5 Membrane Applications in Oil Refining and Petrochemical Industry

A. Brunetti, G. Barbieri, and Enrico Drioli

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a crucial role for the implementation of this strategy. The growth of membrane engineering has been significant in the last few years, and various large unit operations of process engineering have already been redesigned as a membrane unit. With their intrinsic characteristics of efficiency and operational simplicity, high selectivity and permeability for the transport of specific components, compatibility between different membrane operations in integrated systems, low energetic requirement, good stability under operating conditions and environment compatibility, easy control and scale-up, and large operational flexibility, membrane operations are an interesting answer for the rationalization of chemical productions. Membrane reactors (MRs), membrane gas separation (GS), pervaporation (PV), membrane emulsifiers, membrane distillation, membrane crystallizers, membrane contactors, and membrane strippers and scrubbers, in their various configurations and functionalities, are growing in parallel to the molecular separations created with pressure-driven membrane operations. There are already interesting cases where the potentialities of these technologies have been explored. The most important is the success of pressure-driven membrane operations in water and brackish water desalination and in water reuse, where reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) might be considered as dominant technologies. The latest development of immersed bioreactors in the treatment of municipal wastewater is another important example.

There are various applications of membranes in the petrochemical industry and various types of operations that are considered for these applications (Table 5.1). The most important application is membrane GS; this is particularly relevant for hydrogen recovery, since it is also considered as a suitable technology for the recovery of olefins, hydrocarbon separations, natural gas processing, etc. Important potential applications are also covered by MRs, specifically usable for dehydrogenation or hydrogenations of hydrocarbons,5,6 for oligomerizations6,5 and isomerizations,8,9 as well as for hydrogen production in precombustion capture.10 In this latter, many studies report the advantages offered by using MRs. This process based on the continuous removal of hydrogen from the reaction volume by means of a hydrogen-selective membrane allows the production of a retentate stream concentrated and compressed in CO2 and of another stream rich or pure in hydrogen, in dependence on the membrane used in the reactor.11 The separation of liquid organic mixtures, as well as the desulfurization of gasoline, is typically performed in PV processes. The latter are also used for isomer separations such as with mixed xylenes. Another way to separate organic–organic mixtures is by organic solvent nanofiltration (OSN), usually used to separate aromatic and aliphatic hydrocarbons, alcohols, ketones, and esters. A large new application of this technology is in the refining of lubricants with the dewaxing process. Recently, membrane contactors have been receiving a great deal of attention as alternative technology to the other membrane technologies for their application in CO2 separation from the flue gas stream as well as for air purification. The purification of the wastewater produced in the petrochemical industry can be advantageously performed by pressure-driven membrane operations such as MF, UF, and RO and by membrane bioreactors (MBRs) also in combined configurations.

The main aim of this chapter is to show the main applications of membrane technology in the petrochemical industry and the related current research trends, focusing on the impact that membrane technology can have on the process. In addition, a case study is provided to illustrate the analysis of a membrane process in terms of process intensification, showing the advantages that this type of design philosophy can transfer to an important industrial application.

### 5.2 MEMBRANE GAS SEPARATION

In 1950, Weller and Steiner12 considered membrane processes as feasible for the separation of hydrogen from hydrogenation tail gas, enrichment of refinery gas, and air separation. However, commercial membranes capable of performing these separations became available only in 1970.13

| TABLE 5.1 Main Membrane Operations and Their Applications in the Petrochemical Industry |
|------------------------------|---------------------------------|
| **Membrane gas separation**  | Hydrogen recovery in refineries |
|                               | Ammonia purge gas               |
| **Membrane reactors**        | Hydrogen production             |
|                             | Alkane dehydrogenation          |
|                             | Alkene hydrogenation            |
| **Pervaporation processes**  | Oxidations                      |
|                             | Dehydroisomerization of butane  |
|                             | Benzene hydroxylation to phenol |
| **Organic solvent separation** | Gasoline desulfurization      |
| **Membrane contactors**      | Separation of water from organic solutions |
|                             | Isomers separations             |
| **Membrane bioreactors**     | Separation of light hydrocarbons |
|                             | VOCs removal from water         |
|                             | Organic–organic mixtures separations |
| **Membrane bioreactors**     | Removal of VOCs from air       |
|                             | Flue gas treatment              |
| **Reversed osmosis, microfiltration, ultrafiltration, etc.** | Wastewater treatment |

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In 1980, Permea, with its hydrogen-separating Prism membrane, launched the first large industrial application of GS membranes.\textsuperscript{13,14} Since then, membrane-based operations, substituting or to be integrated with the traditional ones, have had a rapid growth, with many companies, such as Cynara-NATCO, UOP Separex, GMS, Generon, Praxair, Air Products, and Ube, involved in this field.\textsuperscript{15–17}

A list of the main industrial applications of membrane technology in GS is given in Table 5.2, along with the membrane materials used and the status of membrane technology updated at 2010.

### 5.2.1 Hydrogen Recovery

Over 50 million tons of hydrogen is produced annually worldwide for use in synthesis gas, ammonia, and methanol production. The most common method of making large-scale hydrogen is steam methane reforming where $H_2$ is separated from $CO_2$. Other sources of low-cost hydrogen are refinery and chemical industry waste gases. Hydrogen demands are growing steadily partly due to the increased use of hydrotreating (to remove sulfur from gasoline and diesel fuels to the new lower standards) and hydrocracking (conversion of heavy hydrocarbons to light hydrocarbons). The unreacted hydrogen from these processes is generally at high pressure, and membrane processes are ideal for their recovery. The first widespread commercial application of membranes in GS was the separation of the hydrogen in the ammonia purge stream, by using Permea Prism™ systems. Nowadays, hydrogen recovery is applicable to several processes and can be divided into three main categories:

- Hydrogen recovery from ammonia purge streams
- Syngas ratio adjustment
- Hydrogen recovery in refineries

In the ammonia process, the purge stream, almost clean and free of condensable vapors, consists of a mixture of hydrogen, nitrogen, methane, and argon, delivered at a high pressure (136 bars). It is, thus, the ideal application for membrane
technology, since hydrogen is highly permeable with respect to the other gases and the stream already provides the necessary driving force for promoting the permeation. Actually, Permea, Inc. (now owned by Air Products & Chemicals, Inc.) designed a two-step membrane process for this separation.

Similar membrane systems are already applied also for syngas ratio adjustment (H₂/CO ratio) of the streams coming out of reformers. Generally, membranes are used for stripping hydrogen out of the syngas in order to reduce the H₂/CO ratio. At 2011, several hundred hydrogen separation plants have been installed.¹⁸

The demand for hydrogen recovery in refineries is rapidly increasing also owing to environmental regulations. The hydrogen content in the various refinery purges and off-gases ranges between 30% and 80%, mixed with light hydrocarbons (C₅−C₆); 90%−95% hydrogen purity is required to recycle it to a process unit. A typical refinery operation is the separation of the hydrogen contained in the stream coming out from the hydrocracker. The membranes can be used alone or together with an absorber system, at a reduced capital cost and better process efficiency. In 2003, it was reported that more than 400 hydrogen permeators were installed worldwide while ~100 were operated in refineries. As there are more than 500 refineries in the world, it is clear that the potential market for these types of membrane application is far from saturated.

The main problems, related to the current limited application of membrane technology, are membrane plasticization by strongly adsorbing components and the condensation of light hydrocarbons on the membrane surface, which strongly affect the membrane performance and durability. The development of new membrane materials more resistant to high-hydrocarbon partial pressure and the introduction of a more efficient pretreatment stage able to reduce pollutant content will rapidly expand this technology.¹⁵ At 2011, the Prism system (using polysulfone hollow fibers with a thin silicone film on it) is dominant on the market for this kind of separation, showing interesting selectivities.¹⁹

5.2.2 Natural Gas Membrane Processing

Natural gas is mainly (from 75% to 90%) composed of methane. It also contains undesired components such as acid gaseous impurities like carbon dioxide or hydrogen sulfide that should be removed to prevent pipeline corrosion; condensable compounds (higher C₅+ hydrocarbons and water) that must be removed in order to prevent condensation troubles, hydrate formation, or corrosion when flowing natural gas in pipelines; and inert gases, such as nitrogen, which lower the calorific value of natural gas.¹⁹

Removal of carbon dioxide (natural gas sweetening) increases the calorific value and transportability of the natural gas stream. Carbon dioxide content in the natural gas obtained from the gas or oil well can vary from 4% to 50%.¹⁹ It has to be reduced down to ca. 2%−5%. This goal is typically achieved by means of absorption with an aqueous alkanolamine solution that has as main drawback the tendency to corrode equipment and to lose amine properties by increases in degradation. Membrane GS systems are an alternative technology for the separation of carbon dioxide from natural gas, particularly for offshore applications,²⁰ since it offers several strong advantages over conventional solvent columns: compactness (which makes membranes particularly well suited for offshore operations), low investment costs, and low maintenance costs, at least with single-stage configurations that do not operate compressors. The current level of CO₂/CH₄ selectivity of commercial membranes is not so high (12−25 in field conditions); therefore, partial losses of treated methane in the low-pressure permeate occur. These losses vary between 10% and 25% on a single-stage configuration and can be from 33% to 80% of the whole operating cost of a membrane unit.¹⁹ Process optimization calculation led to the introduction of two-stage configurations, where at the first stage, the permeate was pressurized and fed to a second permeation stage, recovering a part of the methane. This generally leads to a significant improvement in overall methane recovery (higher than 95%), through introducing extra cost due to the stage compression unit.¹⁹,²¹

Figure 5.1 shows the block diagrams of two typical carbon dioxide membrane systems that treat natural gas with low CO₂ concentration, as proposed by Baker and Lokhandwala.²¹ Both systems are designed to treat a feed stream with 10% carbon dioxide. One-stage systems are preferred for very small gas flows. In such plants, methane loss in the permeate is often 10%−15%. If there is no fuel use for this gas, it must be flared, which is a significant revenue loss. As the flow rate of the natural gas stream increases, the methane loss increases; therefore, usually, the permeate gas

![FIGURE 5.1 Flow scheme of (a) one-stage and (b) two-stage membrane separation systems to remove CO₂ from natural gas.](image-url)
is recompressed and passed through a second membrane stage, which reduces the methane loss to a low percentage.

Membrane systems can also be integrated into traditional units. The design of a hybrid membrane separation system is determined by several considerations, such as membrane permeance and selectivity, CO₂ concentration of the inlet gas and the target required, the gas value (per ca. 30 N m⁻³, the price of gas in 2007 was $6–7 in the United States, whereas in Nigeria, which is far from being well-developed gas market, it may be as low as $0.50 if the gas can be used at all), and the location of the plant (on an offshore platform, the weight, footprint, and simplicity of operation are critical; onshore, the total cost is more significant).²²

Several natural gas reserves are considered subquality because of the high nitrogen content, with gas pipeline specifications fixing a 4% limit.²³ Until now, cryogenic distillation is used for this separation; however, membrane technology could be used here in combination with a cryogenic plant (Figure 5.2). The feed gas, containing 15% nitrogen, is separated by a membrane into two streams: a retentate stream containing 30% nitrogen to be sent to the cryogenic plant and a permeate stream containing 6% nitrogen to be sent to the product pipeline gas. The membrane unit reduces the volume of the gas to be treated by the cryogenic unit by more than half. Simultaneously, the concentrations of water, C₅+ hydrocarbons, and carbon dioxide are brought to very low levels, because these components also preferentially permeate the membrane. Removal of these components prior to cryogenic condensation is required to avoid freezing in the plant. The savings produced by using a smaller, simpler cryogenic plant more than offset the cost of the membrane unit.²⁴

Since the volumes of carbon dioxide are very large (from 140 to 280 N m⁻³ per extracted barrel (reference 29 in Ref. [25]), it is necessary to separate carbon dioxide from the hydrocarbon gaseous phase in order to have it recycled to the reservoir (after pressurization). A typical EOR process starts with >50% CO₂ and high pressure (up to 140 bar); the CO₂ content increases significantly over time. The CO₂ from the CO₂-enriched natural gas is recovered using membrane systems and pressurized and reinjected in the EOR wells. The first membrane plant for this application was installed by NATCO (former Cynara). The plant was designed to reduce CO₂ concentration from 45% down to 28% CO₂ for processing 60,000 N m⁻³/h of gas.²⁵ This plant was later expanded and is processing 120,000 N m⁻³/h of gas, decreasing CO₂ concentration from 80% to less than 10%.

5.2.4 Vapor/Gas Separation

The removal of organic solvents from gas streams has been widely developed at the industrial level. The main industrial applications of vapor/gas membrane separation are²⁶

- Polyolefin plant resin degassing
- Gasoline vapor recovery systems at large terminals
- Polyvinyl chloride manufacturing vent gas
- Ethylene recovery
- Natural gas processing/fuel gas conditioning

The recovery of hydrocarbon monomers from ethylene in polyethylene and polypropylene plants is actually the largest application of vapor separation membranes.²⁶ After the production of the polyolefin resin, there are unreacted monomer and hydrocarbon solvents dissolved in the resin powder that must be separated in order to reuse the polymer. The traditional application involves stripping with hot nitrogen in a column known as a degassing bin. The values of nitrogen and monomer are both high; therefore, the recovery and reuse of these components are of great interest. For this purpose, a membrane operation is profitably used. It consists of two membrane units in series where the off-gas

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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 recycled directly to the degassing bin without further treatment. The residue gas is passed to a second membrane unit to upgrade the nitrogen to better than 99% purity. During the last 10 years, almost 50 of these systems have been installed around the world.

In the polymerization of polyvinyl chloride, side reactions generate unwanted gas, and some small amounts of air leak into the reactors. These inert gases must be vented from the process. However, the vented gas stream, although small, may contain several hundred thousand dollars of monomer values, owing to the high volatility of the vinyl chloride monomer (VCM). 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. The noncondensable gases are mixed with the feed gas and returned to the membrane section. VCM recovery is more than 99% (Figure 5.3). The first unit of this type was installed by Membrane Technology and Research, Inc. (MTR) in 1992. Since then, about 40 similar systems have been installed.

Gasoline vapor recovery has become an important field for membrane application in the last few years. Several hundred retail gasoline stations, in fact, have installed small membrane systems for the recovery of the hydrocarbon vapors during the transfer of hydrocarbons from tankers to holding tanks and then to trucks. GKSS (Helmholtz-Zentrum Geesthacht Zentrum für Material- und Küstenforschung GmbH) licenses have installed about 30 gasoline vapor recovery systems at fuel transfer terminals, mostly in Europe (www.hzg.de). MTR and OPW Fuelling Components (OPW, a Dover Company) have developed a membrane vapor recovery system for the fuel storage tanks of retail gasoline stations. The OPW Vaporsaver™ system, fitted with MTR’s membranes, reduces hydrocarbon emissions by 95%–99% and pays for itself with the value of the recovered gasoline (www.mtrinc.com).

Ethylene oxide is produced through the catalytic oxidation of ethylene with 99.6% pure oxygen; carbon dioxide and water are by-products. The mixture of products 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. Owing 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 inert gases 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. A similar vent gas mixture is created in the production of vinyl acetate. This purge gas can be treated in a membrane-based recovery unit: ethylene preferentially permeates the membrane, producing an ethylene-enriched permeate stream and an argon-enriched residue stream.

### 5.2.5 Olefin/Paraffin Separation

Olefins such as ethylene and propylene are produced in the petrochemical industry by steam cracking of paraffins, followed by repeated compression and distillation to separate the complex vapor mixtures. Ethylene is used to create ethylene oxide, and polyethylene, while propylene is the second highest volume petrochemical feedstock after ethylene and is used for the production of a wide variety of polymers.

Conventionally, the separation of olefins is performed with highly energy-intensive cryogenic distillation in a single- or double-column process with 150–200 trays at temperatures between 233 and 183 K and pressures ranging from 16 to 20 bar. For this reason, several efforts have been made to find an alternative solution, and various researches have been done on the extractive distillation, pressure swing adsorption (PSA) and thermal swing adsorption, etc. Membrane technologies clearly present themselves as an attractive alternative to reduce the large capital and operating costs of the current cryogenic distillation for olefin/paraffin separation, showing a fourfold decrease in operating cost compared to distillation units. The use of polymeric membranes including various materials such as glassy, cellulosic, and rubbery polymers has been studied rather extensively. On the other hand, carbon molecular sieve (CMS) membranes showed promising olefin/paraffin separation compared with polymers, but their development is rather new, and many issues have still to be faced. The last and most important type of membranes for olefin/paraffin separation is facilitated transport.
membranes where olefins are capable of forming reversible chemical bonds with transition metal ions incorporated in the membrane due to the specific interaction between the olefin’s hybrid molecular orbitals and the metal’s atomic orbitals. However, the separation is difficult because of the similar molecular sizes and condensabilities of the components, as well as the challenge of operating the membranes in a hydrocarbon-rich environment under pressure. Thus, the need remains for the identification of membranes able to maintain adequate performance under the conditions of exposure to organic vapors and particularly C$_3$+ hydrocarbons that are common in refineries, chemical plants, or gas fields. At present, sulfur poisoning is the major problem that makes Ag+ containing membranes unfit for industrial use. The functionalization of polyimides is under study for this application.\(^{33}\)

5.2.6 Air Separation

Traditionally, the air separation is done by cryogenic distillation or, alternatively, by adsorption processes.\(^{34}\) Polymeric air separation membranes are by far the most accepted commercial membrane GS application and are used exclusively to generate nitrogen gas of low purities on a small scale and in remote locations. The greater part of the membranes in use is oxygen selective; therefore, the nitrogen-rich stream is recovered in the high-pressure side, whereas an O$_2$-enriched stream is obtained as permeate at a low pressure. Today, nitrogen separation by membrane systems is the largest GS process in use. Membrane selectivity does not need to be high in order to produce a relatively pure nitrogen stream; thus, membrane systems became the dominant technology instead of PSA or cryogenic distillation. At 2011, thousands of compact on-site membrane systems producing nitrogen gas are installed in the offshore and petrochemical industry. Air Products, Norway, has delivered more than 670 PRISM\(^{36}\) systems producing N$_2$ for different ship applications and more than 160 PRISM systems for offshore installations.\(^{35}\) In December 2006, Air Products started with another PRISM production plant in Missouri (United States).\(^{36}\) Another new air separation unit with a capacity of 550 ton/day of oxygen was installed by Air Liquide in Dalian (China).\(^{37}\) In Japan, Ube Industries\(^{38}\) is increasing the production of polyimide hollow fibers for nitrogen separation to introduce a number of ethanol refining plants, mainly in the United States and Europe, driven by the rapid increase in the demand for bioethanol as an additive for oil products.

Membrane GS systems are used in some rare instances for the production of oxygen-enriched air (OEA) with oxygen contents less than 30% O$_2$. For this reason, membranes of quite low selectivity (3–5) and higher oxygen flux are preferred. However, depending on the quality of the oxygen to be obtained, the separation process can be developed in one or two stages (Figure 5.4). However, many studies are focused on new membrane materials exhibiting both high selectivity and high fluxes in order to develop the production of pure oxygen in only one stage.

5.2.6.1 Air Drying

The removal of water vapors from atmospheric air is commercially practiced by the use of refrigeration or adsorption methods. These processes are not energy efficient as a substantial part of the energy is consumed in condensing water vapors to liquid water. In some cases, adsorbents are used to capture water from air and are very effective, especially for the production of very dry air. However, they need a regeneration step (by heat, vacuum, or sweep) to remove adsorbed water. Membrane systems are very attractive for air drying applications since almost all the polymers have higher water permeability than air permeability, even though to make a membrane air drying system with low air loss, the selectivity of the membrane in the module should be >1000. Various commercial products use either a glassy polymer, like polysulfone and polyimide, or ionomers that are fluorine-containing polymer membranes. In these membrane systems, wet air is fed on one side of the membrane, and the water vapors permeate through it retaining dry air in the retentate. Air drying membrane modules are produced by the major membrane manufacturing companies such as Air Products, Air Liquide, Ube, and Asahi Glass. However, most of the air drying business is handled by other equipment manufacturers (OEMs). Commercial membrane modules can handle flows from 0.1 to 2.3 m$^3$/min. Membrane systems are capable of supplying oil and particulate free, dry compressed air to a dew point as low as −40°F (−40°C) at air pressure of 275–2050 kPa (40–300 psig).\(^{39}\)

5.2.7 CO₂ Capture

Today, coal-fired power plants all over the world emit more than 2 billion tons of CO₂ per year. The regulation of the carbon dioxide emissions implies the development of specific CO₂ capture technologies that can be retrofitted to power plants as well as designed into new plants with the goal of achieving 90% CO₂ capture, limiting the increase in cost of electricity to no more than 35%. Therefore, the recovery of CO₂ from large emission sources is a formidable technological and scientific challenge, which has received considerable attention for several years. Currently, the main strategies for carbon dioxide capture in a fossil fuel combustion process are as follows:

- **Oxy-fuel combustion**: This option consists in performing the oxygen/nitrogen separation on the oxidant stream, so that a CO₂/H₂O mixture is produced through the combustion process.

- **Precombustion capture**: This solution is developed in two phases: (1) the conversion of the fuel in a mixture of H₂ and CO (syngas mixture) through, for example, partial oxidation, steam reforming, or autothermal reforming of hydrocarbons, followed by water–gas shift (WGS), and (2) the separation of CO₂ (at 30%–35%) from the H₂ that is then fed as clean fuel to turbines. In these cases, the CO₂ separation could happen at very high pressures (up to 80 bar of pressure difference) and high temperatures (300°C–700°C).

- **Postcombustion capture**: In this case, the CO₂ is separated from the flue gas emitted after the combustion of fossil fuels (from a standard gas turbine combined cycle or a coal-fired steam power plant). CO₂ separation is realized at relatively low temperatures, from a gaseous stream at atmospheric pressure, and with low CO₂ concentration (ca. 5%–25% when air is used during combustion). SO₂, NO₂, and O₂ may also be present in small amounts.

The postcombustion process is by far the most challenging since a diluted, low pressure, hot and wet CO₂/N₂ mixture has to be treated. Nevertheless, it also corresponds to the most widely applied option in terms of industrial sectors (e.g., power, kiln, and steel production). Moreover, it shows the essential advantage of being compatible with a retrofit strategy (i.e., an already existing installation can be, in principle, subject to this type of adaptation). The conventional separation processes for CO₂ separation are absorption (with amines), adsorption (with porous solids with high adsorbing properties such as zeolite or active carbon), and cryogenic separation.

Even though amine absorption is the most common technology for postcombustion capture, its use is by far the best available technology owing to the high energetic cost (in the range 4–6 GJ/ton CO₂ recovered) related, in particular, to the significant energy consumption in the regeneration step. Furthermore, this option requires large-scale equipment for the CO₂ removal and handling of chemicals. Membranes are most often listed as potential candidates for their application in postcombustion capture. However, the main problem related to their limited application is the low CO₂ concentration and pressure of the flue gas, which requires the use of membranes with high selectivities (ca. 100) to satisfy the specification delivered by the [International Energy Agency](https://www.iea.org), that is, a CO₂ recovery of 80%, with purity of at least 80%. The commercial membranes (CO₂/CH₄ selectivity ca. 50) currently used to separate CO₂ from natural gas at high pressures are not suited for one-stage operation, implying a large membrane area and high compression costs.

In 2010, Brunetti et al. introduced some general guidelines to drive the application of membrane GS technology rightly as a suitable operation for CO₂ capture from flue gas emissions. Considering as case study a flue gas stream containing 13% of CO₂, some general maps of CO₂ recovery versus CO₂ purity have been introduced, taking into account the membrane characteristics, the flue gas conditions, and the desired output to be obtained, as a useful tool for an immediate and preliminary analysis on the membrane technology suitability for CO₂ separation from flue gas.

The results showed that, with currently available membranes (selectivity up to 50), it is not possible to obtain, simultaneously, the desired CO₂ recovery and purity (80% CO₂ in the permeate stream). In the context of meeting this target, the operating pressure ratio more than selectivity proved to play a fundamental role. In fact, with a selectivity of 100 (value already reached in the lab by some membrane materials), shifting the pressure ratio from 10 to 20 or 50, the CO₂ recovery passes from 22% to more than 60% or 80%, respectively. A high-pressure ratio is necessary also when many selective (100–150) membranes are operated (Figure 5.5).

5.2.8 Traditional Technologies for Separation of Gases

The traditional technologies for the separation of gases at commercial scale are cryogenic distillation and absorption. Cryogenic separations are universally used for the large-scale separation of atmospheric gases. It requires the liquefaction of the gases that are thus distilled at cryogenic temperatures to separate the gaseous mixture into its components. Absorption technologies are well established for the scrubbing of carbon dioxide and removal of water from natural gases. In gas absorption process, one or more components of the gas mixture are preferably absorbed in a chemical or physical solvent in a gas–liquid contacting device. The separation of the nonabsorbing/nonreacting gases from the gas mixture is thus achieved. Both these methods are complex and capital intensive but cost competitive. The adsorption process consists in the selective adsorption of gaseous species onto the high surface area of solid particles to contact gas mixture where one component of the gas mixture adsorbs, leaving others behind. The main disadvantage of
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this technology is of being a cyclic process; therefore, for continuous separation of gases, one needs to use more than one adsorbent bed. This is due to the required regeneration stage after saturation (or breakthrough). Adsorbent processes are best suited to produce high purity gases, especially for the removal of trace gas impurities from a gas mixture.

Today, membrane technology for GS is a well-consolidated technique, in various cases competitive with traditional operations. Membrane GS processes are simple and operate at a steady state, and they offer low capital costs, low energy requirements, and high modularity.

Gas mixture is fed on one side of the membrane; one or more components of the gas mixture preferentially permeate through the membrane, retaining the rest of the gaseous stream in the retentate. The driving force required for promoting the permeation is achieved either by compressing the feed gas or by using a vacuum on the permeate side. Usually a one-stage process is not sufficient to produce high purity gases. Multistage GS\(^\text{45}\) and membrane hybrid processes\(^\text{46}\) have been developed to produce high purity gases using membrane systems.

The greatest asset to membrane separation is simplicity. And it makes them very attractive in applications where product demand is not constant. Whereas PSA requires the equipment for swinging pressure, cryogenic distillation must endure extreme temperatures, and absorption requires huge amount of sorbent, the only equipment necessary for GS is the membrane and fans. There are almost no moving parts, and the construction is fairly simple. The gaseous stream to be separated generally requires a compression, but this is much smaller than that necessary for PSA.

Actually, the major drawback of the membrane operation concerns just the low selectivity of some membrane materials and a limitation on the suitable operating conditions. A membrane to be useful for H\(_2\) separation from off-gas streams as well as for CO\(_2\) capture should possess a number of properties, such as high permeability, high selectivity, thermally and chemically resistance, plasticization resistance, aging resistance, cost-effective, and ability to be cheaply manufactured into membrane modules. More details on the comparison among these technologies for GS and on the guidelines for the choice more appropriate for a set separation are reported in Section 5.7.

5.3 MEMBRANE REACTORS

In MRs, the membranes are coupled to a chemical reaction carried out in the same unit. The membranes can have the sole function of separating one of the end products, shifting the reaction toward further conversion or also a catalytic function. In most of the applications, the final result is an improvement in productivity. Depending on the type of reaction, the membrane can be organic or inorganic. Organic polymer membranes have a quite limited range of applications mainly consistent in some area of homogeneous catalysis or in bioreactors. Most of the applications in the petrochemical industry foresee harsh conditions, in some cases, accompanied by high temperature, which definitely favors the use of inorganic membranes such as metal, ceramics, and zeolites. Some promising applications using inorganic membranes include dehydrogenation, hydrogenation, and oxidation reactions such as the formation of butadiene from butane by dehydrogenation, styrene production from dehydrogenation of ethyl benzene, dehydrogenation of ethane to ethene, steam reforming, WGS reaction, and oxidative coupling of methane.\(^\text{47}\)

5.3.1 PRECOMBUSTION CAPTURE BY MEANS OF INORGANIC MEMBRANE REACTORS

The precombustion process is one of the technological solutions for allowing CO\(_2\) capture from power plant emissions. It is usually developed in two phases: (1) the conversion of the fuel into a mixture of H\(_2\) and CO (syngas mixture) through, for example, partial oxidation, steam reforming, or autothermal reforming of hydrocarbons, followed by water-gas shift, and (2) the separation of CO\(_2\) (at 30%–35%) from the H\(_2\) that is then fed as clean fuel to the turbines. In these cases, the CO\(_2\) separation could happen at very high pressures (up to 80 bar of pressure difference) and high temperatures.

![FIGURE 5.5 CO\(_2\) permeate purity versus recovery index for pressure ratio of (a) 10 and (b) 50 at different CO\(_2\)/N\(_2\) ideal selectivity from 30 to 300. (Reprinted from J. Membr. Sci., 359, Brunetti, A., Scura, F., Barbieri, G., and Drioli, E., Membrane technologies for CO\(_2\) separation, 115–125, Copyright (2010), with permission from Elsevier.)](image-url)
(300°C–700°C). An alternative solution to traditional technologies is MRs. These devices, able to carry out the reaction and the separation in the same unit once integrated in the power plant, can replace the traditional unit, reducing the number of the stages required for fuel conversion and H₂ separation.

If we consider that, at present, global hydrogen production mainly relies on processes that extract hydrogen from fossil fuel feedstock and, in particular, 96% hydrogen is directly produced from fossil fuels and about 4% is produced indirectly by using electricity generated through them, the impact that this technology can have at the industrial level can be easily figured out.

The MR can be used directly in the conversion of the fuel by carrying out reactions such as steam reforming of partial oxidations or can be placed at the outlet of the reactor for fuel conversion. The stream coming out from a reformer or a coal gasification plant contains around 50% hydrogen (on a dry basis) that must be recovered and between 40% and 45% CO that, usually, is reduced in an upgrading stage, producing more hydrogen at the same time. In traditional applications (Figure 5.6), the upgrading stage is, traditionally, a multi-stage CO-shift process based on a series of catalytic reactors and a separation unit for separating the produced hydrogen from the rest of the stream.

MR use allows this reaction and separation stages to be reduced, obtaining, in the meantime, better performances than traditional operations. In addition, the reaction volume required by the MR is significantly lower than the one required by the whole traditional system. This means the possibility of having an intensified process with a reduced plant size and higher yield. The traditional process can thus be redesigned as more compact and efficient (Figure 5.7). The integrated membrane system can be made up of fewer reaction/separation units than the conventional one. A first MR can be used for carrying out the reforming of the light hydrocarbons and another one for the WGS reaction. The separation stage is avoided, since the hydrogen stream coming out of the MR has already a high purity level. Obviously, the H₂ purity level is strictly determined by the membrane type used in both MRs. Actually, membranes can be distinguished by their selectivity, which can be infinite or finite. The first ones, traditionally Pd based, allow a pure hydrogen stream to be obtained, whereas the others provide a hydrogen-rich stream with a variable purity. If the recovered H₂ stream does not have the purity required, the latter can be increased by adding another purification unit on the basis of the final use of the H₂ stream. Selective CO oxidation is known as an interesting and economical approach for CO removal from H₂-rich gas streams. Also in this field, new studies proposed in the literature have demonstrated how the use of an MR can improve the process by increasing CO conversion as well as the purity of the hydrogen stream. In this context, membrane engineering plays a fundamental role in the integration of these units into a single plant and, at the same time, in the definition of the knowledge necessary to drive the process by maximizing the gains both in terms of efficiency and plant size reduction. The synergic effects offered by MRs through combining reaction and separation in the same unit, their simplicity, and the possibility of advanced levels of automation and control offer an attractive opportunity to redesign industrial processes.
5.3.2 Benzene Hydroxylation to Phenol

One of the important processes in the petrochemical industry is the production of phenol. Phenol is an important raw material for the synthesis of petrochemicals, agrochemicals, and plastics. Examples of employment of phenol as an intermediate are production of bisphenol A, phenolic resins, caprolactam, alkyl phenols, aniline, and other useful chemicals. Current worldwide capacity for phenol production is nearly 7 million metric tons per year. More than the 95% of phenol is produced by the common industrial process known as Hock or cumene process involving three successive reaction steps:

- Benzene alkylation to cumene via propylene
- Cumene oxidation to cumene hydroperoxide (CHP)
- CHP cleavage into phenol and acetone

The rest is produced via toluene oxidation.

It requires high energy consumption and produces an equimolar amount of acetone as a by-product. In this process, the yield of phenol, based on the amount of benzene initially used, is less than 5%. Thus, in the last few years, many studies have focused attention on the development of a new way to produce phenol directly from benzene. Direct hydroxylation of benzene to phenol using oxidant such as H₂O₂ and N₂O has been studied, even though encouraging results have been reported. Among the various techniques, the most promising results were achieved using N₂O as oxidant (AlphOx™ process), but the high cost is the major drawback that limits the industrial growth of this solution. Many types of catalytic systems were proposed: benzene conversion with nitrous oxide and hydrogen peroxide, for example, but none of them produce a benzene conversion and phenol yield that can meet the industrial specifications, or the oxidant was too expensive to make the process competitive on large scale. Another interesting alternative is the production of in situ H₂O₂ either in the liquid or in the gas phase using a mixture of O₂ and H₂.

Niwa et al. produced in situ H₂O₂ using a shell-and-tube reactor, in which a gaseous mixture of benzene and oxygen was fed into a porous alumina tube coated with a Pd thin layer whereas hydrogen was fed into the shell. Hydrogen dissociated on the palladium layer surface permeated onto the back and reacted with oxygen to give active oxygen species, which attack benzene to produce phenol. Vulpescu et al. confirmed the possibility of carrying out the direct hydroxylation of benzene to phenol claimed by Niwa and additionally observed the total oxidation of benzene. Under the process conditions used, side reactions such as total oxidation of hydrogen and benzene to water and CO₂ were favored. With respect to the industrial Hock process, this new route presented the advantage of significantly lower investment costs, but owing to the poor yield, it was much more expensive in terms of variable costs (by about three times). This is, still now, the major barrier to potential commercial application of the concept of in situ H₂O₂ catalytic MR.

A novel reactor design was proposed by Bortolotto and Dittmeyer. the direct hydroxylation of benzene was achieved in a new reactor with separate membranes for distributed dosage of hydrogen (Pdₐg/Cuₐg, 50 μm) and oxygen (Ag 15 μm), respectively, into microstructured reaction channels. The idea was that the H₂/O₂ concentration ratio along the reactor could be kept within an optimum range to maximize the hydroxylation area while limiting the influence of undesired oxidation and hydrogenation reactions. The data showed that there was a clear influence of the H₂/O₂ concentration ratio on the results in particular and that an excess of oxygen greatly reduced the selectivity to phenol: the phenol rate passed through a maximum at H₂/O₂ = 1.4 at which the selectivity reaches its highest value of 9.6%.

Wang et al. tested an MR in which titanium silicalite-1 (TS-1) was incorporated as catalyst in a Pd-based membrane. The direct hydroxylation of benzene to phenol was performed with hydrogen and oxygen as coreactants in the MR, and the effect of reactor configuration was examined.

The reaction results indicated that the direct hydroxylation of benzene required both hydrogen and oxygen coreactants. As already pointed out, the Pd membrane can catalyze the conversion of benzene to phenol as reported by Niwa et al. and the reaction was sensitive to the H₂/O₂ molar feed ratio, and its optimum was governed by membrane permeation rate, reactant composition, and reaction conditions. Nevertheless, benzene conversion and phenol yield remained low.

Another example was given by Sato et al. who investigated the effect of loading metal particles into the pores of an α-Al₂O₃ substrate support tube of the Pd-MR. Likewise, the study demonstrated that the active oxygen species were formed by the reaction with the permeated hydrogen and adsorbed oxygen over the Pd membrane. The active oxygen species were reacted with benzene and directly converted into phenol. The loading of noble metals resulted in the enhancement of the activity of side reactions, that is, complete oxidation and hydrogenation, and a decrease in the hydroxylation activity. In contrast, the loading of Cu suppressed complete oxidation and enhanced the hydroxylation activity. The maximum phenol yield was observed at 140°C (413 K), ca. 8%.

Phenol production through the direct hydroxylation of benzene with hydrogen peroxide using a catalytic MR was carried out in a biphasic system separated by a membrane by Molinari et al. This system consisted of a flat-sheet membrane separating two compartments: one containing an aqueous phase, with an iron catalyst and hydrogen peroxide as the oxidant, and the other one containing an organic phase (only benzene). Benzene had a double task: it was a reactant, and it permeated through the hydrophobic membrane and reacted at the aqueous interface and a solvent, because the phenol produced permeated back through the membrane and dissolved into benzene, where it was protected by overoxidations. However, despite the high phenol selectivity (98%) obtained, thanks to phenol extraction in the organic phase, the low rate of phenol permeation through the membrane caused its further oxidation to overoxidized products such as benzoquinone, biphenyl, and tar (black solid).

Recently, Al-Megren et al. proposed a new MR configuration for the avoidance of TAR formation and the
enhancement of the recovery of the phenol. In their work, a continuous MR was studied, where the phenol produced was recovered by using water on the stripping side of the membrane unit. The influence of the hydrophilic and hydrophobic character of the membrane material on the phenol recovery was investigated at different flow rates of the feed and the stripping phases. Better performance was achieved using a hydrophilic membrane, with a total feed flow rate of 2 mL/min and a stripping flow rate of 1 mL/min, in terms of phenol recovery (25%) and selectivity (94%). In addition, the continuous removal of the phenol from the reaction side reduces the possible formation of by-products such as benzoquinone, avoiding completely biphenyl formation that was not detected in all the tests carried out in the continuous mode.

Despite the positive advantages offered by MRs, the main hurdle that limits the diffusion of MRs for the conversion of benzene to phenol still remains the high cost of oxidants and the limited conversion with formation of by-products.

5.3.3 Dehydroisomerization of Butane to Isobutene

Isobutene is an important intermediate in the petrochemical industry; 649,000 barrels were produced in the United States alone in 2011. Moreover, with the ever-increasing importance of hydrogen, there is extra incentive to research especially dehydrogenative-type reactions of light alkanes due to their high H/C molar ratio. Isobutene, owing to the presence of its reactive double bond, can take part in various chemical reactions, such as hydrogenation, oxidation, and other additions, resulting in a great variety of products. One of the most widely used reactions in the industry is the addition of methanol or ethanol to isobutene, which leads to two well-known fuel additives: methyl tert-butyl ether (MTBE) or ethyl tert-butyl ether (ETBE). Besides this important application, isobutene is also used in a variety of polymerization reactions, as a monomer or copolymer for the formation of various products. Currently, isobutene is obtained on a large scale from crude oil, by petrochemical cracking with the butadiene removed, and from butanes, supplied from natural gas reserves and refinery streams. Butanes are the preferred raw materials for the production of isobutene, and the most common industrial method is by isomerization and catalytic dehydrogenation to isobutene.

The currently practiced process is a two-step process, comprising n-butane isomerization and successive isobutane dehydrogenation. The n-butane dehydroisomerization (Reaction 5.3) involves the dehydrogenation of n-butane (Reaction 5.1) and successive isomerization to isobutene (Reaction 5.2). The main products measured were normal butane, isobutene, and isobutene:

\[
\text{n-butane} = n\text{-butene} + H_2 \quad \Delta H_{\text{Reaction}} (@25^\circ\text{C}) = 130 \text{ kJ/mol} \quad (5.1)
\]

\[
\text{n-butene} = \text{isobutene} \quad \Delta H_{\text{Reaction}} (@25^\circ\text{C}) = -17 \text{ kJ/mol} \quad (5.2)
\]

An interesting alternative is a direct one-step process, allowing the direct conversion of n-butane to isobutene. Some bifunctional catalytic systems, usually considering zeolite-supported Pt catalysts, have been reported in the literature as successful catalysts for such direct conversion including the MRs. Isobutane dehydrogenation using catalytic MRs has been previously studied by a number of researchers. Many types of membranes have been investigated for this type of application. For example, isobutane dehydrogenation has been studied using γ-alumina, zeolite MFI, Pd/Ag and Pd, dense silica, and CMS membranes. The general outcome is that in all cases, a conversion above the equilibrium conversion of a TR could be obtained due to hydrogen removal through the membrane.

Recently, Al-Megren et al. studied by a simulation analysis the exploitation of an MR to carry out the direct conversion of n-butane to isobutene for the reactive system including Reactions 5.1 through 5.3, in a Pd-based MR. The n-butane dehydroisomerization is an endothermic reaction, and therefore, high temperature raises the equilibrium conversion, also in an MR. The peculiarity in the MR of the selective hydrogen removal allowed the exploitation of the positive effect of the reaction pressure on the hydrogen permeation and consequently on the conversion that, on the contrary, in a traditional reactor depleted, since the reaction had an increase in the number of moles. The analysis performed also provided an estimation of the best conditions, in the range of temperature and pressure investigated, which allowed achieving the highest reachable conversions in an MR compared to that of the traditional one. An MR operating at 500°C, 20 and 0.1 bar as reaction and equilibrium hydrogen partial pressures, respectively, showed a conversion seven times higher than that obtainable in a traditional reactor. Even though the research has achieved interesting results, actually, no large-scale applications of the aforementioned technologies are available.

5.4 PV PROCESSES

5.4.1 Gasoline Desulfurization

Nowadays, PV is considered as a promising unit operation for separation of organic–organic liquid mixtures in chemical and petrochemical industries. Its efficiency in separating azeotropic and close-boiling mixtures, isomers, and heat-sensitive compounds makes this operation ideal for various types of separations involving organic–organic mixtures, polar/nonpolar mixtures, aromatic/alicyclic mixtures, aromatic/aliphatic mixtures, and aromatic isomers.

Recently, gasoline desulfurization by PV has been studied as a newly emerged technology in which sulfur components can be preferentially removed from the gasoline feed due to its higher affinity and/or quicker diffusivity in the membrane.

The PV system is made up of a membrane module divided into two chambers by a nonporous polymeric membrane. One side of the membrane is in contact with the gasoline...
feed, whereas the other side is under vacuum or sweep gas to maintain a very low absolute pressure at the downstream side of the membrane. Sulfur components can be preferentially removed from the feed due to its higher affinity and/or quicker diffusivity; they permeate through the membrane and evaporate into the vapor phase that is then condensed. The affinity of the membrane with the sulfur component is determined by its selectivity that can change according to the type of membrane used.

The sulfur content in fluid catalytic cracking (FCC) naphtha consists of aromatic and nonaromatic sulfur-containing compounds. PV can selectively enrich these sulfur compounds in the permeate stream, reducing the quantity of sulfur compounds in the feed stream. A PV process so-called TranSep™ for the removal of sulfur from gasoline has been developed by Trans Ionics Corporation. Instead of the other PV processes, the recovery of the permeate occurs by using a Venturi nozzle and special working fluid with which to create the vacuum required to recover permeate from the downstream side of the membrane. This solution allows the elimination of expensive refrigeration systems generally required to condense light hydrocarbons at high vacuum.

Figure 5.8 shows the integration of S-brane with an hydrodesulphurization (HDS) unit to improve clean gasoline output, producing a sulfur-depleted retentate and a sulfur-enriched permeate. The HDS unit uses hydrogen under high pressure and temperature to convert the sulfur embedded in the sulfur compounds to hydrogen sulfide. The use of a membrane system allows bypassing a large fraction of the feed around the HDS unit, increasing the total quantity of naphtha that can be treated. Grace Davison achieved the first scaled-up installation of this technology in 2001 with the S-brane pilot plant, which had a capacity of 1 bdp treating streams with less than 30 ppm of sulfur. Naphtha was heated to operational temperatures (70°C–100°C), and the permeate was collected in mL/h quantities under full vacuum in condensing traps cooled with liquid nitrogen.

Afterwards, in 2003, an S-brane demonstration plant (300 bdp capacity) was installed at the ConocoPhillips, Bayway Refinery. Figure 5.9 shows a view of the S-brane demonstration plant in operation. Currently, there are commercial systems for S-brane from 5,000 to 40,000 barrels/day. These large-scale systems could require in the order of 10,000 m² of membrane. The actual membrane area is determined by the feed stream composition, volume, target purities, and capabilities of available splitters and hydrogenation units. Given the successful scale-up from lab to pilot to demonstration scale, commercial installations should expect similar performance, with additional cost savings from economy of scale. Capital costs can be 20%–25% of that for other gasoline desulfurization technologies.

5.4.1.1 Other Applications of PV

PV is a quite flexible technology that offers the possibility of separating various solutions, mixtures of components with close boiling points, or azeotropes that are difficult to separate by distillation or other means. For this reason, it can be suitable for various applications in the petrochemical industry. MTR together with USEPA has developed a new ethanol recovery technology called BioSep that combines PV with an innovative condensation technology (dephlegmation). A dephlegmation process consists of partial condensation with a counter current flow of rising vapor and falling condensate. With the dephlegmator, better separation
can be achieved, and only vapor condensing at the top of the column has to be cooled to the lowest temperature. The BioSep process has proved cost-effective and energy efficient in recovering ethanol from biomass and currently, in new projects funded by DOE, is addressing new issues in biobutanol production.\textsuperscript{81}

MTR, Inc. has also developed another commercial PV application using silicon rubber coated on microporous polyimide support membranes for the separation of dissolved volatile organic compound (VOC) from water, achieving very high separation factors for toluene, benzene, chlorinated solvents, esters, and ethers.

Another PV process involves the separation of organics and water. This separation is one of the major separation problems in refineries; however, only few cases are recognized at industrial level.\textsuperscript{77,82} Separex reported the first pilot-plant result for an organic–organic application, the separation of methanol from methyl-\textit{t}-butyl ether/isobutene mixtures, in 1988. More recently, Exxon started a PV pilot plant for the separation of aromatic/aliphatic mixtures, using polyimide/polyurethane multiblock copolycondensates comprising alternate flexible (soft) and rigid (hard) sequence membranes.\textsuperscript{83}

An important process that has been attracting particular attention in the last few decades is the industrial production and recovery of xylene, since it is an important step in several petrochemical processes. Xylene has three isomers that are often used as industrial solvents or intermediates, namely, \textit{para}-, \textit{ortho}-, and \textit{meta}-xylene. However, these isomers have similar molecular structures and close boiling points, implying complex separation processes such as cryogenic crystallization or selective adsorption. PV can provide a simpler alternative to these conventional technologies, if a membrane with ideal separation performance can be obtained.\textsuperscript{84,85} Recently, Qu et al.\textsuperscript{84} demonstrated the effective possibility of separating these isomers by using hybrid membranes made up of poly-(acrylic acid) sodium (PAAS) membranes loaded with surface-modified zeolites. However, this application is, currently, at the laboratory stage.

An interesting analysis on the other potential applications of PV in the petrochemical industry can be found in Smitha et al.\textsuperscript{77}

### 5.5 ORGANIC SOLVENT NANOFILTRATION

The separation of organic mixtures is carried out ever more frequently with another recently introduced membrane technology, called OSN. NF (see Section 5.6) is most often used for water treatment to separate ions and other solutes, and OSN allows the separation of organic–organic mixtures. A study of 2006 demonstrated that its energy duty is only 10% with respect to the traditional distillation columns.\textsuperscript{86} The first large-scale application of this technology was in solvent recovery from the dewaxing operation in lube processing.\textsuperscript{77,88} MAX-DEWAX\textsuperscript{TM} is a large-scale OSN application that is refinery based.\textsuperscript{80} In traditional operations, waxy feed is mixed with a mixture of volatile solvents like toluene and methyl ethyl ketone (MEK) to precipitate the wax components as crystals after successive cooling and refrigeration. Filtration of the chilled wax leaves lube oil dissolved in MEK and toluene. Often, this mixture is separated by multistage flash and successive distillations to recover the solvents cold for recycling to the wax precipitation step. This step is particularly energy intensive, and OSN can reduce these costs, substituting the separation and recovery stage. The mixture of lubes and solvents is fed to the membrane modules. The retentate goes to the conventional recovery section plant, while the permeate stream of clean and cold solvent is integrated into the chilled solvent recycle loop. Since the process runs in solvents, both the membranes and modules were required to have solvent resistance. The feed in MAX-DEWAX at the refinery in Beaumont, TX, takes in a volume of 5,800 m\textsuperscript{3}/day (36,000 barrels/day) (Figure 5.10). The use of membranes allows more solvent to be recycled, thus resulting in a higher lube yield and in a reduced amount of undesirable slack by-products.

![FIGURE 5.10 Scheme of MAX-DEWAX process. (Reprinted from J. Membr. Sci., 286, White, L.S., Development of large-scale applications in organic solvent nanofiltration and pervaporation for chemical and refining processes, 26–35, Copyright (2006), with permission from Elsevier.)](image)

Applications for OSN have been under pilot-plant trial or demonstrated in laboratory experiments in solvent deoiling, homogeneous catalyst recovery, separation of phase-transfer agents, and solvent exchange.\textsuperscript{80} White provides a very interesting review on the large-scale applications of OSN in the chemical and refining processes,\textsuperscript{80} which also provides some guidelines on the convenience of using OSN or PV. In general, the choice between these two technologies depends on the trade-off between selectivity and costs. In some cases, the high throughput of OSN outweighs the higher selectivities of PV. Aromatics-selective membranes can be operated in either PV or OSN mode.\textsuperscript{89} The lower capital and operation cost of OSN suggests that it be considered when streams are high in aromatics content (>80%). On the contrary, when concentrations of aromatics are lower, PV can allow better aromatics enrichment. For reduction to very low levels of aromatics, such as reducing benzene to less than 1% in gasoline, PV is the preferred mode.
5.6 MEMBRANE SYSTEMS FOR WATER RECOVERY

Refineries use large quantities of water. Wastewater production is strongly determined by the process configuration, but for a refinery with cooling water recycle, a production of approximately 3.5–5 m³ per ton of crude can be taken. Uncontrolled discharge of refinery effluent is no longer possible; therefore, various treatment stages are required in each petrochemical industry.

Refinery wastewater includes runoff water, process water, and domestic water. Typically, according to the use, the wastewater can be characterized by significant concentrations of suspended solids, chemical and biochemical oxygen demand (COD, BOD), oil and grease, sulfide, ammonia, phenols, hydrocarbons, benzene, toluene, ethylbenzene, xylene, polycyclic aromatic hydrocarbons (PAHs), and heavy metals. The typical treatment of petrochemical wastewater includes:

- Physical processes for the removal of oil, grease, and heavy hydrocarbons
- Physicochemical processes for the removal of macromolecular and colloidal substances
- Biological wastewater processes aiming to remove organics, nutrients, and particularly lighter hydrocarbons

In addition, the refinery consumes water for cooling, for boilers, and for domestic purposes, and according to the source (surface water, ground water, reused water), the makeup water needs a specific treatment such as sand filtration, iron removal, (partial) softening, desalination, dosing of chemicals to control corrosion, and biofouling.

5.6.1 PRESSURE-DRIVEN PROCESSES FOR THE PURIFICATION OF WATER FROM OIL

One of the methods for EOR is the injection of steam into the oil well. Obviously, the injected water produced with the oil is contaminated and needs to be treated and purified before being reused. In most of the cases, the water is separated from the oil and only slightly treated and sent back into the formation of a poor-quality stream. After some cycles of reuse, the water produced has to be disposed of, and this accounts for ca. 10% of the final cost of the oil production. The disposed water contains large amounts of solutes, including metal and organic compounds, oils, grass, sulfides, and phenols, and its discharge has become a big hurdle requiring, in any case, a pretreatment before discharging underground at a remote site or on the surface. The possibility of treating this water in such a way as to maximize its reuse would imply significant advantages in the reduction of water consumption, particularly in water-stressed regions of the world. The conventional methods for water treatment consist in gravity separation, air flotation, coagulation, flocculation, etc., but have several disadvantages such as high operational costs, low efficiency, use of chemicals, and corrosion. In addition, they are not able to remove low concentrations of residual oil. For this reason, a great deal of attention has been devoted to membrane technologies, also in integrated configuration.

MF or UF or their combined solutions are suitable technologies to separate oils from water. Bilstad and Espedal compared MF and UF membranes in a pilot trial to treat the North Sea oil field–produced water. By UF membrane treatment, the total hydrocarbon concentration can be reduced to 2 from 50 mg/L (96% removal). Benzene, toluene, and xylene (BTX) were reduced by 54%, and some heavy metals like Cu and Zn were removed to the extent of 95%. Lee and Frankiewicz of NATCO group tested a hydrophilic UF membrane to treat oil field–produced water, placing the membrane units after a hydrocyclone used to desand and deoil the wastewater. At the end of the process, the oil and gas concentration was reduced to less than 2 mg/L.

Combined membrane pretreatment and RO technology are effective methods for producing water that can be used for irrigation or domestic purposes. Doran et al. (reference 119 in Ref. [93]) present a pilot process to treat refinery water, making it usable for irrigation. The system is composed of a precipitative softening, a biological oxidation of organic compounds, a filtration stage, an ion-exchange softening, and an RO unit. The system effectively produced irrigation water allowing the reduction of treatment costs of produced water. Another similar example was carried out with success for various purposes, and RO resulted as the best technology for making the water potable or usable for irrigation scopes. However, the main issue limiting the diffusion of this technology is related to the fouling occurring often during the operation. This reduces the lifetime of the membrane and of the process; therefore, the use of RO units needs to be accompanied by pretreatment stages and periodical chemical cleanings, thus increasing the operational costs and limiting the economic efficiency of this technology.

5.6.2 MEMBRANE BIOREACTORS FOR WATER TREATMENT

Activated sludge processes (ASPs) have widely been used for biological wastewater and sewage treatment. However, since the settling of activated sludge for solid–liquid separation is difficult by gravitational settling, the biomass concentration, which can be controlled, is limited when bioreactor volume becomes large. On account of the difficulty of solid–liquid separation in biological wastewater treatment, MBRs have been proposed, and since the 1960s, many researches have been conducted on using MBR for water treatment.

MBRs are combined processes in which a biochemical conversion (by the action of a catalyst of biological origin, i.e., an enzyme) and a physical separation process are simultaneously carried out.

For many applications, the enzyme activity is extremely efficient and selective compared with traditional chemical catalysts; these biological catalysts demonstrate higher reaction rates, milder reaction conditions, and greater stereospecificity.
There are two most common configurations of MBRs: (1) the ones where the membrane controls the mass transport in and out from the reactor bulk and has an indirect effect on the reaction itself and (2) the ones where the reaction takes place at the membrane level and therefore has a direct effect on the reaction in addition to governing the mass transport through itself. These are most properly called biocatalytic MR, owing to the catalytic function of the membrane itself.

MBRs are today an effective technology for wastewater treatment and recycling.

As it combines biological treatment with membrane separation, an MBR is operated similarly to a conventional ASP but without the need for secondary clarification and tertiary steps like sand filtration. The treated water is separated from the purifying bacteria (active sludge) by a process of membrane filtration rather than in a settling tank. Only the treated effluent passes through the membrane; the effluent is then pumped out, while the sludge is recovered. An MBR is a compact facility (up to five times more compact than a conventional activated sludge plant, the membrane module replacing the clarification tank) that produces significantly less excess sludge. The membrane filtration occurs either externally through recirculation (external loop) or within the bioreactor (immersed configuration).

Immersed MBRs have been developed out of a need to simplify the use of these systems and to operate more cost-effectively than the external loops with respect to both energy consumption and cleaning requirements. In these configurations, the membranes are directly immersed in the tanks containing the biological sludge, and the treated permeate is extracted.

This operating mode limits the energy consumption associated with the filtration from 0.2 to 0.4 kW h/m³. Since the membrane is an absolute barrier for bacteria and in the case of UF also for viruses, the MBR process provides a considerable level of physical disinfection. The resulting high quality and disinfected effluent implies that MBR processes can be especially suitable for reuse and recycling of wastewater. Since the early MBR installations in the 1990s, the number of MBR systems has grown considerably. Commercially available systems include the package treatment plant Clereflo MBR (Conder Products, United Kingdom), designed to service populations up to 5000, and the ZeeMOD® (Zenon Environmental, Inc., today General Electric [GE]), which is available for flow rates of up to 7500 m³/day. The development of SMBR technology is also emerging in other fields, including biofuel, pharmaceutical, food, and biotechnology. In refineries, the highly treated wastewater can directly be used in cooling tower makeup, boilers, and utilities. In 2007, Kubota installed in Oman an MBR plant producing 78,000 m³/day of water reused for irrigation. ENI installed the world’s largest centralized MBR plant treating petrochemical wastewater, located in the industrial area of Porto Marghera, Venice. The plant receives wastewater from different petrochemical and chemical industries, and it was upgraded to an MBR in order to meet the strict legislation governing the effluents discharged into the lagoon of Venice (Figure 5.11). Five runs were conducted, initially aiming to represent the operating conditions of the full-scale MBR, and then alternations were introduced, including the addition of more external carbon source, the reduction of the anoxic compartment volume, changes in configuration, and an increase of influent load. The MBR demonstrated to safeguard the effluent quality even under sudden and drastic transient conditions.

The system has now been upgraded with new ClearQ submerged membranes supplied by the water technology company WaterQ, Nijmegen, the Netherlands. The system starts in 2013, and in total, WaterQ will deliver 9 skids with 128 modules, exceeding 100,000 m² allowing the operator to treat 50,000 m³ wastewater per day. The membrane cuts off suspended solids, colloid, bacteria, viruses, and giant molecule organic matter. It is made of lightweight polyvinylidene difluoride (PVDF) thermoplastic providing a good chemical stability and making it easy to clean. The effluent of the municipal WWTP is transported to a special constructed 100 ha wetland for a final polishing step. The construction of the two WWTPs, the wetland, and the pipelines was completed in 2011. Another Italian city, Loano, upgraded a WWTP with GE’s advanced technology making it the second largest municipal MBR plant in Italy.

Borghetto Santo Spirito is a town located in the Province of Savona, in the Italian region of Liguria, and is approximately 60 km west of Genoa. The membrane plant was first constructed 3 years ago initially to treat 7000 m³/day. With the new expansion, using GE’s ZeeWeed technology, the WWTP quadruples the flow and serves approximately 140,000 residents in the towns of Borghetto Santo Spirito, Loano, Torrano, Boissano, Balestrino, and Ceriale. The expanded plant handles a maximum wastewater flow of about 35,000 m³/day, roughly the amount of water required to fill 14 Olympic-sized swimming pools.
5.7 METRICS AND PROCESS INTENSIFICATION

For measuring progress toward sustainability, many efforts are being made to define industrial process indicators. Most of these indicators are calculated in the form of appropriate ratios that provide a measure of impact independent of the scale of the operation or that weigh cost against benefits, and in some cases, they can allow comparison between different operations. Membrane operations are well known for their modularity, compactness, and flexibility; therefore, they can be considered as new operations developed in the logic of PI. Recently, new metrics for comparing membrane performances with those of conventional units have been introduced. With respect to the existing indicators, these new metrics take into account the size, the weight, the flexibility, the yield, and the modularity of the plants. They are useful for an immediate indication of the eventual gain that a membrane operation can offer with respect to a traditional one. In this sense, they are useful also for indicating which of membrane and traditional operation is more suitable for a specific process.

5.7.1 CASE STUDY: HYDROGEN SEPARATION IN REFINERIES

The hydrogen upgrading in refineries is traditionally carried out by means of PSA and cryogenic separation processes. However, the application of membrane systems for this type of separation is rapidly growing toward the commercial level, owing to the advantages related to the low capital costs, low energy requirements, and modularity. The choice of the best technology can be driven by evaluating some parameters, such as those reported in the following, introduced by Miller in 1989, still useful and valid:

5.7.1.1 Operating Flexibility

It is the ability to operate under variable feed quality conditions, either on a short- or long-term basis. The changes in feed composition occur very often in refinery applications, particularly when the source of the feed is a catalytic process or when the feedstock to the upstream unit changes.

In membrane processes, the increase in feed impurity concentrations can induce a decrease in product purity, which, however, can be maintained for small feed composition changes by adjusting the feed-to-permeate pressure ratio. The response time of membrane systems is essentially instantaneous, and corrective action has immediate results. The start-up time required by the process is extremely short.

The PSA process shows a great ability to maintain hydrogen purity and recovery under changing conditions. The process is self-compensating, and even relatively large changes in feed impurity concentrations have little impact on performance. As the concentration of a feed impurity increases, its partial pressure increases, increasing also the amount of the impurity, which will be adsorbed. The purity of the hydrogen can be maintained constant by a simple cycle time adjustment. The response time to variations is rapid but not abrupt, generally requiring 5–15 min for responding to a step change in feed quality. The new steady state upon restart following shutdown is reached in about 1 h.

The cryogenic process has very low flexibility, because changes in the concentration of the lower boiling components of the feed affect the product purity directly. Recovery is not strongly affected. Response time is not as rapid as for PSA or membrane systems. Start-up is 8–24 h depending on the procedure used.

5.7.1.2 Turndown

It is the capability of the system to operate at reduced capacity. Membrane systems are highly capable of maintaining product purity even though the capacity is reduced down to 10% of the initial design. This is done by either reducing feed pressure, increasing permeate pressure, or isolating modules from the system. No provisions are required in the design phase.

PSA units can maintain both recovery and product purity at throughputs of ca. 30%–100% of design by adjustment of the cycle time. Between 0% and 30% of design product rates, purity can be maintained, but recovery is reduced unless special provisions are made in the design.

The turndown capability of cryogenic systems is strongly determined by the design. Partial condensation units can maintain product purity at slightly reduced recovery at flows down to 30%–50% of design.

5.7.1.3 Reliability

It takes into account the on-stream factors that can cause unscheduled shutdowns. It is an important project consideration, particularly if the process is a primary source of makeup hydrogen to a hydro processor or other mainstream refinery processes.

Membrane systems are extremely reliable with respect to the on-stream factor. The membrane separation process is continuous and has few control components that can cause a shutdown. Typically, the response to unscheduled shutdowns is rapid.

PSA systems are moderately reliable. The numerous valves associated with the process can cause unexpected shutdowns. The new PSAs are designed with alternate modes of operation, in which 100% of design capacity can be achieved while bypassing any failed valve or instrument, with only a slight loss of recovery. Failures are automatically detected and bypassed by the microprocessor-based control system. However, stronger and periodic control cycles are required.

The cryogenic process is considered by refiners to be less reliable than the PSA or membrane processes; this is mainly due not to the process itself but to the need for feed pretreatments. Failure of the pretreatment system usually results in contaminants freezing in the cold box, leading to shutdown.

5.7.1.4 Ease of Expansion

In some case, future expansion is contemplated even during the initial phase of a project.
Membrane system expansion is very easy, since this only requires the addition of identical modules.

PSA systems can also be expanded, but it requires additional design considerations and adds cost in the initial phase of the project.

The cryogenic units cannot be expanded if it is not foreseen during the design phase.

### 5.7.1.5 By-Product Value

It is the capability of producing a high-value tail gas.

In many refineries' hydrogen upgrading processes, the impurities to be rejected include hydrocarbons that have value significantly above fuel value. This is particularly true for olefin-containing streams. The relative amounts of high-value hydrocarbons and the incremental cost of further separation determine whether by-product recovery is an important parameter to be considered.

The cryogenic process is best suited to applications involving by-product hydrocarbon recovery. It is possible to separate hydrocarbon streams containing C2/C3 and C4+ components, with recovery of these components generally quite high, with typical overall values of 90% for the C2/C3 components and up to 100% of the C4+.

The membrane process is not capable of providing separate streams rich in specific hydrocarbon fractions; however, it is also used in these applications, since the hydrocarbon-rich stream is available at high pressure.

By-product hydrocarbon recovery is normally not economical when the PSA process is used, because the single hydrocarbon-rich tail gas is delivered at too low a pressure.

Table 5.3 summarizes the comparison among the project parameters described earlier for the three operations considered in the case of H2 separation.

The selection of the hydrogen purification process may be driven by specific considerations, strictly related to the output to be obtained. The feed composition (H2%), the feed conditions (pressure and temperature), the product purity, and the final destination of the product strongly affect the choice (Table 5.4).

The composition of the feed and its variability has a large impact on the selection of a hydrogen separation process because it influences the performance, reliability, and pretreatment required by the three upgrading processes. Membrane systems are suitable for a wide range of feed compositions, owing to the possibility of driving the process acting on different parameters such as feed and permeate pressure, temperature, and flow configuration. Streams with 75–90 vol% hydrogen are most economically upgraded also by PSA with the selection being based on flow, pressure, and pretreatment requirements. Cryogenic upgrading is applicable to large streams with 30–75 vol% hydrogen.

**Feed pressure and product flow rates** are best considered together when selecting a hydrogen purification process because the three processes have drastically different economies of scale.

The membrane systems are the lowest capital cost alternative for small (less than 30,000 m3/h product) flow rates, since the cost of a membrane system is proportional to the number of modules required. If the feed gas is already at high pressure or if there is downstream hydrocarbon recovery from the nonpermeate, where the high pressure of this stream can be used to advantage, the membrane systems can be used also for larger flow rates. For small flow rates at high pressure, such as a purge stream from the high-pressure separator of a hydro processor, membrane systems are the most economical.

PSA systems can be economical for flow rates from 1000 to 107 m3/h already compressed at 15–30 bar. Differently from membrane systems, PSA units cannot take advantage of high available feed pressures (50–70 bar), and the capital and operating costs associated with feed, product, and/or tail gas compression are almost always a significant portion of the total separation costs and globally higher than that required by membrane systems. Cryogenic systems have high capital

<p>| TABLE 5.3 |
| Comparison among Some Important Project Parameters |</p>
<table>
<thead>
<tr>
<th>Membrane System</th>
<th>PSA</th>
<th>Cryogenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating flexibility</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Response to variations</td>
<td>Instantaneous</td>
<td>Rapid (5–15 min)</td>
</tr>
<tr>
<td>Start-up after the variations</td>
<td>Extremely short (10 min)</td>
<td>1 h</td>
</tr>
<tr>
<td>Turn-down</td>
<td>Down to 10%</td>
<td>Down to 30%</td>
</tr>
<tr>
<td>Reliability</td>
<td>100%</td>
<td>95%</td>
</tr>
<tr>
<td>Control requirement</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Ease of expansion</td>
<td>Very high (modularity)</td>
<td>Moderate</td>
</tr>
<tr>
<td>By-product value</td>
<td>Moderate</td>
<td>Not economical</td>
</tr>
</tbody>
</table>


<p>| TABLE 5.4 |</p>
<table>
<thead>
<tr>
<th>Comparison among the Three Units as a Function of Feed and Product Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane System</td>
</tr>
<tr>
<td>Feed composition (H2%)</td>
</tr>
<tr>
<td>Feed pressure and product flow</td>
</tr>
<tr>
<td>Product purity</td>
</tr>
<tr>
<td>Product purity</td>
</tr>
</tbody>
</table>

The relative economic feasibilities are driven by specific considerations, strictly related to the output to be obtained. The feed composition (H2%), the feed conditions (pressure and temperature), the product purity, and the final destination of the product strongly affect the choice (Table 5.4).
membrane units are most often selected, whereas the cryogenic system is not suitable.

Apart from the economic considerations, the choice among the three separation processes is generally made taking into account the specific process from which the hydrogen is produced, the specific requirements that the upgraded H₂ must have also considering the final destination of the stream. Table 5.5 reports some selection guidelines of the most important processes of hydrogen production in refineries.¹⁷

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TABLE 5.5
Selection Guidelines for Specific Application Processes

<table>
<thead>
<tr>
<th>Process Application</th>
<th>Feed Conditions</th>
<th>Membrane System</th>
<th>PSA</th>
<th>Cryogenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic reformer off-gas</td>
<td>70%–90% vol. H₂</td>
<td>H₂ purity: 98%, Final destination: uses such as catalyst regeneration</td>
<td>H₂ purity: 99%</td>
<td>Not used due to the necessity of pre-treatment for aromatic removals</td>
</tr>
<tr>
<td></td>
<td>30%–10% vol. C₂ to C₂+</td>
<td>Room temperature</td>
<td>H₂ recovery: 82%–90%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ppm of aromatics and HCl</td>
<td>Pressure: 15–30 bar</td>
<td>Final destination: primary source of make-up hydrogen for hydrocracker</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Room temperature</td>
<td></td>
<td>Not used because of the high feed pressure</td>
<td>Not used due to the low flow rates</td>
</tr>
<tr>
<td></td>
<td>High pressure purge gas:</td>
<td>H₂ purity: 92%–98%, H₂ pressure: 20–40 bar, 85%–95% hydrogen compressor</td>
<td>H₂ purity: 99%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75%–90% vol. H₂</td>
<td>Room temperature</td>
<td>H₂ pressure: 1 bar</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrocarbon balance</td>
<td></td>
<td>H₂ recovery: 80%–90%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pressure: 50–200 bar</td>
<td></td>
<td>Final destination: primary source of make-up hydrogen for hydrocracker</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Room temperature</td>
<td></td>
<td>Not used because of the low H₂ concentration in the feed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low pressure purge gas:</td>
<td>Not used because of the low feed pressure</td>
<td>H₂ purity: ≥95%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50%–75% vol. H₂</td>
<td></td>
<td>H₂ pressure: 15–30 bar</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrocarbon balance</td>
<td></td>
<td>Recovery of a mixed stream containing ≥99+% of C₂+ components</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pressure: 5–20 bar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Room temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydro processor purge gases</td>
<td>15%–50% vol. H₂</td>
<td>Feed compression: ≥25 bar</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrocarbon or olefins balance</td>
<td>H₂ purity: 80%–90%, H₂ pressure: 5–20 bar, 50%–85% hydrogen compressor</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pressure: 5–20 bar</td>
<td>Final destination: low pressure hydrotreaters</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Room temperature</td>
<td>The tail gas is sent to downstream hydrogen recovery units</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FCC off-gas and other refinery purge streams</td>
<td>80%–90% vol. H₂</td>
<td>H₂ purity: 95%–97%, H₂ recovery: 80%–90% hydrogen compressor</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO, CO₂, CH₄ balance</td>
<td>Final destination: make-up hydrogen compressor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene off-gas</td>
<td>15%–50% vol. H₂</td>
<td>H₂ purity: 99.5%, H₂ recovery: 80%–90%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Room temperature</td>
<td>Final destination: primary source of make-up hydrogen for hydrocracker</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pressure: 15–30 bar</td>
<td>Final destination: make-up hydrogen compressor</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The largest source of easily recovered hydrogen in a refinery is the off-gas from catalytic reforming. This off-gas typically contains from 70 to 90+ vol% hydrogen with the balance being C\(_3\)-C\(_6\) hydrocarbons. If large quantities of reformer off-gas are to be upgraded for use as a primary source of makeup hydrogen for a hydrocracker or hydrotreater, the PSA process is normally used. The high hydrogen content makes the adsorbent requirements low, and the hydrocarbons in the tail gas sent to the fuel are relatively small with respect to the feed gas. The aromatic and HCl content of the feed do not require special pretreatment. In some cases, there is a requirement for relatively small quantities of hydrogen at 98+ vol% purity for uses such as catalyst regeneration. Membrane systems using feed compression may be most economical for these applications requiring less than about 1000 m\(^3\)/h of hydrogen product, owing to low capital costs. For large flows, cryogenic upgrading has sometimes been used. However, the feed hydrogen purity is often too high, and external refrigeration is required. Aromatic removal in the pretreatment section is also an important design consideration. Unless recovered hydrocarbons are of high value, the cryogenic process is not normally used to process reformer off-gas alone.

The high-pressure and low-pressure purge gases from high-pressure hydrocrackers and hydrotreaters are good candidates for hydrogen upgrading. The recovered hydrogen is returned to the hydro processor with the makeup hydrogen. Many hydro processors have both high- and low-pressure purge streams. The high-pressure purge streams are available at 50–200 bar and contain 75–90 vol% hydrogen, with the balance being hydrocarbons. Low-pressure purge streams are available at much lower pressures, typically 5–20 bar, and have hydrogen contents ranging from 50 to 75 vol%.

The membrane process is the most economical process for high-pressure purge gas upgrading. The product delivery pressure is chosen to allow the product to enter one of the stages of the makeup hydrogen compressors. Low-pressure purge gases are usually upgraded by the PSA process. The PSA process is better suited than the cryogenic process because the flow rates are relatively small and the stream composition can be highly variable. The combination of lower pressure and lower hydrogen content makes the PSA system less economical than the membrane system. The membrane system usually gives the highest rate of return on investment, the tail gas being at high pressure.

Hydrogen can be recovered from FCC off-gas and other low-pressure refinery purge streams of low hydrogen content. According to flow rate, feed composition and variability, feed pressure and required hydrogen product purity, either the cryogenic or membrane process can be used. In almost all cases, the stream is not upgraded for its hydrogen content alone, but also the tail gas is of value. If there are valuable hydrocarbons, particularly olefins, which can be recovered in addition to hydrogen, or if a hydrogen product purity in excess of 90 vol% is required, the cryogenic process is normally used. However, feed quality variations and contaminant levels are important considerations in determining whether the cryogenic process is appropriate. The membrane process can recover hydrogen efficiently from these streams at a hydrogen purity 80–90 vol%. The low purity hydrogen product can be used effectively in some applications, such as low-pressure hydrotreaters, and the tail gas can be sometimes sent to downstream hydrocarbon recovery units, being already compressed.

The ethylene production process produces large amounts of hydrogen, which can be easily upgraded for refinery use if the ethylene plant is in close proximity to the refinery. The ethylene process uses a series of cryogenic units to separate the products from the ethylene furnace, and a high purity hydrogen stream is produced. Typically, only a small fraction of the available hydrogen is used in the ethylene plant (for acetylene hydrogenation), and the balance is sent to fuel unless it can be exported. The hydrogen-rich ethylene off-gas normally contains 80–90 vol% hydrogen, with CO, CH\(_4\), ethylene, and nitrogen as impurities. In few cases, the cryogenic system is employed, producing a hydrogen purity as high as 95 vol% with the same impurities through the use of external refrigeration. Regardless of the hydrogen purity, the ethylene off-gas must be processed to remove CO to ppmv levels for general refinery use. For off-gas with 80–90 vol% hydrogen, the membrane systems are the most suitable for upgrading. The pressure and the high H\(_2\) concentration, in fact, allow a high purity product to be produced, even though lower (95–97 vol%) than for the PSA system. Furthermore, the retenate gas stream is already compressed, on the contrary to the PSA systems that require tail gas compression, from 0.1 to 0.3 bar to fuel system pressure. The choice between the membrane and PSA processes will primarily be determined by the cost of compressing the membrane hydrogen product compared to the cost of compressing the PSA tail gas, assuming high hydrogen recovery is desired in both cases. The product purity from the membrane system will be lower (95–97 vol%) than for the PSA system.

For the process selection, general selection guidelines can be helpful, at least in eliminating an inappropriate process. In order to use such guidelines, feed characteristics, contaminant levels, required product purity, allowable product impurities, pressure levels, and flow rates must be known. These parameters can be used in conjunction with experience-based, application-specific guidelines to select the optimum process. The membrane systems, owing to their high flexibility, reliability, modularity, and ease of control, compete well with the other two consolidated technologies, in particular, for some specific applications typical of refinery hydrogen upgrading.

### 5.8 Conclusions

An important contribution to a sustainable industrial growth might come not only from the development of new materials but also from the redesign of process engineering, following the principles of the green process engineering. As already done in large part of processes in nature, membrane operations can serve in molecular separations, chemical transformations, and water and energy transfer between different phases. Various are the successful examples of processes that have moved from lab scale to pilot plant up to
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a demonstration unit in refinery. These processes like the MAX-DEWAX offer significant gains with respect to the traditional technologies in terms of quality, energy saving, easiness of operation, and environmental impact.

In this context, membrane engineering plays a fundamental role in the integration of the units in a single plant and, at the same time, in the definition of the knowledge necessary to drive the process by maximizing the gains both in terms of efficiency and plant size reduction.

REFERENCES

98 Handbook of Membrane Separations: Chemical, Pharmaceutical, Food and Biotechnological Applications

35. www.airproducts.com
36. www.airproducts.no


101. [http://www.thembrsite.com](http://www.thembrsite.com)


