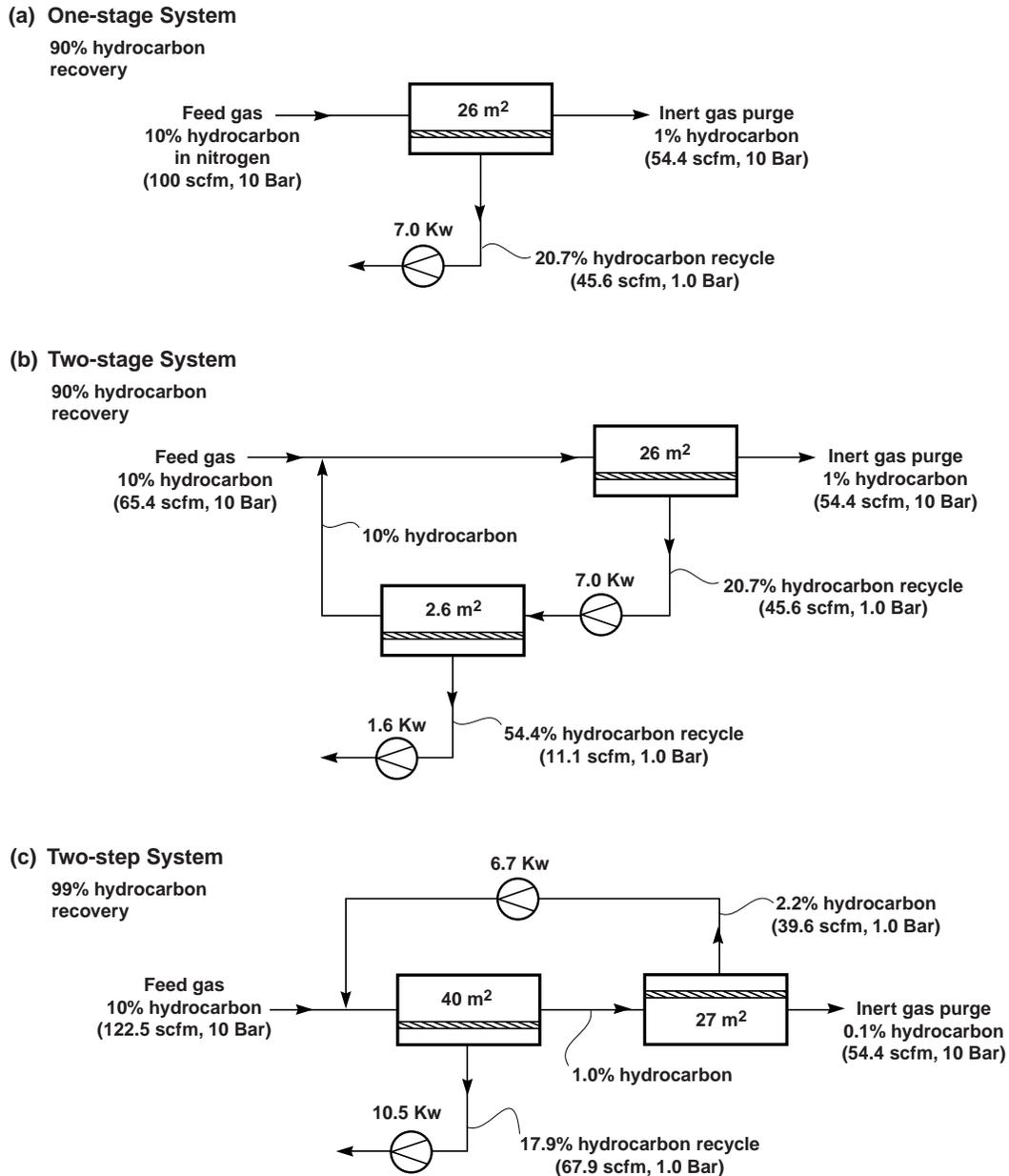


Figure 5. Comparison of one-stage, two-stage and two-step membrane processes, all producing the same volume of inert gas purge (54.4 scfm). These calculations are performed using a computer process simulation package (ChemCAD 5.0, Chemstations, Inc., Houston, TX) modified with code written at MTR for the membrane separation step.

The one-stage system [Figure 5(a)] divides the feed gas into two roughly equal streams: a residue inert gas purge, from which 90% of the hydrocarbon has been removed; and a permeate recycle stream, enriched about two-fold in hydrocarbons, that is recycled to the reactor. The two-stage system [Figure 5(b)] also achieves 90% removal of hydrocarbons from the inert gas purge. However, the first stage permeate gas, after compression to 10 bar, is passed through a second membrane stage. The residue from the second stage is mixed with the feed gas and recycled to the first membrane stage. In the design shown, the second membrane stage is used to produce a recycle

The feed gas is first compressed and then sent to a vapor condenser, operating at -20°C . On cooling the gas, a portion of the vapor contained in the feed gas (in this case propylene), condenses and is removed as liquid. The condenser off-gas, containing uncondensed propylene, is sent to the membrane unit, which preferentially permeates the hydrocarbon vapor, leaving a 99% pure nitrogen residue stream. The propylene-enriched permeate gas is recycled to the incoming feed gas. The gas sent to the membrane unit comes directly from the chilled vapor condenser and is, therefore, saturated with propylene and cold. Under these conditions, the solubility of the hydrocarbon in the membrane is enhanced, and the membrane selectivity is high.

The raw propylene condensate produced in the condenser contains some dissolved nitrogen, so the liquid is flashed at low pressure to remove this gas. The flash step off-gas is recycled to the feed as shown. After flashing, the propylene product has a purity of better than 99.5%. The hybrid design takes advantage of the ability of condensation to produce a high-purity liquid and of membrane separation to produce a high-purity residue stream. If condensation alone were used, the only way to avoid loss of propylene in the condenser off-gas would be to cool it to extremely low temperatures, requiring multiple stages of refrigeration. If membrane separation alone were used, it would be almost impossible to achieve both a high-purity residue and a high-purity permeate stream, without resorting to a cascade of many membrane stages. The hybrid design offers flexibility to adjust the operating parameters of each unit for optimized efficiency and product quality.

In the example of Figure 6, the inert gas is nitrogen, so there is no possibility of creating flammable gas mixtures in the process. However, in some applications the inert gas is air, so precautions must be taken to eliminate dangers caused by the vapor/air mixture entering the flammable-explosive range. This type of problem exists in the separation of gasoline/air mixtures. The specific system designs used to circumvent this problem are described for the treatment of gasoline vapor/air mixtures in the application section that follows.

APPLICATIONS

The two principal suppliers of vapor/gas membrane separation systems are MTR and the licensees of GKSS (Borsig, Sihi and Dalian Eurofilm). The major markets serviced by these companies are described briefly below.

Polyolefin Plant Resin Degassing

Probably the largest single application of vapor separation membranes is in the recovery of hydrocarbon monomers from ethylene and polyethylene and polypropylene plants. These plants make polyolefins, principally from ethylene and propylene. After the polyolefin resin is produced, it contains unreacted monomer and hydrocarbon solvents, dissolved in the resin powder. The dissolved hydrocarbon must be removed before the polymer can be used, and this is done by stripping with hot nitrogen, in a column known as a degassing bin. In early polyolefin plants, the vent gas from the degassing bin—containing 10 to 20 mol% hydrocarbon—was used as boiler fuel. Since the development of vapor separation membranes, most new polyolefin plants have installed hydrocarbon recovery units. In a modern polyolefin plant, the value of the monomer in the nitrogen

resin bin off-gas is on the order of \$1 to 2 million/year; the value of the nitrogen can represent another \$0.5 million/year. Recovery and reuse of these components is well worthwhile.

A process flow stream and a photograph of a typical membrane system fitted to a polyolefin plant resin degassing bin are shown in Figure 7.⁽¹³⁾ The off-gas from the bin is compressed to 200 psi, dried, and cooled to -30°C. A portion of the propylene then condenses. The condenser overhead stream (propylene and nitrogen) is sent to the membrane section, which contains two membrane units in series. The first membrane unit produces a permeate stream enriched in propylene and a purified residue stream containing ~97-98% nitrogen. The vapor-enriched permeate stream is recycled to the inlet of the compressor. The nitrogen-rich residue can often be directly recycled to the degassing bin without further treatment. However, in the example shown, the residue gas is passed to a second membrane unit to upgrade the nitrogen to better than 99% purity. The waste hydrocarbon stream from the second membrane unit is sent to flare. The performance of the system is summarized in Table 1. During the last 10 years, almost 50 of these systems have been installed around the world.

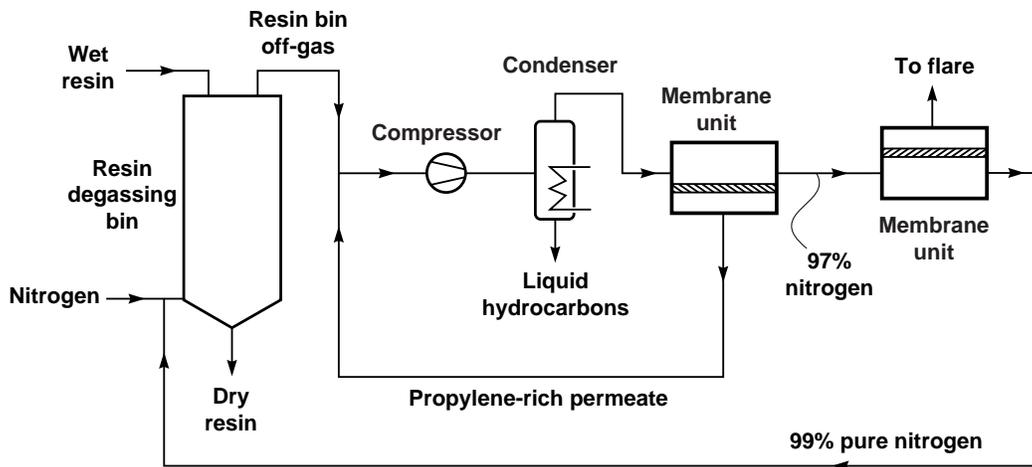


Figure 7. Photograph and process flow diagram of a membrane propylene recovery system installed at a modern polypropylene plant. The front portion of the unit is the compressor package. The spiral-wound membrane modules are contained in the horizontal tubes above and behind the compressor. This unit recovers approximately 1,000 lb/h of hydrocarbons.

Table 1. System Performance of a Typical Membrane Resin Degassing Bin Recovery Unit (1999 data).

Feed Flow Rate (lb/h)	5,000
Feed Gas Composition (vol%)	
Hydrogen	1.0
Nitrogen	84.4
Propane	0.3
Propylene	14.0
Water	0.3
Hydrocarbon Recovery ~1,000 lb/h	
	91%
Nitrogen Recovery ~2,000 lb/h	
	50%
Value of Recovered Hydrocarbons*	\$1.75 million/year
Value of Recovered Nitrogen*	\$0.6 million/year
Capital Cost**	\$2.7 million

* Value of recovered nitrogen at \$75/ton; hydrocarbons at \$400/ton.

** Includes cost of the low temperature refrigeration unit.

Gasoline Vapor Recovery Systems at Large Terminals

An important early application of membrane vapor recovery systems was the recovery of gasoline vapors from vent streams produced at large oil and gasoline terminals. During the transfer of hydrocarbons from tankers to holding tanks and then to trucks, off-gases are produced. The off-gas stream volume and vapor concentration vary widely, but the average emissions resulting from each transfer operation are large—in the range 0.03 to 0.05% of the hydrocarbon transferred.^(2,4)

The hydrocarbon concentration of the emitted gas is generally quite high, in the range 10 to 30 vol%, depending on the type of hydrocarbon and type of transfer. A typical off-gas composition for gasoline loading or unloading is shown in Table 2. Because the off-gas is an air-hydrocarbon mixture, the potential for creating an explosive composition has to be considered in the design of the membrane vapor recovery system.

Table 2. Typical Gasoline Vapor Vent Gas Composition (vol%).⁽²⁾

Component	(%)	Component	(%)
Methane	0.01	<i>i</i> -Pentane	4.43
Ethane	0.03	Hexane	1.51
Propane	0.69	C ₇ ⁺	0.14
Butane	6.66	Benzene	0.29
<i>i</i> -Butane	3.69	Oxygen	16.71
Pentane	2.60	Nitrogen	63.24

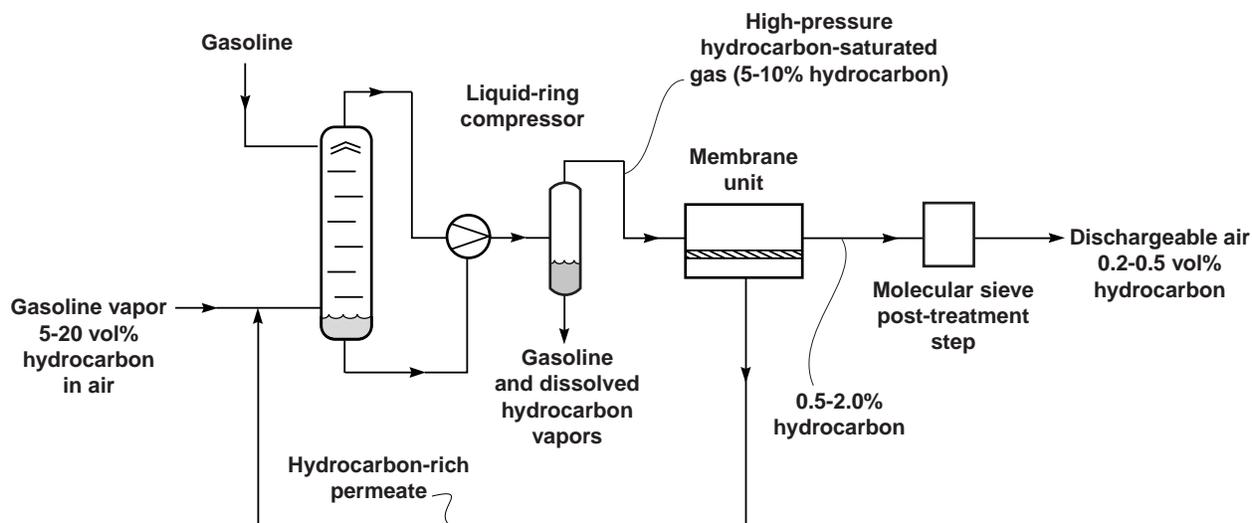


Figure 8. Flow schematic of a gasoline vapor recovery system, using a combination of absorption and membrane separation to recover 98+% of the hydrocarbons in the vent gas, followed by a molecular sieve pressure swing absorption (PSA) unit to remove the final 1-2% hydrocarbon.

Hydrocarbon vapor/air mixtures containing from 3 to 15% hydrocarbon are in the flammable range. Below 3% hydrocarbon vapor, the mixture is too hydrocarbon-lean to burn. Above 15% hydrocarbon vapor, the mixture does not contain enough oxygen to burn. Problems occur in the intermediate range, where a chance spark can cause an explosion. The usual solution to this problem is to saturate the incoming feed mixture with additional hydrocarbon vapor in a small contactor tower. This ensures that the feed to the compressor needed to operate the membrane unit is always comfortably above the upper explosion limit, regardless of the composition of the feed gas.

As an additional safeguard, liquid-ring compressors are usually chosen. In a liquid-ring compressor, the seal between the rotating vane of the compressor and the compressor chamber is formed by a film of liquid—in this case, liquid gasoline. The liquid seal minimizes metal-to-metal contact and the possibility of sparks. As the gas is compressed, some hydrocarbon vapor is absorbed by the gasoline sealing fluid of the compressor. The fluid leaving the compressor is then a two-phase mixture of gasoline containing dissolved vapors and hydrocarbon-saturated air. A phase separator, after the compressor, separates the hydrocarbon liquid and gas phases. The vapor-saturated gasoline is removed; the saturated vapor then passes to the membrane unit. As with the condensation-membrane separation unit shown in Figure 6, hydrocarbon vapors are removed by using a hydrocarbon-selective membrane. The hydrocarbon-enriched permeate is recycled to the front of the feed gas compressor; the hydrocarbon-stripped residue contains 0.5 to 2% hydrocarbon, mainly the light gases methane, ethane and propane. To meet air discharge regulations, this gas is usually sent to a final polishing step, most commonly a small, molecular sieve, pressure swing absorption unit (PSA), which reduces the hydrocarbon level to 0.2 to 0.5 vol%. As Figure 8 shows, the gas under treatment passes through the flammable range from the hydrocarbon-saturated feed (5-10% hydrocarbon) to the hydrocarbon-stripped residue (0.5-2% hydrocarbon) within the membrane module. Since there are no moving parts within the module, the chance of a spark causing an explosion is minimal.

GKSS's licensees have installed about 30 gasoline vapor recovery systems at fuel transfer terminals, mostly in Europe. The alternative technology is to use some sort of thermal oxidizer, and this approach seems to be the most widely used technology, especially in the United States. A related gasoline vapor recovery application in which membranes are finding it easier to compete is at retail gasoline stations. Many new gasoline stations are using vacuum-assisted dispensing systems to control the release of hydrocarbon vapors to the atmosphere. These systems use a small pump to draw air and vapors from the gasoline dispensing nozzle. For every liter of gasoline dispensed, as much as two liters of air and gasoline vapor are returned to the storage tank. The air that builds up in the tank must be vented to the atmosphere. Membrane systems are used to control the vapor emissions.

In the last few years, several hundred retail gasoline stations have installed small membrane systems to treat their tank vents. A flow scheme of this type of system is shown in Figure 9. Air from the gas station dispenser is collected and sent to the gasoline storage tank. When the pressure in the tank reaches a preset value, a pressure switch activates a small compressor that draws off excess vapor-laden air. A portion of the hydrocarbon vapors condense and is returned to the tank as a liquid. The remaining hydrocarbons permeate the membrane and are returned to the tank as concentrated vapor. Air, stripped of 95-99% of the hydrocarbons, is vented. In addition to eliminating hydrocarbon emissions, the unit essentially pays for itself with the value of the recovered gasoline.⁽¹⁴⁾

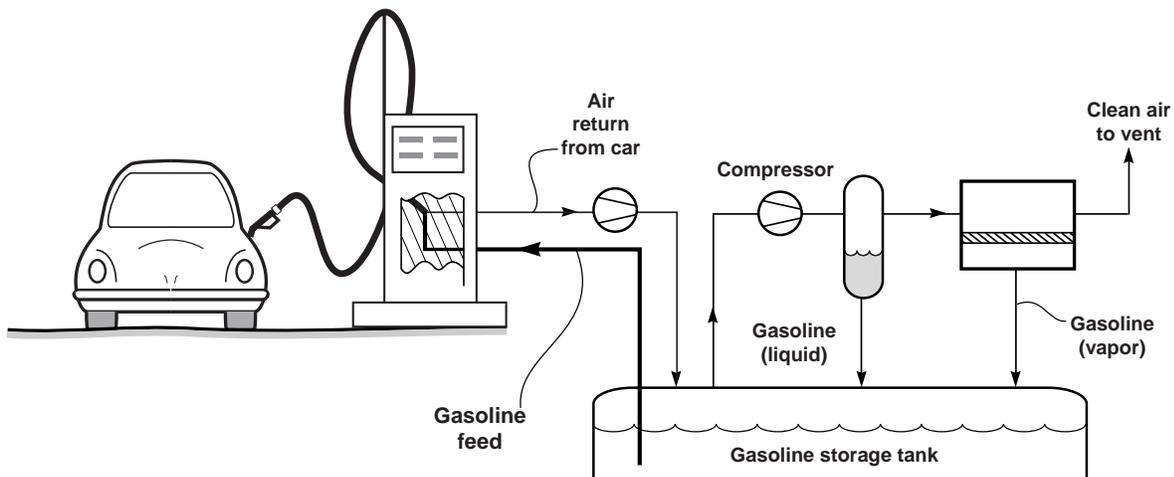


Figure 9. Flow diagram of a membrane gasoline-vapor recovery unit suited to a retail gasoline station tank vent. Typical systems are small, containing a single 1-2 m² membrane module and costing from \$5,000 to 15,000. Several hundred, perhaps as many as 1,000 of these systems have been installed around the world.⁽¹⁴⁾

Polyvinyl Chloride Manufacturing Vent Gas

In the polymerization of polyvinyl chloride, unwanted gas is generated by side reactions, and some small amounts of air leak into the reactors. These inerts must be vented from the process. Because vinyl chloride monomer (VCM) is extremely volatile, the purge gas, although it is typically at 4 to 5

bar pressure, can contain as much as 50 vol% monomer. As a consequence, the vented gas stream, although small, may contain several hundred thousand dollars worth of monomer values. A typical process flow scheme to recover VCM is shown in Figure 10.⁽¹⁵⁾

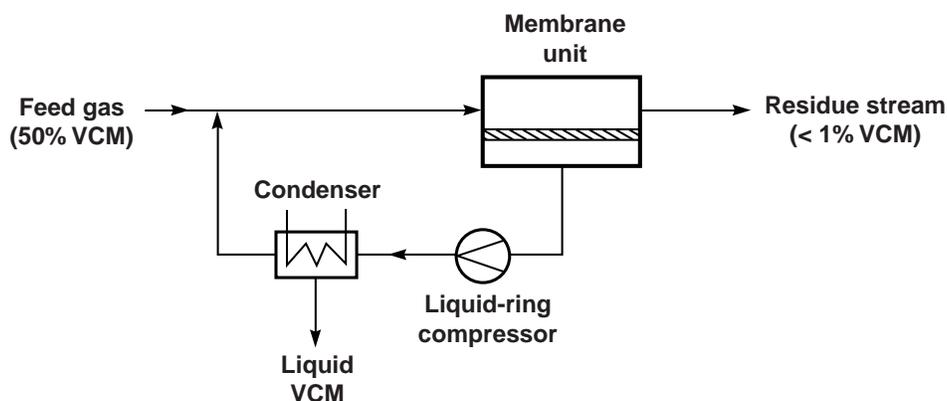


Figure 10. Recovery of VCM monomer in a polyvinyl chloride plant.

Feed gas containing VCM and air is sent to the membrane system. The VCM-enriched permeate from the membrane system is compressed in a liquid-ring compressor and cooled to liquefy the VCM. A liquid-ring compressor is used because of the flammable nature of vinyl chloride. The non-condensable gases are mixed with the feed gas and returned to the membrane section. The residue stream is sent to the incinerator, where the remaining VCM is destroyed before venting the inerts. VCM recovery is more than 99%. The first unit of this type was installed by MTR in 1992. Since then, about 40 similar systems have been installed.

Ethylene Recovery in Ethylene Oxide and Vinyl Acetate Manufacturing Plants

Ethylene oxide: Ethylene oxide is produced through the catalytic oxidation of ethylene with 99.6+% pure oxygen. Ethylene, oxygen and methane are fed into the reactor. Methane is added to moderate the reaction kinetics and keep the gas mixtures outside the explosive range. Ethylene oxide is produced, along with carbon dioxide and water as by-products. The mixture is sent to a water-based scrubber to recover the ethylene oxide. Carbon dioxide is then removed by absorption with hot potassium carbonate, fresh ethylene and oxygen are added to the unreacted gases and the mixture is recycled back to the reactor. Due to the presence of argon in the incoming oxygen and ethane in the incoming ethylene, a portion of the gases in the reactor loop must be purged to keep the concentration of these inerts under control.

The purge gas for a typical ethylene oxide plant contains approximately 20-30% ethylene; 10-12% argon; 1-10% carbon dioxide; 1-3% ethane; 50% methane; and 4-5% oxygen. This purge gas can be treated in a membrane-based recovery unit, as pictured in Figure 11. The purge gas enters the membrane system at approximately 20 bar and 30°C. Ethylene preferentially permeates the membrane, producing an ethylene-enriched permeate stream and an argon-enriched residue stream. The permeate stream is then recompressed back into the reactor loop via the reclaim compressor. As ethane also preferentially permeates the membrane, there is the potential for build-up of ethane in the system. However, this build-up is mitigated by two factors: the ethane concentration in polymer

grade ethylene is very low; and, as long as the recovery of ethylene is not too high (not greater than 90%), the remaining ethane will be removed from the reactor loop through the residue stream. Based on actual field data from operating units, no ethane buildup has been observed. The residue stream, which has been stripped of ethylene, is used in a boiler or incinerator.^(16,17)

The performance of a typical ethylene recovery unit is summarized in Table 3. The system cost was approximately \$550,000, resulting in a simple payback time of less than eight months.

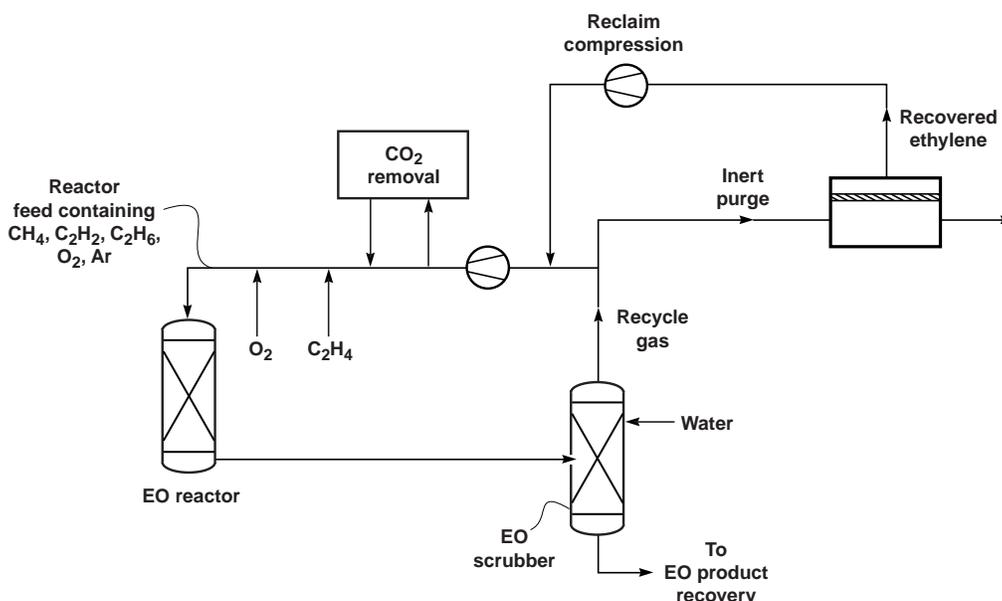


Figure 11. Schematic of the ethylene oxide plant ethylene recovery unit.

Table 3. Performance of a Typical Ethylene Oxide Plant Ethylene Recovery Unit.

Ethylene Recovery (lb/h)	290
Ethylene Recovery (%)	75
Methane Recovery (lb/h)	150
Value of Recovered Ethylene*	\$620,000/year
Value of Recovered Methane**	\$215,000/year
System Cost	\$550,000
Simple Payback (months)	< 8

* Based on \$500/ton

** Based on \$7.00/1,000 ft³

Vinyl acetate: A similar vent gas mixture is created in the production of vinyl acetate. Most vinyl acetate is produced by a catalytic vapor-phase reaction of ethylene and acetic acid in the presence of oxygen. The gases leaving the reactor are cooled, partially condensing the mixture, and the

condensed liquid is then purified in a downstream distillation section. The vapor from the condenser is sent to a carbon dioxide removal system, then returned to the reactor, where the unreacted gases are combined with the feed gases. In like manner to the ethylene oxide process, a purge stream must be taken from the reactor loop to remove argon, ethane and other impurities. The purge gas from vinyl acetate reactors contains a much higher concentration of ethylene (more than 65%), and the remaining components are carbon dioxide (20%), argon (5%) and methane (10%). The feed pressure and temperature are 10 bar and 35°C, respectively. Table 4 summarizes the performance of the ethylene recovery unit, which provides a payback period of less than nine months.

Table 4. Performance of a Typical Vinyl Acetate Plant Ethylene Recovery Unit.

Ethylene Recovery (lb/h)	460
Ethylene Recovery (%)	70
Value of Recovered Ethylene*	\$980,000
System Cost	\$700,000
Simple Payback (months)	< 9

* Based on \$500/ton

Natural Gas Processing/Fuel Gas Conditioning

Raw natural gas is often saturated with propane, butane, higher hydrocarbons and water. Separation of these components is necessary to prevent formation of hydrocarbon liquids and hydrates in the pipeline, as well as to control Btu content. In addition, their removal is desirable on economic grounds; the hydrocarbons have more value as recovered natural gas liquids (NGLs).

Membranes can be used to bring raw natural gas to pipeline quality by removing water and higher hydrocarbons. A simple, economical membrane system can lower the dew point of the gas by 80-120°F (30 to 50°C). The current alternative technology cools the gas using a refrigeration unit and separates the heavy hydrocarbons by condensation. Thus far, membrane systems have had difficulty replacing refrigeration for removing heavy hydrocarbons from large-volume gas streams, but a number of membrane units have been installed to treat gas used as on-site fuel for remote gas compressor engines.^(18,19)

Raw unprocessed natural gas is widely used to power field compressor engines and generator sets. Oftentimes this gas has a low octane rating because of the presence of propane and C₄₊ hydrocarbons in the gas. These components lead to pre-detonation and coking problems, requiring derating of the engines so that they can run smoothly. Engine and turbine manufacturers characterize the quality of natural gas in a number of ways, most commonly by calculating the methane number or Wobbe number of the gas. These numbers are equivalent to the octane rating used to characterize gasoline. Good gas has a methane number of greater than 65; a methane number of 40 or below can be used as engine fuel but will usually require derating of the engine. Another measure of gas quality is its Btu value. Below 600-700 Btu/scf, gas is considered very lean; above 1,200 Btu/scf, gas is normally too

rich to be used in standard gas-powered equipment. Finally, most engine manufacturers will have a limit on the hydrogen sulfide content of the gas.

The amount of gas used by field engines is usually in the 0.5 to 2.0 MMscfd range—too small to make treatment of the gas by refrigeration economical. As a consequence, many engine users are forced to live with the problem gas and the resulting low reliability and high maintenance costs.

A membrane-based fuel gas conditioning unit designed to upgrade raw gas used as engine fuel is illustrated in Figure 12. In this simple example, the gas to be treated was being used to power a field gas compressor engine. The raw gas was very rich, resulting in engine knocking, damage and frequent shutdown. A portion of the high-pressure compressed gas (450 psia) was diverted from the pipeline and passed across the surface of a rubbery membrane selectively permeable to the heavier components of the gas. Methane and ethane are retained by the membrane; propane, butane, C₅₊ hydrocarbons and the BTEX aromatics all preferentially permeate the membrane. The system removes 80% of the C₃₊ hydrocarbons, lowering the gas hydrocarbon dew point by 75°F.

As membrane-based fuel gas conditioning technology gains credibility, opportunities to compete with low-temperature condensation, or to provide membrane-augmented hybrid systems should open up.

Other Applications

The five categories of applications described above cover the bulk of the current membrane vapor/gas separation market. For various reasons, several environmental vent gas applications developed in the 1980s did not materialize commercially, but a number of smaller applications and new applications are currently under development. These are listed in Table 5, together with brief descriptions; more detailed discussions can be found in the cited references.

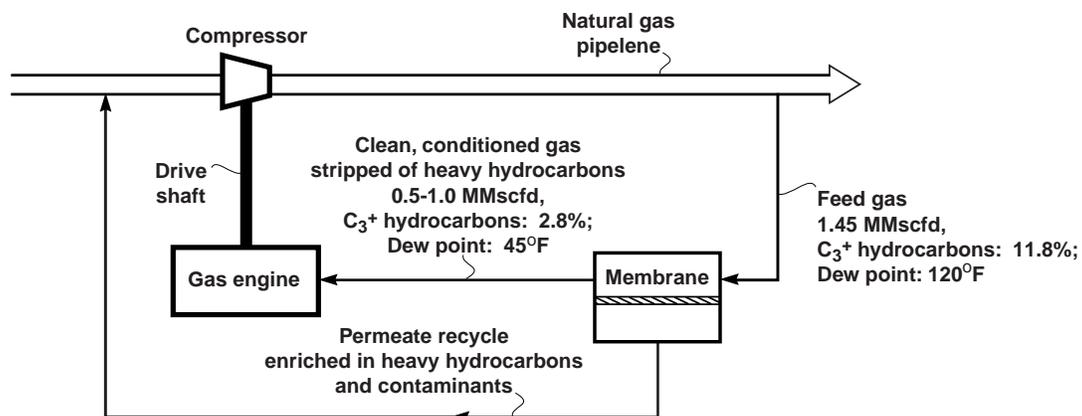


Figure 12. Flow diagram and shop photograph of a membrane fuel gas conditioning unit used for a field gas compressor engine. The membrane modules are contained in two horizontal pressure vessels. The unit can produce 0.5 to 1.0 MMscfd of clean gas.

Table 5. Minor and Developing Applications of Membrane Vapor/Gas Separation Technology.

Application	Separation	Description
Early Commercialization Efforts		
CFC, HCFC (Freon) from Refrigeration Vents and Other Process Streams.	CFC, HCFC/air (1-10%)	When the ozone hole in the atmosphere above the Antarctic was discovered, CFC and HCFC fluorocarbons (Freon [®]), widely used as industrial refrigerants, were progressively banned. For a few years a market existed to treat the fluorocarbon/air vents for these units, with approximately 50-100 small systems sold. With the phase-out of CFC and HCFC liquids, this market has disappeared. ⁽²⁰⁾
Semiconductor Plasma Cleaning Gas	C ₂ F ₆ /N ₂ -related separations, including SF ₆ /N ₂ , CF ₄ /N ₂	Vent gas from semiconductor plasma cleaning operations contains 0.5 to 1.0% C ₂ F ₆ . C ₂ F ₆ is a high-value chemical (\$30/lb) and an egregious global warmer (10,000 times worse than CO ₂). This is an interesting application because the best membranes to date are nitrogen-permeable/C ₂ F ₆ -rejecting membranes. Pilot systems have been demonstrated, but the market evaporated when the semiconductor industry switched to NF ₃ for plasma cleaning. ⁽²⁴⁻²⁶⁾
Pilot Plant or Small-Scale Commercial Development		
Chlorine Recovery From Chlor-alkali Plant Tail Gas	Cl ₂ /air (~20%)	Chlorine produced in chlor-alkali plants is liquefied by compression and cooling. A tail gas containing uncondensed chlorine and air is produced. Silicone rubber membranes can be used to recover the chlorine vapor in a condensation-membrane hybrid unit. Pilot plants for the process have been installed. ⁽²¹⁻²³⁾
Vacuum Pump Exhausts	Hydrocarbons, toluene, chlorinated solvents/air	A few systems sold. ^(29,30)
Separation of Volatile Organic Compounds (VOCs) from Effluent Air Streams	0.1 to 1.0 vol% toluene, hexane, chlorinated solvents, and the like from air	VOC recovery from VOC-containing air streams was a major driver for the early development of vapor separation membranes. However, in this low-concentration range, membranes were not able to compete with incineration, thermal oxidation, carbon adsorption, etc. A few systems have been sold, but the market is now largely abandoned by membrane companies. ^(3,27,28) If lower-cost, higher-permeance membranes are developed, this market may be revisited.
Significant Market Potential		
LPG Recovery in Refineries	C ₃₊ Hydrocarbons/CH ₄ , H ₂	Recovery of heavy hydrocarbons or liquefied petroleum gas (LPG) from refinery purge or fuel gas is significantly more profitable than using these components as waste fuel. If the gas contains hydrogen, it can also be recovered. This application is a long-standing area of research; pilot plants for the process are installed. This could become a significant market.

CONCLUSIONS

The first commercial membrane vapor separation systems were installed in 1988; four years later, about 20 systems had been installed, and to date (2006), more than 100 large units and several hundred smaller systems have been installed. Currently, the total membrane vapor separation equipment market is at least \$20 to 30 million/year, and growing and diversifying. Although these statistics are unlikely to excite most venture capitalists, the creation of a new market segment in the conservative world of chemical engineering is an unusual achievement. The modest but solid growth of market share for membranes over the last 15 years, and the opportunities for development of new product lines are optimistic indicators for a bright future.

REFERENCES

1. R.W. Baker and J.G. Wijmans, "Membrane Separation of Organic Vapors from Gas Streams," in *Polymeric Gas Separation Membranes*, D.R. Paul and Y.P. Yampolskii, Eds., CRC Press, Boca Raton, FL (1994).
2. K. Ohlrogge, J.B. Rockmiller, J. Wind and R.D. Behling, Engineering Aspects of the Plant Design to Separate Volatile Hydrocarbons by Membrane Vapor Separation, *Sep. Sci. and Technology* 28, 227 (1993).
3. R.W. Baker, J.H. Kaschemekat, and J.G. Wijmans, "Membrane Systems for Profitable VOC Recovery," *CHEMTECH* 26, 37, (July 1996).
4. K. Ohlrogge and K. Stürken, "The Separation of Organic Vapors from Gas Streams by Means of Membranes," *Membrane Technology*, S.P. Nunes and K-V. Peinemann (eds), J. Wiley, Chichester, UK (2001).
5. R.D. Behling, K. Ohlrogge, K-V. Peinemann and E. Kyburz, "The Separation of Hydrocarbon From Waste Vapor Streams," in *Membrane Separation in Chemical Engineering*, A.E. Fouda, J.D. Hazlett, T. Matsura and J. Johnson (Eds) AIChE Symposium Series Number 272, 85, 68 (1989).
6. I. Pinnau, Z. He, A.R. Da Costa, K.D. Amo, and R. Daniels, "Gas Separation using C₃₊-Hydrocarbon-Resistant Membranes," U.S. Patents 6,361,582 and 6,361,583 (March 2002).
7. J. Schultz and K.-V. Peinemann, "Membranes for Separation of Higher Hydrocarbons from Methane," *J. Memb. Sci.* 110, 37 (1996).
8. I. Pinnau, Z. He, T. Masuda and T. Sakaguchi, "Pure and Mixed-gas Permeation Properties of Poly(p-tert-butyl diphenylacetylene)," in *Advanced Materials for Membrane Separations* p. 167 ACS Symposium Series 876, I. Pinnau and B.D. Freeman (Eds.) American Chemical Society, Washington D.C. (2004).

9. A. Morisato, Z. He and I. Pinnau, "Mixed-Gas Properties and Physical Aging of Poly(4-methyl-2-pentyne)," in *Polymer Membranes for Gas and Vapor Separation: Chemistry and Materials Science*, ACS Symposium Series 733, B.D. Freeman and I. Pinnau (Eds.), ACS, Washington, DC (1999).
10. R.W. Baker, K.A. Lokhandwala, M.L. Jacobs, and D.E. Gottschlich, "Feedstock and Product Recovery from Reactor Vent Streams," *Chemical Engineering Progress* 96, 51 (December 2000).
11. J.G. Wijmans, "Process for Removing Condensable Components from Gas Streams," U.S. Patent 5,199,962 (April 6, 1993) and 5,089,033 (February 1992).
12. R.W. Baker, J.G. Wijmans, and J.H. Kaschemekat, "The Design of Membrane Vapor-Gas Separation Systems," *J. Memb. Sci.* 151, 55-62 (1998).
13. R.W. Baker and M. Jacobs, "Improve Monomer Recovery from Polyolefin Resin Degassing," *Hydrocarbon Processing* (March 1996).
14. K. Ohlrogge and J. Wind, "Method and Apparatus for reducing Emissions from Breather-lined Storage Tanks, U.S. Patent 6,059,856 (May 2000).
15. R.J. Lahiere, M.W. Hellums, J.G. Wijmans, and J. Kaschemekat, "Membrane Vapor Separation: Recovery of Vinyl Chloride Monomer from PVC Reactor Vents," *Ind. Eng. Chem. Res.* 32, 2236-2241 (1993).
16. R.W. Baker and D. Gottschlich, "Membrane Process and Apparatus for Argon Purging from Oxidation Reactors," U.S. Patent 6,018,060 (January 25, 2000).
17. M. Jacobs and B. Billing, "Achieving Ethylene Efficiency," *Hydrocarbon Engineering*, (August 2005).
18. R.W. Fenstermaker, Engine Performance Operating on Field Engine Gas as Engine Fuel, U.S. Patent 4,370,150 (January 1983).
19. K. Lokhandwala, A. Jariwala and R.W. Baker, "Only Raw Sour Gas Available for Engine Fuel," GPA Annual Meeting Proceedings (2006).
20. J.G. Wijmans and R.W. Baker, "Refrigeration Process with Purge and Recovery of Refrigerant," U.S. Patent 5,044,166 (September 3, 1991).
21. M-B Hägg, "Purification of Chlorine Gas with Membranes—An Integrated Process Solution for Magnesium Production," *Separation and Purification Technology* 21, 261 (2001).
22. I. Pinnau, K.A. Lokhandwala, P. Nguyen, L.G. Toy, and M.L. Jacobs, "Membrane Process for Treatment of Chlorine-Containing Gas Streams," U.S. Patent 5,538,535 (July 23, 1996).

23. K.A. Lokhandwala, S. Segelke, P. Nguyen, R.W. Baker, T.T. Su and I. Pinnau, "A Membrane Process to Recover Chlorine from Chloralkali Plant Tail Gas," *Ind. Eng. Chem. Res.* 38, 3606-3613 (1999).
24. J. G. Wijmans, Z. He, T. T. Su, R.W. Baker and I. Pinnau, "Recovery of Perfluoroethane from Chemical Deposition Operations in the Semiconductor Industry," *Separation and Purification Technology* 35 , 203-213 (2004).
25. Y.-E. Li, J.E. Paganessi, D. Vassallo and G.N. Flemming, Recovery and System for Separation and Recovery of Perfluoro Compound Gases, U.S. Patents 5,785,741 (July 28, 1998; 5,858,065 (January 12, 1999); and 5,919,285 (July 1999).
26. I. Pinnau, J.G. Wijmans, Z. He, S. Goakey, and R.W. Baker, "Process for Recovering Semiconductor Industry Cleaning Compounds," U.S. Patent 5,779,763 (July 14, 1998).
27. J.G. Wijmans, H.D. Kamaruddin, S.V. Segelke, M. Wessling, and R.W. Baker, "Removal of Dissolved VOCs from Water with an Air Stripper/Membrane Vapor Separation System," *Sep. Sci. and Tech.* 32 (14), 2267-2287 (1997).
28. X. Wang, R. Daniels, and R.W. Baker, "Recovery of VOCs from High-Volume Low-Concentration Air Streams," *AIChE Journal* 47, 1094 (2001).
29. R.W. Baker and J. Kaschemekat, "Membrane Process for Treating Pump Exhausts," U.S. Patent 5,127,926 (July 7, 1992).
30. G. Hauk, Device for Continuously Purifying the Waste Gas from a Vacuum Unit, U.S. Patent 5,194,074 (March 1993).