Permselective Membranes for Gas Processing Replacing the Conventional Methods

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Abstract: Membrane technology has gained acceptance for gas separation and recovery as membranes are friendly to the environment and less expensive. Membranes are starting to play a great role in industries such as separation and production of gases, sweetening of natural gas, processing of biogas and syngas, and oil refineries. This article evaluates the replacement of the conventional methods for gas processing by perm selective membranes and also offers an overview of the membrane technology in current use for gas processing in industries.

Keywords: Synthetic membranes, Natural gas, separation of gases, polymeric membranes, inorganic membranes, membrane contractor, Olefin-paraffin separation.

1. INTRODUCTION

Nature provides human beings with air and water which are their life line. Both are being polluted day by day, threatening the future of human survival. In particular, air pollution can result from both human and natural activities. Forest fires, volcanic eruptions, wind erosion, pollen dispersal, evaporation of organic compounds and natural radioactivity are the cause from the natural events, but they do not occur very often. On the other hand, the human activities result in air pollution more often by:

1. Emissions from industries and manufacturing activities,
2. Burning fossil fuels,
3. Household and farming chemicals.

Environmental scientists are seriously worrying about the ocean acidification. The atmosphere is made up of air which is composed of oxygen 21%, nitrogen 78%, argon 0.9% and carbon dioxide (CO_2) 0.04%. The concentration of CO_2 in the atmosphere has increased tremendously since the industrial revolution. CO_2, CO, SO_2, NO_2, H_2S and particulate matter are the common air pollutants. Gas processing industries are also contributing to the pollution by emitting hazardous gases which cannot be removed effectively by the conventional separation methods. Membrane gas separation processes may offer the solution to this environmental challenge.

The separation of gas mixtures plays now a significant role in industries such as natural and biogas processing, separation of air, applications in oil refinery, etc. The conventional methods are not environmentally friendly since they release waste gases which pollute the atmosphere. Membrane technology has gained acceptance for gas separation and recovery. This includes carbon dioxide separation from flue gas, hydrogen separation/recovery for fuel cell application, hydrogen sulfide separation from natural gas and recovery of helium and methane from biogas etc. [1]. There is growing industrial interest in the use of synthetic membranes for gas processing. These processes are less costly, less space covering and friendly to environment. The materials that are currently being investigated for these applications include organic polymer-based membranes, porous carbon, and inorganic membranes made of ceramics, zeolites, metals or glass.

Membrane gas separation process has emerged as a viable technology on industrial scale when Prism® was introduced in 1978. Since then the utilization of membrane technology in gas separation has rapidly expanded and undergone broad usage/interest in the industrial sector.

Permeability and selectivity are the two main parameters that characterize the performance of membrane material. They are directly connected, from an application point of view, to productivity and purity, respectively.

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Membranes are being used to separate gases from their mixtures by the differential permeation of the components through them.

Following are the main advantage of membrane systems;

1. Simple.
2. Minimal or no operator attention.
3. Small footprint and low weight.
4. Low maintenance.
5. Ambient temperature operation.
6. Lower capital and operating cost.
7. Environmentally friendly.

In addition gas separation membranes can be an alternative to more conventional separations such as cryogenic distillation, absorption, and pressure swing adsorption.

Several operating parameters affect gas separation by membrane, including feed-gas flow rate and composition, pressure differential across the membrane, gas temperature, online membrane area, and sales-gas specification. A good understanding of the effects of these process parameters is important to maximize the efficiency of the gas separation.

Membranes are employed in [2].

- The separation of nitrogen or oxygen from air (yielding up to 99.5% of nitrogen).
- Separation of hydrogen from gases like nitrogen and methane.
- Recovery of hydrogen from product streams of ammonia plants.
- Recovery of hydrogen in oil refinery processes.
- Separation of methane from the other components of biogas.
- Enrichment of air by oxygen for medical or metallurgical purposes.
- Removal of water vapor from natural gas and other gases.
- Removal of SO_2, CO_2 and H_2S from natural gas.
- Removal of volatile organic liquids (VOL) from air of exhaust streams.

Membranes are prepared from many different materials (both organic and inorganic).

1.1. Organic

Most widely used membrane materials for gas separation are polymers. Polymeric membranes are generally non-porous and gas permeation is described by the solution -diffusion mechanism. This is based on the solubility of specific gases within the membrane and their diffusion through the dense membrane matrix. In other words, separation is not just dependent upon molecular size but also depends on the interaction between the gases and the polymer. Polymeric membranes are in two types i.e. rubbery and glassy. Rubber is an example of an elastomer type polymer, which has the ability to return to its original shape after being stretched or deformed. The elastic properties in rubbery polymers arise from its ability to stretch the chains apart. However, on releasing the tension, chains snap back to its original position. On the other hand, the chains of glassy polymers are rigid. On heating, the glassy polymers will soften and become rubbery. But glassy polymers are not elastomer type polymer. The selectivity of gases through rubbery is based on the solubility, while in glassy polymer it is based on diffusion. Glassy polymers show very attractive separation properties, namely high selectivity combined with medium/low permeability. Polymers are easy to make membrane modules, which are mechanically strong and have thermal and chemical resistance [3].

1.2. Inorganic

Inorganic membranes are also versatile. They can operate at elevated temperatures, with metal membranes stable at temperatures ranging from 500-800ºC and with many ceramic membranes usable at over 1000ºC. They are also much more resistant to chemical attack. Because of the wide variety of materials that may be used in the fabrication of inorganic membranes and resistance to corrosive liquids and gases, even at elevated temperatures, inorganic membranes can be utilized for many purposes. Inorganic membranes compete with organic membranes for commercial use. Inorganic membranes demonstrate high performance under research conditions but module fabrication is still too costly in comparison with current polymeric modules. Inorganic membranes refer to membranes made of materials such as ceramic, carbon, silica, zeolite, various oxides (alumina, titania, zirconia) and metals such as palladium, silver and their alloys. Inorganic membranes can be classified into two major categories based on its structure: porous inorganic membranes and dense (non-porous) inorganic membranes. Microporous inorganic membranes have two different structures: symmetric and asymmetric; and include both amorphous and crystalline structures. The most important inorganic membranes are ceramic gas separation membranes which are based on microporous silica, zeolite or microporous carbon. Graphene is an emerging material for gas separation membrane which will compete with all other materials.

2. TARGETED SEPARATION

2.1. CO_2 Removal

Carbon dioxide (CO_2) is the main gaseous component of the greenhouse gases in the atmosphere, and it is known that about 80% of global warming is contributed by CO_2. It is essential to capture CO_2 from other gases in an effective and economical way. Following techniques are common for the separation of carbon dioxide from other gases.

1. Wet scrubbing.
2. Dry-generable solvents.
3. Cryogenics.
4. Pressure and temperature swing adsorption (PSA, TSA).
5. Chemical adsorption and gas separation membranes.

The common conventional gas absorption process for removal of CO_2 is chemical absorption by reactive absorbents. It is carried out by packed tower, spray tower, venture scrubber and bubble column. There are many problems such as flooding, foaming, and high capital and operating costs with these methods. Gableman and Hwang [4] suggested that these problems can be overcome by using hollow fiber membrane contactors (HFMC).

The presence of carbon dioxide is common in natural gas and must be removed to a level of <8% (usually <2%) to minimize corrosion of the pipe line [5]. Membranes for natural gas processing were first commercialized in the 1980s for CO_2 removal, and have been the dominant membrane gas separation process since then [6].

Various CO_2 separation/capture technologies are available. However, advanced polymer separation membranes are more favorable to monoethanolamide (MEA) absorption, cryogenics and PSA or TSA in terms of cost and energy demand. Separation membranes continue to offer considerable advantages for process integration with ease of operation and a smaller environmental impact than other separations techniques which often result in pollutant by-products. Currently membranes are being considered for separating CO_2 from natural gas [7].

There are three main types of membranes commercially available for CO_2 removal: i) cellulose acetate, ii) polyimides, and iii) perfluoro-polymers. There are two major membrane manufacturers currently supplying cellulose acetate based modules; these are Cynara® (part of Cameron) and UOP Separex® (part of Honeywell) [8].

Atchariyawut *et al*. [9] reported the potentiality of the gas-liquid membrane contactor for the separation of CO_2/CH_4 and reported that the CH_4 recovery from the CO_2/CH_4 mixture was approximately 100% in the membrane contactor. As they used small membrane module, the retentate selectivity obtained was not satisfactory. On increasing the CO_2 concentration in the feed gas stream, the CO_2 flux was enhanced as the driving force of the system was increased.

The removal of CO_2 by membrane-based natural gas separation process is currently practiced on a large scale and; more than 200 plants have been installed. The membrane system operates on the principles of selective permeation [10]. The Cakerawala production platform, an offshore processing facility in Block A18 of the Malaysia Thailand Joint Development Area in the Gulf of Thailand, installed semipermeable membranes to lower the CO_2 content in its produced gas. The CO_2-removal process on the Cakerawala production platform (CKP) uses Cynara semipermeable membranes. The facility was successfully commissioned in December 2004 and is currently continuing to operate [11]. The largest membrane plant for natural gas processing (CO_2/CH_4 separation) was installed in Pakistan in 1995, which was based on spiral wound modules. Its expansion is a clear example of the easy scale-up of the membrane technology.

The NETL (National Energy Technology Laboratory), an energy research laboratory owned and operated by the U.S. Department of Energy's (DOE) Office of Fossil Energy, is developing a technology based on RTI's (RTI International is a nonprofit organization, headquartered in the Research Triangle Park in North Carolina, that provides research and technical services) CO_2 capture membrane process and hollow-fiber membrane 'module design' to remove CO_2 from pulverized coal (PC) used in power plants (Figure **1**). Capture of CO_2 is a challenging application due to the low pressure and dilute concentration of CO_2 in the waste stream, and trace impurities in the flue gas (Nitrogen Oxides [NOx], Sulfur Oxides [SOx], particulate matter [PM]) that affect removal processes [12].

2.2. H_2S Removal

Hydrogen sulfide (H_2S) is a smelly, corrosive, highly toxic gas. Beside this it also deactivates industrial catalyst. H_2S is commonly found in natural gas and is also made at oil refineries, especially if the crude oil contains a lot of sulfur compounds. Hydrogen sulphide can be converted to non-toxic and useful element sulfur as it is an obnoxious substance. The process used to convert H_2S into elemental sulfur is the Claus Sulfur Recovery process.

In this process, H_2S is separated from the host gas stream using amine extraction. Then it is fed to the Claus unit, where it is converted to sulfur in two steps:

1. Thermal Step. The H_2S is partially oxidized by air. This is done in a reaction furnace at high temperatures (1000-1400°C). Sulfur is formed, but some H_2S remains unreacted, and some SO_2 is formed.

2. Catalytic Step. The remaining H_2S is reacted with the SO_2 at low temperatures (about 200-350°C) over a catalyst to produce more sulfur. The reaction is as follows:

$$2H_2S + SO_2 ==> 3S + 2H_2O$$

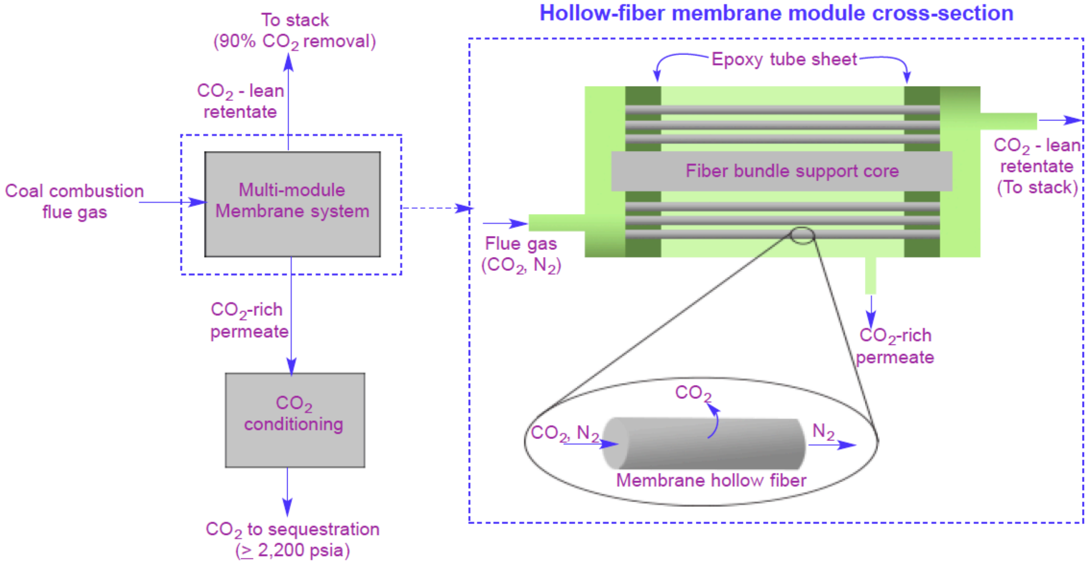

Figure 1: RTI's CO_2 capture membrane process and hollow-fiber membrane module design [12].

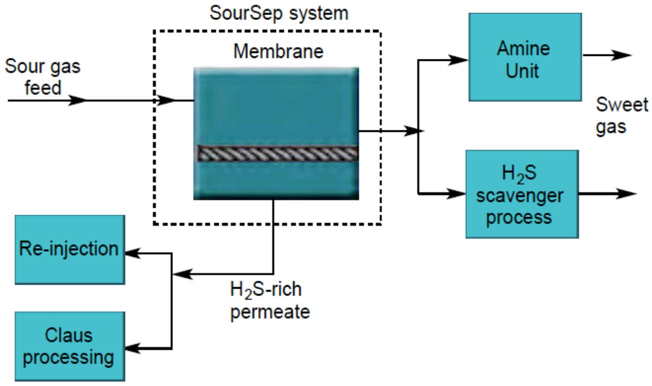

Figure 2: MTR's SourSep™ systems for H_2S removal [13].

Membrane technology for H_2S removal from natural gas was started by MTR (Membrane Technology and Research). MTR's SourSep™ systems removes bulk H_2S from pressurized sour gas in a simple single stage process (Figure **2**). Bulk H_2S removal (>75%) will generate a very sour permeate which can be re-injected or processed in a Claus plant (Figure **2**). Peculiarity of this unit is as follows:

1. Simple.
2. No moving parts.
3. No absorbents or adsorbents.
4. Process only gas.
5. Either no solids or liquids are produced
6. No solids or liquids are used or produced.

The incoming high pressure sour stream is split into a moderately sweetened high pressure product stream and a low pressure H_2S rich reject stream [13].

SourSep™ bulk H_2S removal can be combined with (i) reinjection or (ii) Claus processing for bulk H_2S disposal. Moderately sweetened product gas can be polished using (iii) lightly loaded conventional amine units with Claus process or, (iv) H_2S scavenger processes. SourSep™ unit was installed on an Indonesian remote production field.

UOP has developed polymeric membranes that can be used for bulk removal of H_2S from natural gas even at very high H_2S concentrations and at high operating pressures. UOP developed cellulose acetate membranes for the removal of H_2S. The simplest membrane processing scheme is a one-stage flow scheme. A feed gas is separated into a permeate stream rich in acid gas and a hydrocarbon-rich residual stream (Figure **3**). In high H_2S applications, hydrocarbons permeating with the acid gases may be re-injected. If re-injection is not possible then multistage system can be used to achieve higher hydrocarbon recoveries. Figure **4** shows a two–stage design where the first-stage permeate is compressed and processed in a second stage membrane (for both CO_2 and acidic gases removal).

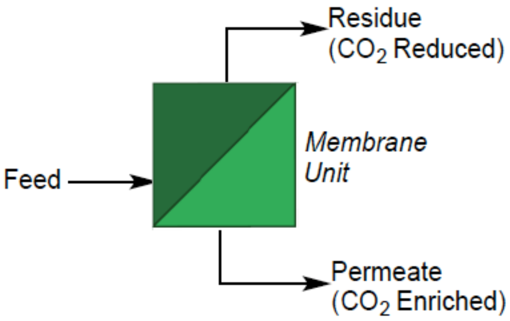

Figure 3: One-stage flow schemes (for both CO_2 and H_2S removal) [14].

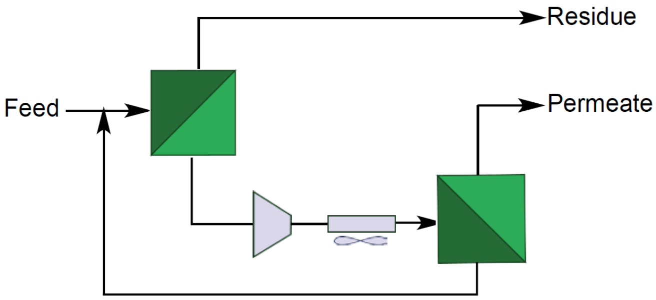

Figure 4: Two stage flow scheme (for both CO_2 and H_2S removal) [14].

UOP LLC has been developing membranes for the large scale treatment of highly sour natural gas streams. Existing membrane materials in some cases can be used for high partial pressures of H_2S, though care must be taken to make sure that all components in the membrane system are compatible with the application [14]. Membrane systems in natural gas service are currently used for the co-removal of CO_2 and H_2S when the sulfur levels are as low as the following examples.

- Pakistan, Kadanwari: 24ppm H_2S
- Pakistan, Qudirpur: 60ppm H_2S
- Mexico 4600ppm H_2S
- USA, West Texas: 2.8% H_2S

2.3. SO_2 Removal

Various absorption techniques are used for the removal of SO_2 from exhaust gases. One of them is "double alkaline process" which can be applied as membrane absorbers. Pilot tests for an installation of the output of $100m^3/h$ are carried out by TNO (Holland) using the gas coming from the installation for biogas combustion, which contains SO_2. Sulfur dioxide, which is being recovered by membrane absorption in the form of sodium sulfite, may be again used in the production process [15].

2.4. Hydrogen Recovery/Production

Hydrogen is a valuable commodity in oil refining and petrochemical processes which must be economically generated, purchased, or recovered from numerous process streams. Hydrogen can be generated from a readily available source: water electrolysis based on a proton-exchange membrane (PEM). PROTON developed a PEM called FuelGen® to produce high purity hydrogen by electrolysis [16, 17]. PRISM membrane separators are capable of recovering high purity hydrogen from purge gas streams in oil refineries and petrochemical plants [18]. Air-Products were the first for the application of a commercial membrane (Prism® system) for hydrogen recovery from the ammonia purge gas.

Undesired components such as light hydrocarbons, CO and CO_2 are present in hydrogen in large quantity when it is produced either from chemical processes or from fossil fuels. These components are currently separated by the following methods.

I. Pressure swing adsorption (PSA) is the most common method used today for hydrogen separation. PSA is based on an adsorbent bed that captures the impurities in the syngas stream at higher pressure and then releases the impurities at low pressure. Multiple beds are utilized simultaneously so that a continuous stream of hydrogen at purities up to 99.9% may be produced [19].

II. Temperature swing adsorption is a variation on PSA, but it is not widely used because of the relatively long time it takes to heat and cool sorbents.

III. Electrical swing adsorption has been proposed as well, but it is currently in the development stage.

IV. Cryogenic processes also exist to purify hydrogen, but they require extremely low temperatures and are, therefore, relatively expensive.'

Processes i) and iv) are industrially used but both processes produce relatively impure hydrogen and are very costly.

The purification or separation of hydrogen from industrial gases by means of membrane technology serves several purposes, including the improvement of existing processes and cheaper production of pure hydrogen. Only hydrogen can penetrate through the membrane because of the inherent properties of the material used for membrane preparation. The mechanism depends on the type of membrane in question (material rubbery or glassy). Most membranes rely on the partial pressure of hydrogen in the feed stream as the driving force for permeation, which is balanced with the partial pressure of hydrogen in the product (permeate) stream.

Membranes are already being used for the separation of H_2 and N_2 in ammonia production and for separating H_2 from hydrocarbons in petrochemical plants [20]. Johnson Matthey produces palladium-silver alloy membranes up to 60cm in size, commercially useful for the production of ultra-pure hydrogen in the electronics industry [21, 22].

Dense inorganic membranes with mixed protonic–electronic conduction – typically oxides – find prospective use in high-temperature hydrogen separation membranes [23]. Commercially available membranes for hydrogen separation have been summarized by EERC (Energy and Environmental Research Center®) as follows [24].

1. Air Liquid has technology called MEDAL™ that is typically used in refinery applications for hydro treating. The membrane is selective to components other than hydrogen, including H_2O, NH_3, and CO_2 and, therefore, would probably not be a good fit in most coal gasification applications.

2. Air Products offers a line of hydrogen recovery membranes referred to as PRISM® membrane systems [25]. The PRISM membrane is intended for separations in hydrocracker and hydro-treater systems or for CO purification in reformer gases. The systems are for low-temperature and not intended for processing of coal-derived syngas.

3. Wah-Chang offers small-scale Pd–Cu membranes for commercial sale that are capable of producing an ultrapure stream of hydrogen from syngas. The one drawback of the membrane (like many Pd-based membranes) is that it has a very low tolerance to H_2S and HCl, both of which are commonly found contaminants in coal-derived syngas.

Kim *et al*. [26] developed a membrane with an exceptionally high hydrogen permselectivity, exceeding

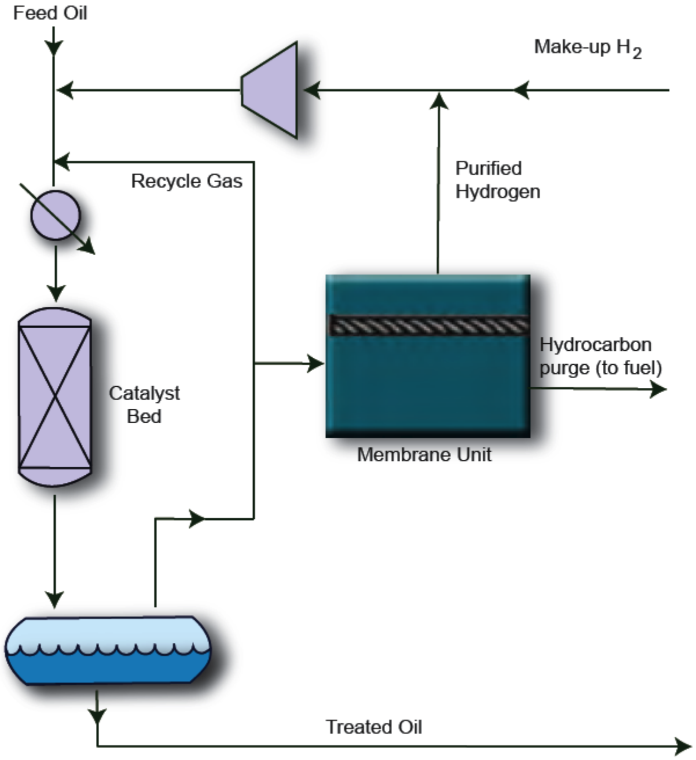

Figure 5: Schematic diagram for hydrogen recovery using VaporSep-H2™ membrane [27].

those of any polymeric or porous inorganic systems, which was achieved using an ionically cross-linked multilayer polymer thin membrane (layer-by-layer assembled PEI/PAA). They claimed that the membrane performs beyond Robeson's upper bound limit despite being made of only homogenous polymer. The membrane separates molecules based on size. The smaller ones such as hydrogen pass through, while larger ones such as CO_2 and N_2 are slowed down. Kim *et al*. also claimed that this unique thin film overcomes the drawbacks of common polymeric membranes (i.e., low selectivity and poor mechanical properties), making it a significant advance in polymeric membranes for gas separation This invention is under the process of patent and it has a large potential to separate H_2 from light gases, and for the purification of natural gas, sour gases etc.

For the recovery of H_2 from refinery streams, membranes are the simplest, most reliable, and economic methods. Refinery hydrogen requirements are growing due to the increased use of hydro treating (to remove sulfur) and hydrocracking (to convert heavy hydrocarbons to lighter, higher-value fuels). Residual gas from these processes contains a significant amount of unused hydrogen at high pressures, and membranes provide an economic recovery method. MTR's hydrogen-permeable. VaporSep-H2™ membranes can provide 90% to 99% pure hydrogen with greater than 90% recovery [27]. Figure **5** shows a schematic diagram for hydrogen recovery using VaporSep-H2™ membrane for refinery streams to separate hydrogen from refinery streams.

VaporSep-H2™offers a simple method for recovering hydrogen from refinery streams. Hydrogen permeates preferentially through the membrane, producing a purified hydrogen "permeate" stream and a hydrocarbon-enriched "residue" stream.

The available pressure for the purified hydrogen depends on the feed conditions, and can be as high as 1500psi. The hydrocarbon-enriched "residue" is recovered at close to the feed pressure, and can be sent directly to fuel, or treated for liquefied petroleum gas (LPG) recovery if these components have value.

China's first hydrogen recovery unit by membrane technology from refinery's hydrocracking dry gas and PSA resolving gas was run successfully as a trial production plant in Sinopec Zhenhai Refining Plant [28].

2.5. Oxygen Production (Enriched Oxygen Production, Nitrogen Purification)

Oxygen is having very important role in the life of human being and all the living and non-living objects available on the earth. Membrane oxygen plants are finding increasingly broad application in various industries all over the world. Still, oxygen production by membrane systems is not developed well to meet the requirements. With moderate requirements to oxygen purity in product - up to 30-45%, membrane systems generally prove more economically sound than adsorption and cryogenic systems. Most of the industrial O_2 applications require purity higher than 90%, which is easily achieved by adsorption (PSA, vacuum swing adsorption (VSA) and PSA/VSA) or cryogenic technologies with >99% oxygen, but not by a single-stage membrane process. New materials are being developed aimed at higher permeability and selectivity than conventional polymeric membranes. Promising oxygen permeation has been obtained in many perovskite systems. The dense perovskite type membranes transport oxygen as lattice ions at elevated temperatures with infinite selectivity ratios of O_2 over N_2 [29, 30].

Membrane air separation is now widely accepted as an economic process to produce moderate purity streams containing up to 99.5% nitrogen or 30-50% oxygen [31]. The commercial production of nitrogen was started in the mid-1980s when Generon introduced a membrane system to separate nitrogen from air. This first air separation system was based on poly (4-methyl-1-pentene) (TPX) membranes with an oxygen/nitrogen selectivity of about 4. These membranes could only produce 95% nitrogen, but in 1990, Generon, Praxair and Medal had all produced the second generation of tailor-made membranes having selectivities of 6-8 and were able to generate a 99% nitrogen product [32].

Oxygen enriched air with oxygen content higher than in atmospheric air is used in many applications worldwide such as medical devices, steel and chemical manufacturing, and most recently carbon capture on a large scale. The size of the operation and the required purity of oxygen determine the method of separation [33].

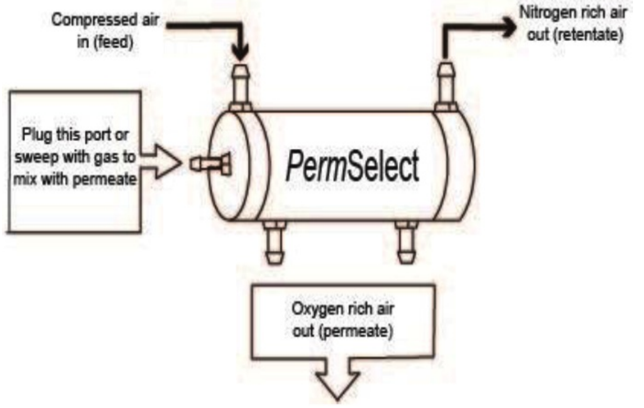

Figure 6: Oxygen-enrichment/nitrogen-enrichment using a PermSelect® membrane module [35].

Grasys produces high-efficiency system for oxygen production from air on the basis of membrane technology. Membrane oxygen plants allow producing oxygen with the purity of up to 45%; the application of these systems is considered extremely economically expedient. Companies involved in fish, shrimps, crabs and mussels farming use membrane oxygen plants for incubation support purposes [34].

PermSelect® silicone membranes are common and simple examples for oxygen enrichment and nitogen enrichment. It was noticed that oxygen is roughly twice as permeable as nitrogen, when supplying a feed of compressed air to a PermSelect® module. In a single pass, the separation properties of silicone can get a maximum permeate oxygen up to a concentration of 34% and retentate nitrogen concentration as high as 99.9%. Figure **6** shows oxygen-enrichment/nitrogen-

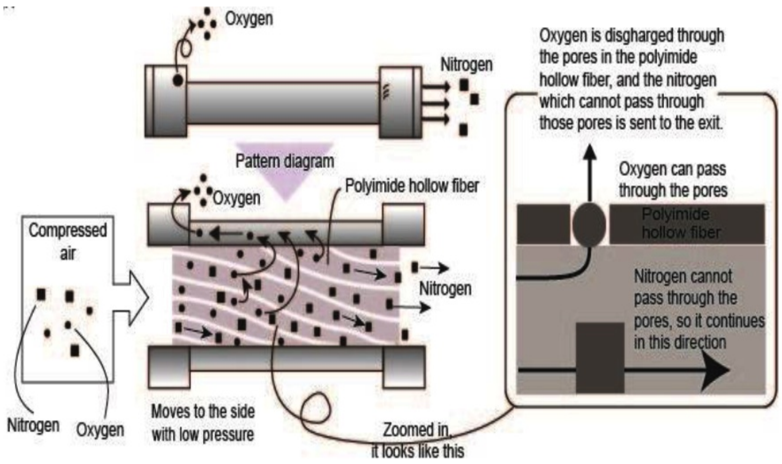

Figure 7: Separation membrane mechanisms [36].

enrichment using a PermSelect® membrane module [35].

A functional polymer such as polyimide shows oxygen selective gas permeability. These polymers are used in a variety of systems for producing pure nitrogen from air. Figure **7** shows mechanism of the oxygen and nitrogen separation membrane.

The Essential Chemical Industry (ECI) reported that oxygen and carbon dioxide diffuse more rapidly than nitrogen and argon through a polymeric membrane {often made of poly(methylpentene)} and this allows the remaining gas to become richer in nitrogen and argon. Eventually, the nitrogen concentration becomes over 95% [37].

2.6. Olefin-Paraffin Separation

Light olefins such as ethylene and propylene are very important to petrochemical industries. These chemicals are the source of main raw materials for many essential chemicals and products for industrial and domestic consumptions. Approximately, 80% of ethylene produced in the United States and Europe is used to create ethylene oxide, ethylene dichloride, and polyethylene. Ethylene oxide is a key raw material in the production of surfactants, detergents, and automotive anti-freeze solution. Propylene is a raw material for a large variety of products including polypropylene, which is considered as a versatile polymer used in packing and other important applications such as textiles, laboratory equipment, and automotive components. Propylene is the second highest volume petrochemical feedstock after ethylene. The production of polymers and other special chemicals from mono –olefins such as propylene requires the olefin to be extremely pure (>99.9%), and since light olefins are commonly produced together with paraffin hydrocarbons, i.e. ethane and propane, the techniques for separating both hydrocarbons are of primary importance to the petrochemical industry [38].

In general, olefin/paraffin separation technique is carried out by distillation units. It is reported that over 2000 articles (including patents which are about one third) have been published on the use of membranes for hydrocarbon separations and removals over the span of the 30 years before 2004 [39]. In other words, it reflects that researchers are still looking into the enhancement of the available membrane technology for olefin/paraffin separation before possible commercialization. The membranes used for this technology can be classified into three main groups: i) polymeric; ii) inorganic; and iii) facilitated transport membranes.

2.6.1. Polymeric Membrane

A large number of articles on the use of polymeric membranes for olefin/paraffin separation, as well as those for pervaporation for hydrocarbon separation have been reported in the literature [40]. Glassy, cellulosic, and rubbery polymeric membranes are widely used for olefin/paraffin separation. The properties of both permeant molecules and polymers; such as size and shape of permeating molecules and the polymeric structure such as packing density and rigidity control the permeation and separation of hydrocarbons. In general glassy polymers have been studied intensively for olefin/paraffin separation, including the separation of aromatic, alicyclic, and aliphatic hydrocarbons. Rubbery polymers are mainly used in gas/vapor separation applications such as hydrocarbon extraction from their aqueous solutions. Asymmetric hollow fiber membranes are attractive than other membrane configurations due to their high flux.

2.6.2. Inorganic Membrane

Inorganic membranes are promising and becoming commercial to separate gas mixtures. It is well known that inorganic membranes have appreciable thermal and chemical stability including higher gas fluxes as compared to polymeric membranes. Basically there are two types of inorganic membranes i.e. dense (nonporous) and porous membranes. Commercial porous inorganic membranes are ceramic membranes, such as alumina, silica, titanium, and glass and non-porous metals, such as stainless steel and silver. These membranes have shown high permeabilities and low selectivities. On the other hand, dense inorganic membranes are very specific in their separation behaviors. For example Pd metal based membranes are hydrogen specific and metal oxide membranes are oxygen specific. Potential membrane materials such as palladium and its alloys are widely studied and reported.

Ma *et al*. [41] separated propylene/ propane mixture by using high quality carbon molecular sieve (CMS) membranes prepared on mesoporous γ-alumina supports at different feed pressures (up to 100 psia), feed compositions, and permeation temperatures. The membrane exhibits a mixture propylene/propane selectivity of above 30 under the studied conditions, with no plasticization effect observed at feed pressures up to 100 psia (~700 kPa). In another study Ma *et al*. [42] reported that the separation of propylene/propane through ultrathin (down to 300nm) CMS membranes supported on mesoporous γ-alumina support. It was noticed that the 520nm CMS membrane exhibited its C_3H_6/C_3H_8 mixture selectivity around 31 and permeability of C_3H_6 was around $1.0x10^{-8}$ mol m^{-1} s^{-1} Pa^{-1}.

Kwon *et al*. [43] discussed the high-quality nanoporous molecular sieve membranes that distinguish molecules based on the size difference between propylene and propane. The membranes exhibited unprecedented propylene/propane separation performances, which can potentially lead to the significant savings in energy.

Air products and Chemical Inc. developed the selective surface flow (SSF) membranes. It consists of a thin layer (2– 3 mm) of nanoporous carbon supported by a macroporous alumina tube [44]. The effective pore diameter of the carbon matrix is 5–7 Ǻ [45]. The membrane separates the components of a gas mixture by selective adsorption–surface diffusion–desorption mechanism [46].

Carbon molecular sieves (CMS) membranes open a new avenue for the separation of olefin/paraffin. These membranes are usually prepared by the pyrolysis of polymeric precursors for which polyimide materials are frequently used. CMS composite membranes composed of a selective carbonized layer on top of an inorganic support seem to have excellent mechanical strength but suffer from complicated preparation procedures.

Carbon molecular sieve (CMS) membranes have been studied for more than 20 years as a promising candidate for energy-efficient gas separation technology. Much interest has been shown in the preparation of carbon membranes for separation of gas mixtures such as CO_2-N_2, O_2-N_2 and CO_2-CH_4 [47]. Ma *et al*. [48] reported the physical characteristics and gas transport properties for a series of pyrolyzed membranes derived from an intrinsically microporous polyimide containing spiro-centers (PIM-6FDA-OH) by step-wise heat treatment to 440, 530, 600, 630 and 800°C, respectively. At 440°C, the PIM-6FDA-OH was converted to a polybenzoxazole and exhibited a 3-fold increase in CO_2 permeability (from 251 to 683 Barrer) with a 50% reduction in selectivity over CH_4 (from 28 to 14). At 530°C, a distinct intermediate amorphous carbon structure with superior gas separation properties was formed. A 56% increase in CO_2-probed surface area accompanied a 16-fold increase in CO_2 permeability (4110 Barrer) over the pristine polymer.

2.6.3. Facilitated Transport Membrane

In general, the separation of olefin/paraffin systems is carried out by low temperature distillation and extractive distillation. These systems are expensive, energy consuming and only attractive for streams containing high amounts of olefins. This provides an incentive to develop cost effective separations, e.g. membrane-based separations like gas–liquid membrane contactors. Gas–liquid membrane contactors offer a unique way to perform gas–liquid absorption processes in a controlled way: gas and liquid flow can be controlled independently, giving large operational flexibility [49]. Separation of the olefin /paraffin mixture is achieved by the selective absorption of olefins in a concentrated silver salt solution, a separation based on the ability of silver ions to complexate with the double bond of the olefin [49, 48].

Nymeijer *et al*. [50] reported that the selective composite membranes containing sulfonated poly(ether ether ketone) (SPEEK) layers on top of a hydrophobic, polypropylene support can be applied as absorber and desorber in a gas–liquid membrane contactor system for the separation of paraffins and olefins. The water present in the absorption liquid swells the hydrophilic polymer sufficiently, making the membranes olefin-selective. As a result, even at high liquid velocities where the membrane determines the selectivity of the process, high selectivities can be obtained in combination with high productivities. Continuous contact between the absorption silver nitrate solution and the SPEEK layer prevents the layer from drying out and subsequent loss of selectivity. Previously unknown high ethylene/ethane selectivities (>2700) are obtained in combination with reasonable ethylene productivities (7.6x $10^{-10}cm^3/cm^2$ s Pa ($1x10^{-6}$ cm^3/cm^2 s Hg). Due to carrier poisoning and short life span of the polymeric membranes, this technique is still not feasible for the commercialization for olefin/paraffin separation.

3. APPLICATIONS

3.1. Natural Gas Treatment

Natural gas consists primarily of methane as the prevailing component but it also contains considerable amounts of light and heavier hydrocarbons as well as contaminating compounds such as CO_2, N_2, Hg, He, H_2S. Thus, the impurities must be removed to meet the pipe-line quality standard specifications as a consumer fuel, enhance the calorific value of the natural gas, avoid pipelines and equipment corrosion and further overcome related process bottle necks.

Gas wells typically produce raw natural gas by itself, while condensate wells produce free natural gas along with a semi-liquid hydrocarbon condensate. Whatever the source of the natural gas, once separated from crude oil (if present) it commonly exists in mixtures with other hydrocarbons; principally ethane, propane, butane, and pentanes. In addition, raw natural gas contains water vapor, hydrogen sulfide (H_2S), carbon dioxide, helium, nitrogen, and other compounds [50].

The actual practice of processing natural gas to pipeline dry gas quality levels can be quite complex, but usually involves four main processes to remove the various impurities:

- Oil and Condensate Removal.
- Water Removal.
- Separation of Natural Gas Liquids.
- Sulfur and Carbon Dioxide Removal.

Figure **8** shows a schematic block flow diagram of a typical natural gas processing plant. It shows the various unit processes used to convert raw natural gas into sales gas pipelined to the end user markets. The block flow diagram also shows how processing of the raw natural gas yields byproduct sulfur, byproduct ethane, and natural gas liquids (NGL) propane, butanes and natural gasoline (denoted as pentanes +) [51].

Natural gas processing is a complex industrial process designed to clean raw natural gas by separating impurities and various non-methane hydrocarbons and fluids to produce what is known as pipeline quality dry natural gas. Generally, natural gas contains low molecular weight hydrocarbon compounds; examples include methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}), as well as acid gases such as CO_2, H_2S and water. Composition of natural gas varies substantially from source to source. Non-hydrocarbons such as carbon dioxide, nitrogen, helium (rarely), and hydrogen sulfide must also be removed before the natural gas can be transported.

"UOP is focused on developing technologies that help natural gas producers maximize their output at minimal cost," said Rebecca Liebert, vice president and general manager of Honeywell's UOP Gas Processing and Hydrogen business unit. "UOP's new Separex Flux+ membrane element increases gas processing capacity over existing technology, translating to increased revenue and reduced operating costs for natural gas producers" [52].

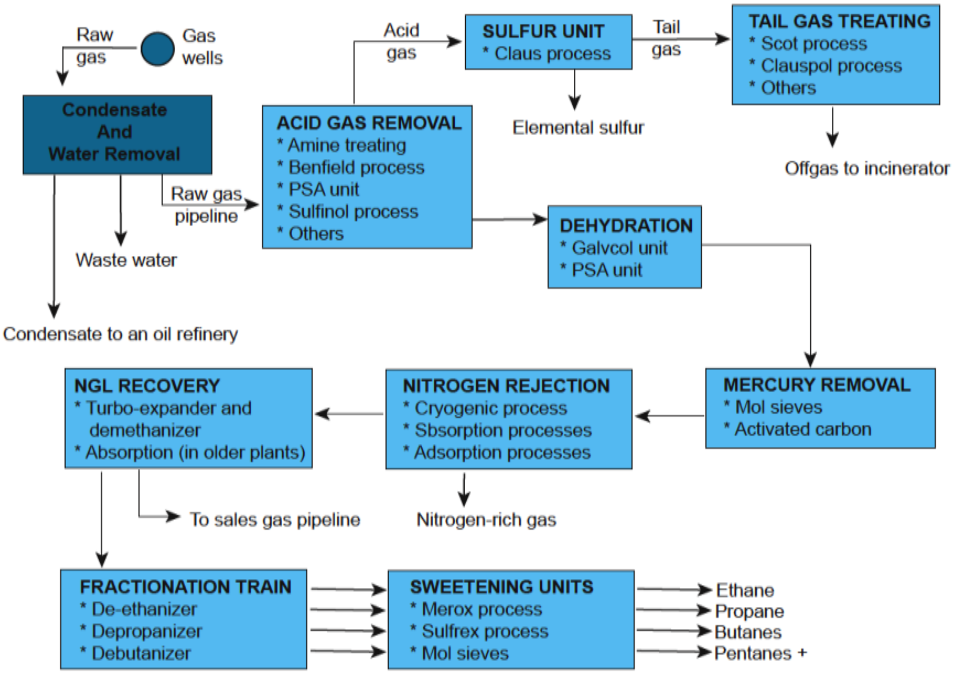

Figure 8: Schematic block flow diagram of a typical natural gas processing plant [51].

3.1.1. Separation of C_{+3} Hydrocarbons

Cooling and condensation, or lean oil absorption is the current technology to separate heavy hydrocarbons from natural gas. To recover the individual components by fractional distillation and storage is very costly. The alternative can be membrane gas separation. The competitiveness of membrane system in this application is sensitive to the selectivity of the membrane for propane, butane, and other hydrocarbons. These selectivities, in turn, are dependent on the pressure and composition of the gas being processed [6]. Currently, silicon rubber membranes with a typical mixed-gas propane/methane selectivity of 3-5 and a butane/methane selectivity of 5-10 are used.

Walter [53] patented a process for separating ethane and other higher hydrocarbons from a natural or produced gas stream, having methane as its major constituent. A rubbery permselective membrane, having propane/methane selectivity of 8 or above, is contacted on its feed side with a gas mixture typically containing methane, ethane, propane, butane, and small amounts of other hydrocarbons, water vapor, hydrogen sulfide and carbon dioxide. Carbon dioxide, water vapor, ethane and the other higher hydrocarbons permeate preferentially through the membrane, and the retentate stream is correspondingly enriched in methane. The membrane was a multilayer membrane comprising a microporous support onto which is coated an ultrathin permselective layer of a rubbery polymer. Polymers that may be used include, but are not limited to, nitrile rubber, neoprene, polydimethylsiloxane (silicone rubber), chlorosulfonated polyethylene, polysilicon-carbonate copolymers, fluoroelastomers polyvinylchloride, polyurethane, cis-polybutadiene, cispolyisoprene, poly(butene-1), polystyrene-butadiene copolymers, styrene / butadiene / styrene block copolymers, styrene / ethylene / butylene block copolymers, thermoplastic polyolefin elastomers, and block copolymers of polyethers and polyesters.

Reyes *et al*. [54] invented a membrane selective for the separation of methane ("CH_4") from higher carbon number hydrocarbons ("HHC"s) in streams containing both methane and higher carbon number hydrocarbons (e.g. ethylene, ethane, propylene, propane, etc.) utilizing a zeolitic imidazolate framework ("ZIF") material. Preferably, the stream to be separated is fed to the present process in a substantially gaseous phase. In preferred embodiments, the current invention is utilized in a process to separate methane from higher carbon number hydrocarbons in natural gas streams. Figure **9**(**a**) shows a schematic diagram of a conventional gas conditioning unit.

The schematic diagram Figure **9**(**a**) is the application for associated gas, the low pressure gas produced as a byproduct of oil production. The gas is usually compressed and dried by glycol absorption and

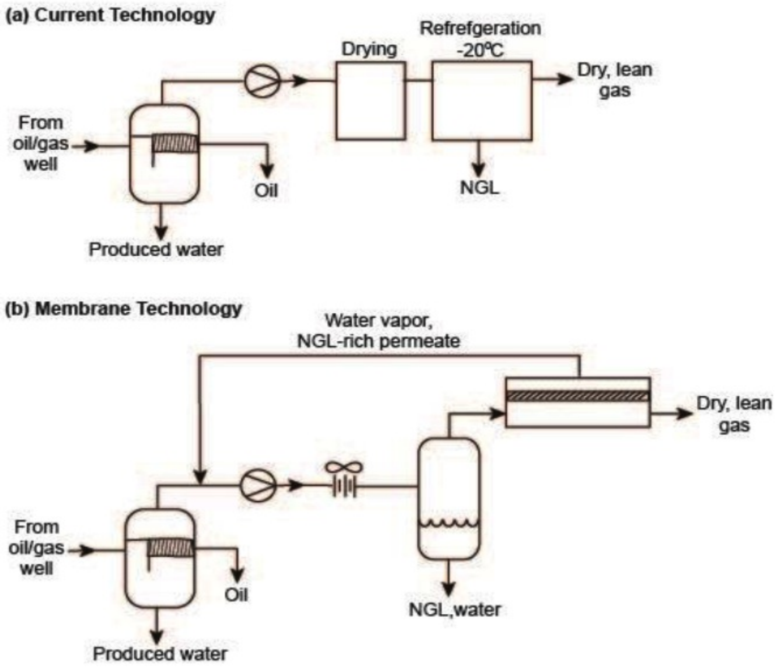

Figure 9(a): Current conventional technology and, (**b**) the membrane approach to the removal of water and heavy hydrocarbons from associated gas [55].

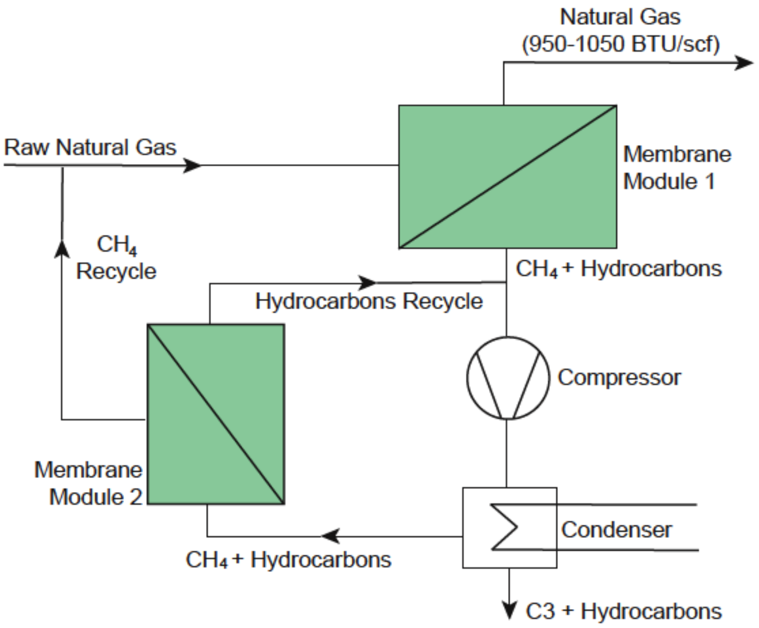

Figure 10: Design of a membrane system for separation of heavy hydrocarbons from natural gas [8].

then cooled to -20°C in a propane refrigeration plant: dry, lean gas is produced. The membrane process is shown in Figure **9**(**b**). After compression and cooling to about 30°C by an air cooler, a portion of water and C_{3+} hydrocarbons is condensed and recovered.

The process design for removing heavy hydrocarbons from raw natural gas is relatively simple, as shown in Figure **10** [8]. The standard design is for a single membrane separation step to recover and concentrate the majority of the heavy hydrocarbons into the permeate stream. This stream is then compressed and a simple condenser stage is used to remove the heavy hydrocarbons from the methane that passed through the membrane. The methane is then recirculated to the feed.

Engine fuel gas conditioning is currently the most widely used application of membranes for heavy hydrocarbon separation [56].

A flow diagram of the membrane to condition raw natural gas to be used in gas engine is shown in Figure **11**. The gas, at a pressure of100 psig, is compressed to 1000 psig and cooled in an air-cooled after cooler. The heavy hydrocarbons are condensed and recovered as a liquid [57].

Liquefied petroleum gas (LPG) contains chemical compounds different from natural gas even though they are both hydrocarbons. LPG consists of propane and/or butane. Propane (C_3H_8) contains three carbon atoms and eight hydrogen atoms. MTR's LPG-Sep™ systems efficiently recover LPG from associated gas —

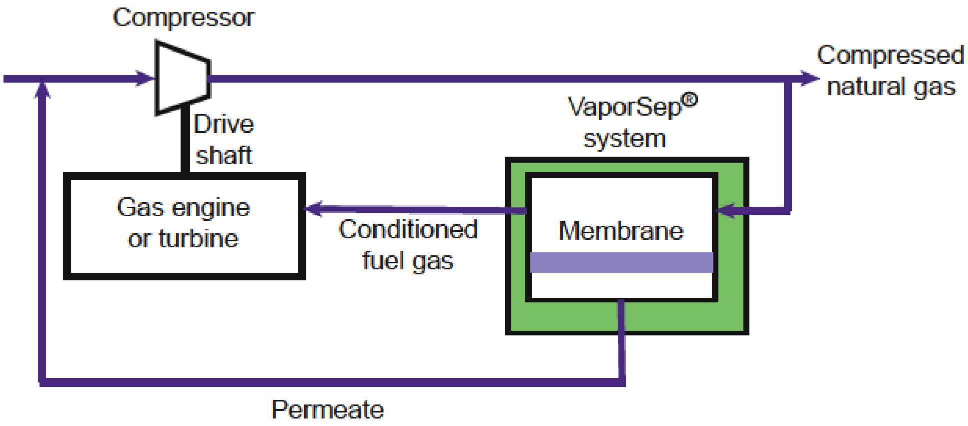

Figure 11: Block diagram of a membrane fuel gas conditioning unit used for a field gas compressor engine [57].

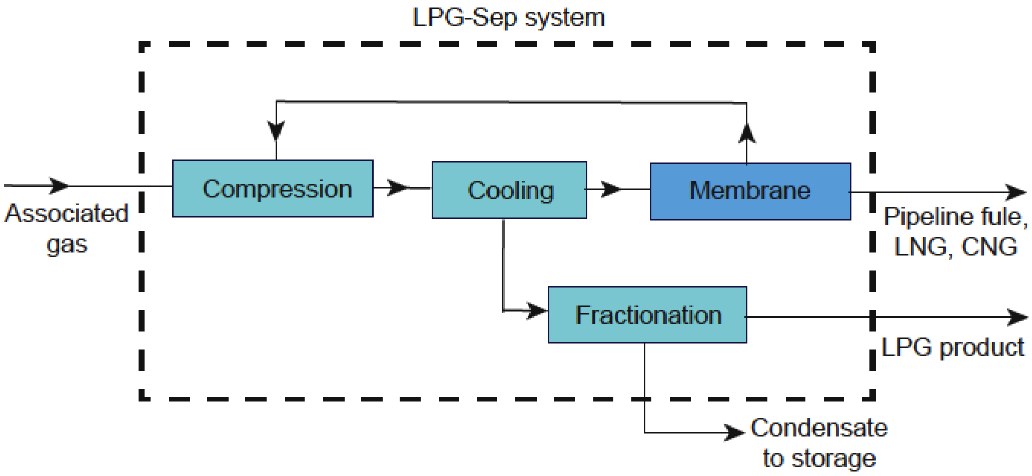

Figure 12: MTR's LPG-Sep™ system [58].

an attractive option since LPG is easy to store and transport and can often be used locally. Figure **12** shows the schematic diagram. Associated gas is rich in heavy hydrocarbons, so removing LPG and heavier fractions from the flare gas massively reduces carbon emissions and the bulk of the BTU value in the gas is recovered for local use. In some situations use of LPG-Sep™ enables the remaining methane to be easily recovered in simple LNG or CNG units, to be used as fuel gas or to be piped to a nearby consumer [58].

LPG-Sep™ Process, LPG-Sep™ unit operations comprise (i) Conventional compression to 350psi;

a. Cooling and C_{3+} condensation by chilled water at 60°F.

b. Membrane gas separation to lean Out of gas.

c. Fractionation to produce spec LPG and condensate.

U.S. Energy Information Administration revealed that there were 493 operational natural gas processing plants till 2010 in the United States with a combined capacity of 77 billion cubic feet (bcf) per day [59].

3.1.2. Dehydration

Raw natural gas requires dehydration in order to avoid the formation of hydrates, reduce corrosion and meet sales specifications before it can be sold to the market and be used to heat homes, run hot water tanks and fuel barbeques. Until now, a process using a chemical called glycol has been used for natural gas dehydration.

The most widely used technology for dehydration is through absorption by diethylene or triethyleneglycol [60].

Gas dehydration processes remove water vapor from natural gas. Removing water vapor prevents hydrate formation and corrosion, and maximizes pipeline efficiencies. Natural gas dehydration is the process of removing water vapor from a natural gas stream to lower the water dew point of natural gas at which water will condense from the stream. In general most widely-used technology is to absorb the water with a liquid solvent flowing in countercurrent inside columns.

There are two types of contactor columns.

a. Bubble cap column.

b. Packed column.

Bubble cap column usually consists of 4 to 12 trays. The greater number of trays, more moisture can be removed. Each tray has opening with bubble cap bolted over them. The up flowing gas is forced through these caps and bubbles through the down flowing glycol. The gas gives up water and becomes dryer as it passes upward through each subsiding tray. The glycol becomes more saturated with water as it flows downward over each tray.

Packed column utilizes the same process as tray column where liquid glycol flows down over the packing and the gas flows up through the packing. Packed columns are less expensive however they tend to channel and have poor flow distribution. "Channeling" occurs when liquid glycol flows in streams throughout the random packing. Channeling limits the surface area where the glycol and gas come into contact.

Beside above mentioned method, there are other methods also. Methanol injection gas dehydration method involves the injection of methanol in the gas stream to absorb water. The methanol and water mixture is disposed of in the environmentally safe manner. Methanol injection is rarely used on dehydration because it is toxic, expensive and the disposal can be complicated.

Another gas dehydration method uses solid bed desiccant instead of liquid desiccant. The common example of this is the molecular sieves which are made of pellets that are electronically poured to water. When placed in line with the gas stream the polarity of the pellets attracts the water out of the gas into molecular size pore on the surface of the pellets. The water is held there until the pellets are saturated. The pellets themselves are then dehydrated by a small volume of heated gas so that they can be used again.

In the last ten years, research has been developing new dehydration systems based on selective membranes in order to lower plant costs, increase separation efficiency and reduce emissions. The membrane system proved more cost-effective for low feed gas flow rates and more environment-friendly. Membrane dehydration technologies are currently commercially available: however these technologies are hampered by performance degradation, high energy consumption, hydrocarbon losses, equipment complexity, and high capital costs. Air Products and Petreco seek to resolve these imperfections, developing hollow-fiber membranes for natural gas dehydration [40, 61]. Susceptibility of the membrane material (polymeric) to plasticization by water is also a main problem [62]. The potential for the application of membranes to large scale dehydration of natural gas is large, and so far there are some successful units that have been reported for commercial use already [62-64].

Figure **13** represents the schematic for natural gas dehydration by membrane. If the pressure of natural gas is low, a compressor and an after cooler are needed between the filter and the membrane. If the dehydration system has low pressure fuel consumption system, the design shown in Figure **13**(**a**) would be suitable. Most plants do not need that much fuel gas, and the permeate gas should be recompressed, as shown in Figure **13**(**b**).

Mostly polyimide and sulfonated polymers are used in the dehydration process. However, there are some limitations such as materials susceptible to plasticization due to water and methane loss.

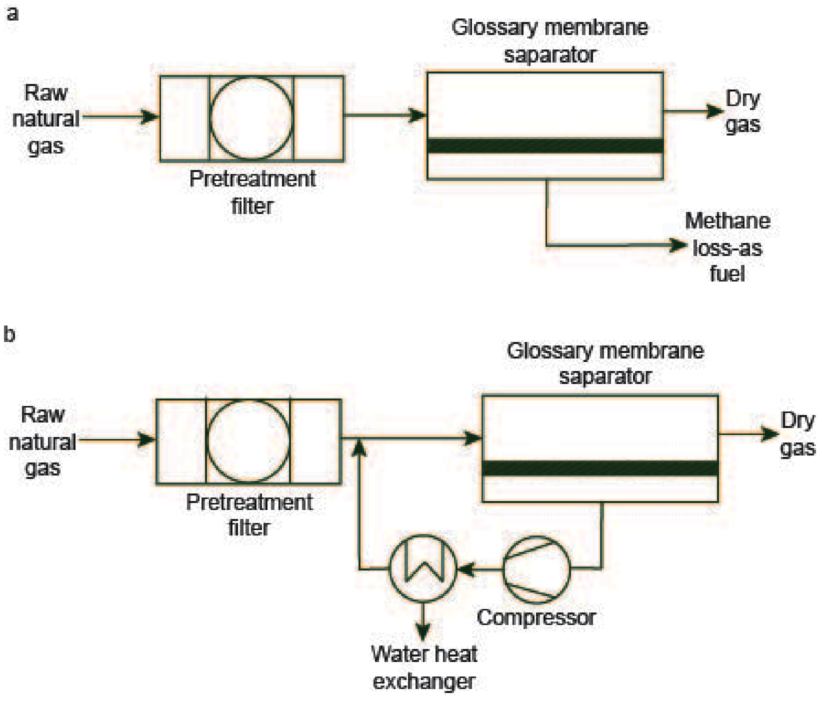

Figure 13: Schematic of natural gas dehydration by membrane under different situations [62].

Lin *et al*. [64] reported hydrophilic microphase-separated block copolymers (Pebax®) with promising H_2O/CH_4 separation properties, which were made into industrial thin film composite membranes. PEEK-SEP™ hollow fiber membranes can be used for vapor phase dehydration processes. PEEK-SEP™ membranes allow for highly selective and cost efficient separation of water vapors from numerous gas streams and vapor mixtures [63].

Morgan *et al*. [65] from Air Products patented a hollow fiber dehydration method and apparatus using an internal sweep of the permeate side by a dry gas product. This invention works well under high operation pressures (above 7 bars).

Zhao *et al*. [66] built a pilot scale air dehumidification system which was based on PAN/PDMS hollow fiber membrane modules. It was claimed by Zhao *et al*. that this membrane system is better than polysulfone (PSF) fibers in comparison with materials costs made by Air Product US or Generon UK. Lin *et al*. [67] discussed the feasibility of membrane for dehydration of natural gas.

3.1.3. Dew Pointing of Natural Gas

The hydrocarbon dew point is the temperature (at a given pressure) at which the hydrocarbon components of any hydrocarbon-rich gas mixture, such as natural gas, will start to condense out of the gaseous phase. It is often also referred to as the Hydrocarbon dew point (HDP or the HCDP). The maximum temperature and the pressure at which such condensation takes place are called the "cricondentherm". The hydrocarbon dew point is a function of the gas composition as well as the pressure.

Some liquids may condense out in the gas pipeline, if the hydrocarbon dew point of pipelined natural gas is too high. It will degrade the heating value of the remaining gas, and increases the potential for problems in the pipeline transmission systems. This will cause problems for the end users of the gas such as industrial combustion equipment and household gas appliances.

By managing hydrocarbon dew point, hydrocarbon condensation can be prevented in cold spots under rivers and lakes where the liquids condensed in the low temperature areas and then often move as a slug through the system, over pressuring the pipe, and overpowering liquid handling facilities, flowing into compressors and end user sales points. Removing pipeline liquids helps prevent pipe corrosion in the low areas where water is trapped under the hydrocarbon liquid layer and slowly destroys the pipe integrity.

There are a number of methods accepted for measuring HCDP;

a. Cooled mirror dew scope.

b. Gas chromatography.

c. Optical condensation dew-point hygrometer, such as the Michell Instruments Condumax II.

But these methods have their own limitation and are not perfect as well as expensive. Membrane technology can open a new avenue for lowering the dew point of natural gas. Membranes are usually glassy polymers, and have very high selectivities for water, generally orders of magnitude greater than both CO_2 and CH_4. Liu *et al*. [68] [patented a membrane prepared from the polymer of intrinsic microporosity (PIM) to selectively remove hydrocarbons from C_3 to C_{35} to control the dew point of natural gas.

MTR developed membranes which can reduce both hydrocarbons and water dew point in one process. The schematic diagram of the whole process is described in Figure **14** [69].

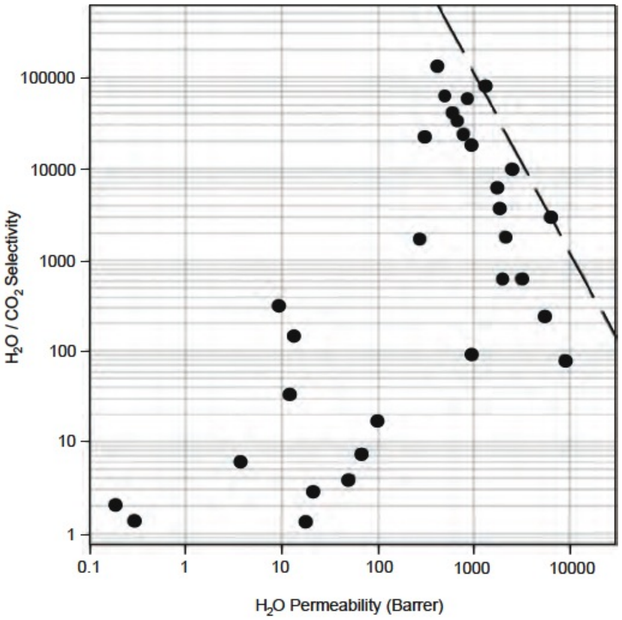

Figure 14: Both hydrocarbon and water dew point reduced in one process [69].

Borsig Membrane Technology GmbH, a member of the BORSIG group developed a membrane process to adjust the dew point in gas processing [70].

It has been estimated that a simple economical membrane system could lower the dew point of the raw gas by 30-50°C [71]. This approach has been commercialized by Air Products using their Prism® polysulfone membrane.

3.1.4. Mercury Removal

Mercury in natural gas is present predominantly as elemental mercury. However, in theory, the mercury could be present in other forms: inorganic (such as $HgCl_2$), organic (such as CH_3HgCH_3, $C_2H_5HgC_2H_5$) and organic-ionic (such as $ClHgCH_3$) compounds. The primary reason for removing mercury from natural gas is to protect downstream aluminum heat exchangers, such as those used in cryogenic hydrocarbon recovery natural gas plants and in natural gas liquefaction plants. Mercury has caused numerous aluminum exchanger failures. It amalgamates with aluminum, resulting in a mechanical failure and gas leakage. Since the level of mercury that can be tolerated is not established, most operators want to remove it “all.” That is, remove it to a level where it cannot be detected with the available analytical capability. Currently, this means reducing the mercury level to the less than 0.01µg/Nm^3 which corresponds to about 1ppt by volume [72].

Mercury is removed from gas by an irreversible chemical reaction with a metal sulfide. The metal sulfide may be formed *ex-situ* or *in-situ* by the reaction between a mixed metal oxide and hydrogen sulfide by means of a desulfurization reaction. The resulting compound, mercuric sulfide, is one of the most stable forms of mercury and can be readily recycled through established routes within the metal recovery industry.

$$M_xO_y + H_2S \rightarrow MS_z + H_2O \quad (1)$$

Metal Oxide Reaction with H_2S

$$MS_x + Hg \rightarrow MS_{(x-1)} + HgS \quad (2)$$

Metal Sulfide Reaction with Hg

UOP offers two ways to remove mercury for the feed gas. UOP HgSIV™ adsorbent can be incorporated into the TSA unit. This regenerative adsorbent can remove mercury to the less than 0.01µg/Nm^3. While this is typically the most economical location for mercury removal, it does expose upstream equipment and piping to mercury. Addition of HgSIV adsorbent does not affect the size of the pretreatment system for moderately contaminated feed gas streams (mercury level less than 100µg/Nm^3). High levels of mercury can also be handled, but there may be a small increase in the overall size of the TSA unit [73].

UOP GB adsorbents and UOP Separex TM membrane systems have been successfully employed to remove mercury, water contaminants and acid gases offshore [74]. On March 12, 2013, UOP LLC, a Honeywell (NYSE: HON) company [75] announced a new membrane element which can extract mercury together with water, sulfur and carbon dioxide from raw natural gas.

3.2. Biogas Treatment

Biogas is considered to be one of the most efficient means of utilizing renewable energy and reducing greenhouse gas emissions. The composition of biogas varies depending on the origin of the anaerobic digestion process, and the main components are methane (CH_4) and carbon dioxide (CO_2) as shown in Table **1** [76].

There are several techniques of upgrading biogas to bio-methane. The most common technologies to process biogas include high-pressure water scrubbing, chemical absorption, PSA, cryogenic separation and membrane separation [77]. Each technology has its advantages and disadvantages that often depend on the place of biogas production, the capacity of processed biogas etc. The advantages of membrane

Table 1: Typical Biogas Composition from Different Sources

Process	Composition (vol. %)*					H_2S/SO_2 (ppm)
	CO_2	CH_4	N_2	O_2	H_2O	
Farm biogasplant	37-38	55-58	<2	<1	4-7	32-169
Sewage digester	38.6	57.8	3.7	0	4-7	62.9
Landfill	37-41	47-57	<1	<1	4-7	36-115

separation mainly include the simplicity of the process, low energy demands, low maintenance requirements, independence from the changes in the biogas composition and no need to use any liquids and to regenerate or eliminate them. On the whole, membrane separation is environmentally friendly. Today, however, most biogas upgrading plants in Sweden are using PSA [77].

3.3. Syngas Treatment

Syngas is produced *via* partial oxidation of a carbon source (coal, natural gas, or biomass) using oxygen (or air) and steam. Syngas produced from gasification or steam methane reforming (SMR) contains mostly hydrogen and carbon monoxide, desirable constituents that are used as feedstock in refineries, chemical processes and power generation. However, a significant amount of CO_2, a greenhouse gas, is also produced as a by-product. Removal of CO_2 is desired due to downstream process requirements or to reduce CO_2 emissions. Until recently, membranes could not be used in these applications because previously available membranes could not separate CO_2 from syngas.

MTR's unique Polaris™ membrane is the first commercially available membrane that separates CO_2 from syngas. The Polaris™ membrane is much more permeable to CO_2 than to other syngas constituents and can be used to recover and purify CO_2 for sequestration, enhanced oil recovery (EOR), or for use in chemical and industrial applications. The resulting CO_2 enriched stream can be produced in gas or liquid form, depending on the final use for CO_2. Figure **15** shows CO_2 removal from Syngas using Polaris™ [78].

4. LIQUID MEMBRANE (EMPHASIS ON IONIC LIQUID MEMBRANE)

Liquids are much more permeable than solid polymers. This is due to the high gas diffusion coefficients in liquids (about 1000 times greater than in solid polymers) and the high gas/vapor solubility's in liquids. Immobilized liquid membranes (ILMs), composed of liquids immobilized in a porous polymer matrix, have high permeabilities and are also highly selective unlike polymer membranes [79]. If membranes are viewed as semipermeable phase separators, then the traditional concept of membranes as polymer films can be extended to include liquids. They are defined as liquid membranes (LMs). Liquid membrane system involves a liquid which is immiscible with the source (feed) and receiving (product) solutions and serves as a semi permeable barrier between these two phases [80, 81]. Conventional supported liquid membrane (SLMs) are composed of porous membranes filled with organic liquids, which often leads to higher permeabilities due to the favorable diffusivities of gases in liquids compared to solids. The major drawback with SLMs is the loss of the liquid *via* evaporation during operation. Use of non-volatile ionic liquids (SILMs) instead of organic solvents overcomes this problem [82].

Ionic liquid based membranes can be classified in four [82, 83] categories.

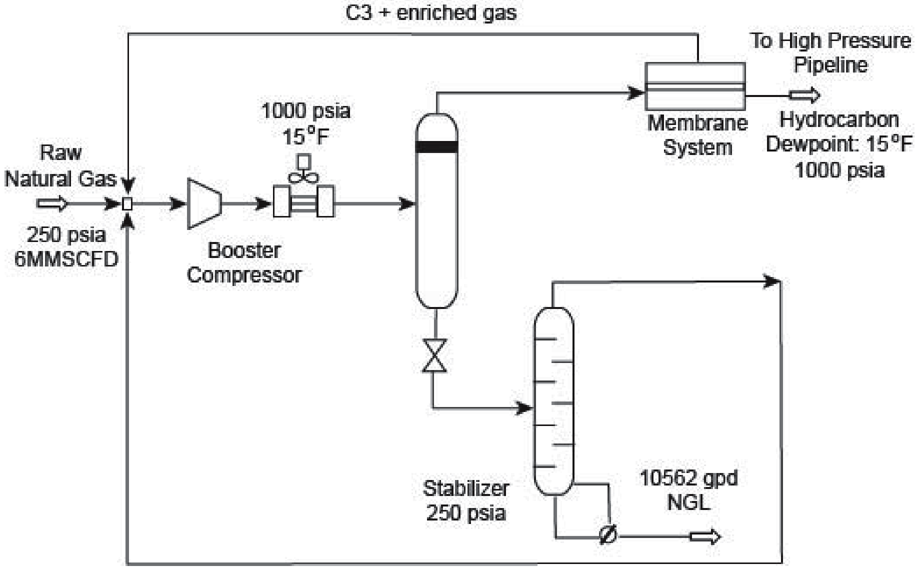

Figure 15: CO_2 Removal from Syngas using Polaris™ [78].

a. Bulk ionic liquid membranes (BILMs).

b. Emulsion ionic liquid membranes (EILMs).

c. Supported ionic liquid membranes.

d. Polymerized ionic liquid membranes.

4.1. Bulk Ionic Liquid Membranes (BILMs)

In the bulk liquid membrane an organic membrane phase separates two aqueous or gaseous phases. Bulk ionic liquid membranes contain ionic liquids as the membrane phase and have relatively high selectivity due to tunable nature of the ionic liquids. For a certain separation task the ionic liquid with the best separation properties can be selected [80].

4.2. Emulsion Ionic Liquid Membranes (EILMs)

Emulsion (or surfactant) liquid membranes are prepared by the intensive mixing of two non-miscible phases (phase 1 and phase 2) and then the addition of some strong surfactant as it is shown in Figure **16**. In this case phase 2 will be the liquid membrane, which can contain facilitating agents that promote separation through formation of chemical complexes from the agents and the components. Fabrication of emulsion liquid membranes is complicated and the decomposition of the emulsions after the separation is also difficult in the case of relatively strong surfactants. So far the application of this type is limited to laboratory scale [84].

Li [85] patented emulsion liquid membrane (ELM). If the aqueous medium is ionic liquid, it is called emulsion ionic liquid membrane (EILMs).

4.3. Supported Ionic Liquid Membranes (SILMs)

SILMs are porous membranes whose pores are filled with ionic liquid (IL). These membranes have been shown to be a very attractive transport media of organic compounds involved in the synthesis of pharmaceutical and fine chemicals. They can also be used for gas separation [86].

SILMs have shown high selectivity for some industrially important gas pair such as CO_2/CH_4, CO_2/N_2 and SO_2/CH_4 with higher permeabilities than polymer membranes. However, both SLMs and SILMs are susceptible if the pressure differential across the membrane is high enough to overcome the interactions between the liquid and the support and, thus, push the liquid through the pores of the support [83]. Numerous concepts in the design and performance of liquid-membrane systems for gas separation and purification have been proposed [87].

Supported ionic liquid membranes have distinctive advantages over conventional supported liquid membranes (SLMs) because the non-volatile viscous nature of ionic liquids means that they cannot be easily displaced from supporting media to cause contamination of the gas streams. Jiang *et al*. [88] measured the permeability of sulfur dioxide (SO_2) in five imidazolium-based ionic liquids supported on the

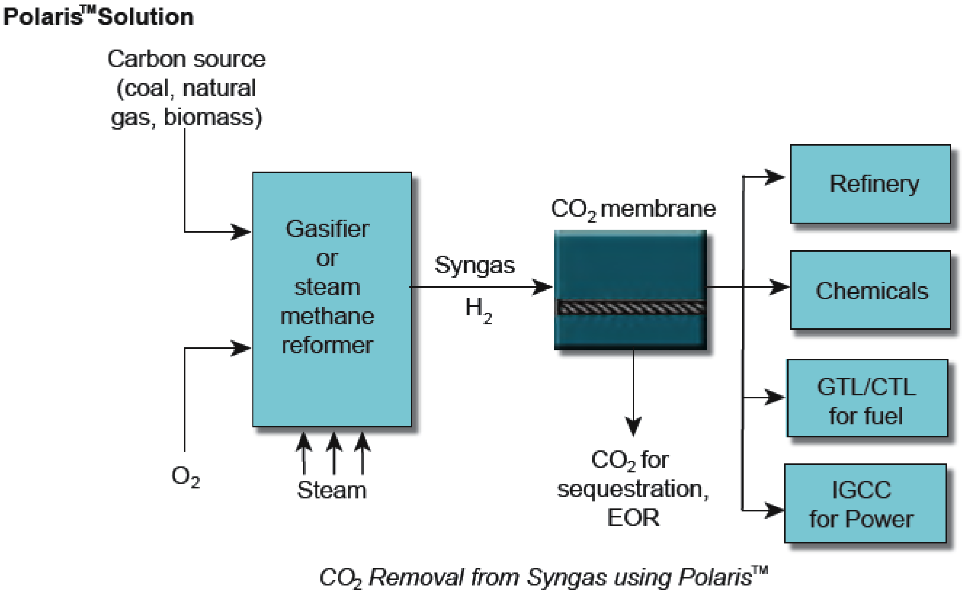

Figure 16: Formation of emulsion liquid membranes [84].

polyethersulfone microfiltration membranes at temperatures from 25 to 45°C and atmospheric pressure. It was observed that under the same conditions, the SO_2 selectivity over CO_2 was 9-19.

4.4. Polymerized Ionic Liquid Membranes

During the last few years, the introduction of the functional groups associated to ILs (i.e. cations such as imidazolium, pyrrolidonium, pyridinium and anions such as tetra fluoroborate, hexafluorophosphate, triflates) into functional polymers is giving rise to a new family of materials with particular properties and interesting applications. By looking at their chemical structures, PILs are polyelectrolytes, polymers whose repeating unit bear an electrolyte group (cation or anion). Although there is not a clear definition for PILs, we will consider those polymers synthesized from IL monomers in opposition to polyelectrolytes which are synthesized from solid salt monomers. PILs present some of the unique properties of ILs (ionic conductivity, thermal stability, tunable solution properties and chemical stability) together with the intrinsic polymer properties [89]. Bara *et al*. [90] used this technique for CO_2/N_2 and CO_2/CH_4 separation and reported very significant data.

Liang *et al*. [83] and Carlisle *et al*. [91] used CILPMs (composite ionic liquid and polymer membranes) fabricated from poly (pyromellitimide-co-4, 4′-oxydianiline) (PMDA-ODA PI) and polybenzimidazole (PBI) in combination with the ionic liquid, [C4mim] [NTf2], to determine permeabilities and selectivities for H_2, N_2, CO, CO_2 and CH_4 over a range of pressures and temperatures. The fabricated CILPMs were shown to maintain excellent mechanical and thermal stability over a wide range of processing conditions. Temperature was shown to greatly affect both permeability and selectivity of the membranes, whilst pressure had less influence. The incorporation of [C4mim] [NTf2] into the membranes was found to significantly increase CO_2 permeation and, therefore, it is anticipated that these CILPMs hold significant potential for CO_2 separation applications. Recently more work has been reported in literature for the gas processing by PILs and it opened a new avenue for the separation of gases in industrial level [92, 93].

5. MEMBRANE CONTACTOR

There are two types of membrane contactors. One is to remove gas from liquid (mostly water). The other is to remove a component (or components) of a gas mixture by absorption into liquid. The latter process can be used for gas separation. Membrane contactors are devices that allow a gaseous phase and a liquid phase to come into direct contact with each other, for the purpose of mass transfer between the phases, without dispersing one phase into the other. For removal of dissolved gases from an aqueous stream, membrane contactors are operated with the aqueous fluid flow on one side of a hydrophobic membrane and a sweep gas and / or a vacuum applied to other side of the membrane. Since the microporous membrane is hydrophobic, the membrane will not allow liquid water to pass through the pore into the gas side of the membrane. In true sense, membrane acts as a support between the gas and liquid phases that allows them to interface at the pore.

In a membrane contactor the membrane acts as an interface between the feed gas and the absorption liquid. For example, in the case of CO_2/CH_4 separation, CO_2 diffuses from the feed gas side through the membrane and is then absorbed in the selective absorption liquid. The loaded liquid circulates from the absorber to the disrober, which can be a traditional stripper or a second membrane contactor, in which desorption of CO_2 occurs. The selectivity of the process is not only determined by the absorption liquid, but also the membrane can play a significant role and contribute to the selectivity, depending on whether selective or non-selective membranes are used. Figure **17** shows the schematic representation of a

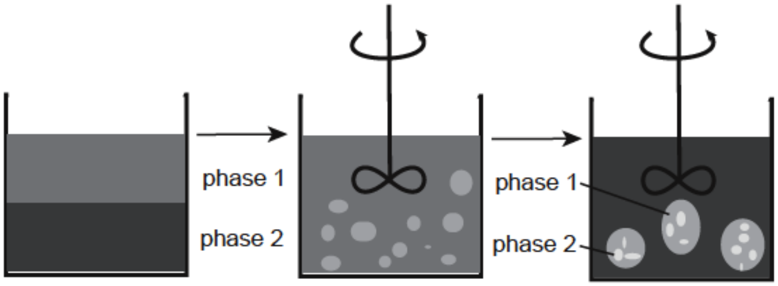

Figure 17: Schematic representation of a membrane contactor for the separation of CO_2 and CH_4 [94].

membrane contactor for the separation of CO_2 and CH_4 [94].

The early development of membrane contactors was aimed at the separation of CO_2. Simons *et al*. [94] used both commercially available porous PP hollow fiber membrane and asymmetric PPO hollow fiber membranes in membrane contactor for the separation of CO_2 and CH_4 (CO_2/CH_4 20/80 vol.%). Monoethanolamine (MEA, 10 wt.% aqueous solution) was used as absorption liquid.

Chilukuri *et al*. [95] described a conceptual design for propylene/propane separation process (300kton/yr. at 99.9 wt.% propylene purity) based on a gas/liquid membrane contactor. A selective silver salt solution ($AgBF_4$) was used as an absorption liquid. The process flow sheet for the required separation is given in the following Figure **18**.

Figure **19** shows propylene/propane separation using a silver salt solution and a gas/liquid membrane contactor as absorber. Gas and liquid phases were separated by a composite membrane consisting of a dense polymeric top layer on a porous support. Propylene and propane diffuse through the membrane, and propylene selectively reacts with silver ions, resulting in a silver-propylene complex. The reaction is based on the ability of silver ions to reversibly form a complex with propylene *via* a combination of a π- and σ bond between silver ions and propylene. Propane is only physically absorbed in the silver salt solution. The propylene rich silver salt solution leaves the absorber at the bottom. By changing the temperature and/or pressure, the equilibrium of complexation can be influenced, allowing desorption of propylene in a desorber. The lean silver solution is cooled and recycled back to the absorber. The propane rich gas

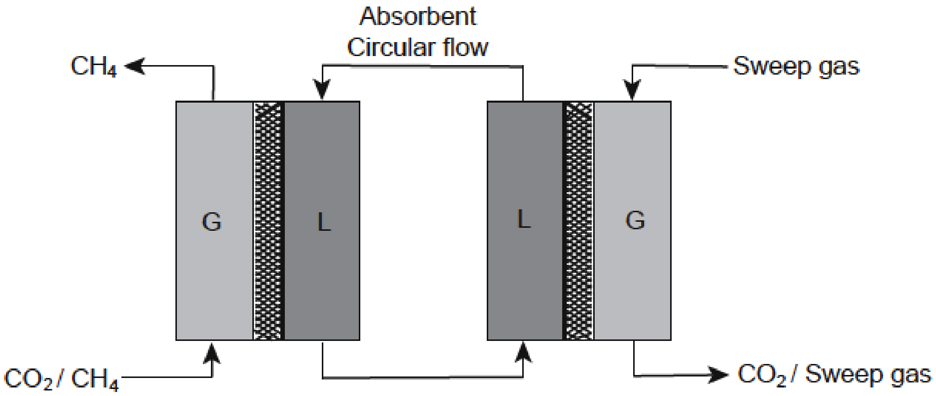

Figure 18: Steps to create process flow sheet [95].

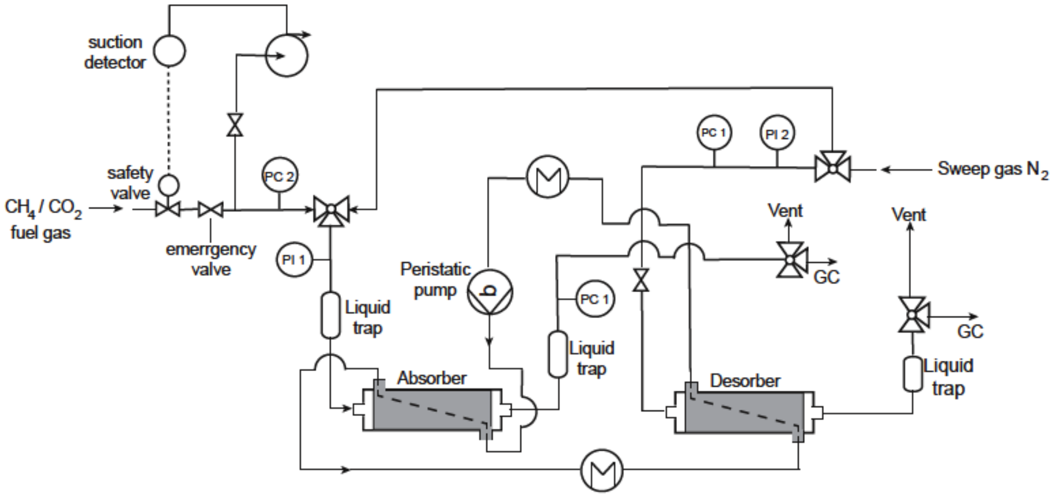

Figure 19: Scheme of propylene/propane separation using a silver salt solution and a gas/liquid membrane contactor as absorber [95].

stream leaves the absorber at the top. Figure **20** shows the functional diagram of propylene / propane separation process based on a gas / liquid membrane absorber using a silver salt solution.

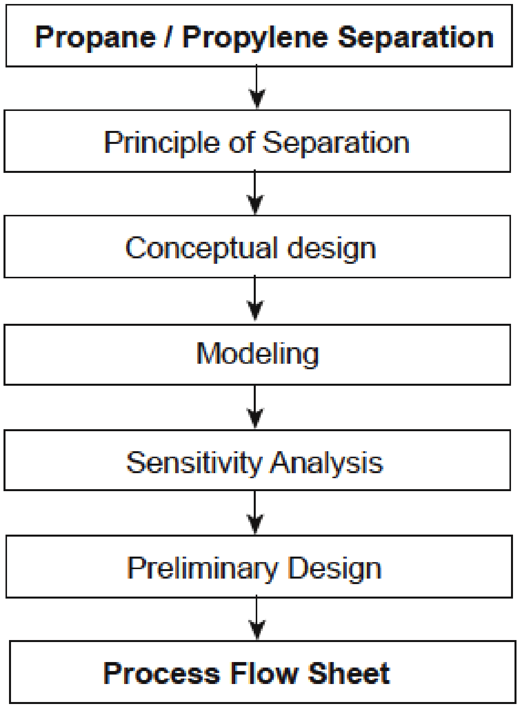

Figure 20: Functional diagram of propylene / propane separation process based on a gas / liquid membrane absorber using a silver salt solution [95].

The conceptual design resulted in the use of a 5.5 M $AgBF_4$ solution at an absorber temperature of 308 K in combination with a desorber temperature of 353K. This gives the best separation of propylene and propane regarding cost and purity. Modeling of the gas / liquid membrane contactor showed that a membrane area 80,000m^2 is required to achieve the desired propane and propylene purities. A brief economic evaluation shows that the difference between the feed and product prices should be at least 175$ / ton to make the proposed propylene / propane separation process economically feasible.

Zein *et al*. [96] designed a system for the separation of propane and propylene based on chemical absorption. The results showed that the chemical absorption technique for propane/propylene separation is a promising alternative over the distillation technique.

Table **2** gives a short review of membrane contactors, characteristics, properties of membrane materials and introduction in membrane contactor application in gas separation [97].

6. CRYOGENIC PROCESSOR DISTILLATION

The production of oxygen has become increasingly important as the world tries to produce clean energy. Currently there are three major alternatives for Air Separation Units (ASU): cryogenic distillation, adsorption-based processes, and membrane technologies. Cryogenic distillation is considered the most economical large-scale process and can produce very pure gas and liquid products [98].

Table 2: Summary of Membrane Contactor

Membranes	Porous (hydrophobic or hydrophilic), nonporous, or composite
Thickness	20 – 100μm
Pore size	Nonporous or 0.05-1.0μm
Driving force	Concentration or vapor pressure difference
Separation principle	Distribution coefficient
Membrane material	Hydrophobic (polytetrafluoroethylene, polypropylene, silicon rubber), polyolefin
Application	G-L contactors
	– SO_2, CO_2, CO, NO_x from flue gases
	– CO_2 and H_2S from natural gas
	– VOC from off gas
	– Saturated / unsaturated (ethane/ethylene)
	– LG contactors
	– O_2 removal from water

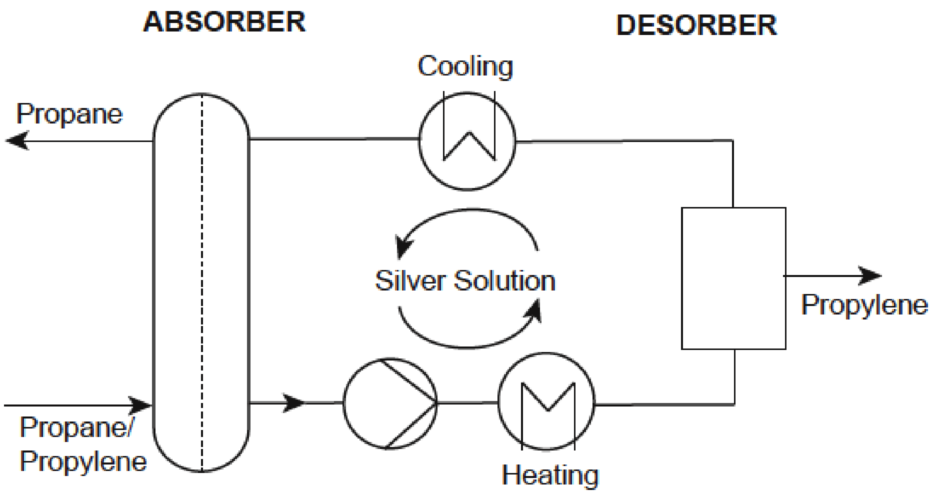

Figure 21: Cycle sequence of a two-permeator pressure swing permeation process [103].

Burdyny and Struchtrup [99] discussed a hybrid membrane/cryogenic separation of oxygen from air for use in the oxy-fuel process. It was claimed by them that the hybrid system would be more productive in small to medium scale applications than in large scale applications. Ye *et al*. [100, 101], for the first time, used ultra-thin MFI zeolite membranes to evaluate the air separation at low feed pressures ranging from 100 to 1000 mbar at cryogenic temperature. This work has demonstrated the potential of MFI zeolite membranes for O_2 / N_2 separations at cryogenic temperature. Several hybrid membrane-cryogenic distillation processes for the recovery of He from NG and / or the rejection of N_2-rich streams from NG have been suggested in the open and patent literature [102].

7. PRESSURE SWING PROCESS

A novel process for gas separation, called pressure swing permeation was introduced by Feng *et al*. [103] to evaluate the relatively low permeate pressure by pressurization with high-pressure feed gas. The novel process is not really a hybrid process but obviously the authors have attempted to apply the principle of PSA to membrane the gas separation. Hence, the pressure swing permeation process is an analogue of the pressure swing adsorption. Though the pressure swing permeation process can be run as a batch process, it is more efficient to operate the membrane system in a continuous fashion. In a continuous pressure swing permeation process, the membrane system, in a simple form, comprises two membrane modules A and B (Figure **21**) to perform a gas separation in a steady-state cyclic fashion. Each module contains two distinct void spaces separated by the membrane for the admission and removal of gas streams, respectively. After the high-pressure feed gas is introduced to membrane module A, permeation takes place, and the permeate from module A, which is at a relatively low pressure level as compared to the feed pressure, is received by module B. As the permeation in module. A proceeds with time, the pressure of permeate collected in module B increases. Then the gas feeding to module A is stopped, and permeate stored in module B is pressurized with the high-pressure feed gas, during which period the permeate product at a desired elevated pressure is displaced out of module B. In the meantime, the residue in module A is released. The two modules are arranged such that the void space in one module used for receiving the permeate from the other module will receive the feed gas when the two modules are switched to reverse their functions in terms of feed admission and permeate reception. Thus the membrane system is ready for the next cycle of operation. It should be mentioned that the membrane modules should be properly designed and the pressurization and displacement steps should be carried out in a sufficiently short period of time to prevent any breakthrough of feed gas into the permeate product. Hollow-fiber membranes are preferred because the lengthwise gas mixing in the membrane module is very limited. The two membrane modules can be synchronized, and each undergoes five basic operating steps:

1. Collection of the low-pressure permeate from the other module.
2. Pressurization of permeate by the high-pressure feed gas.

Table 3: Cycles Steps in a Two-Module Pressure Swing Permeation Process

Step	Module A	Module B
1	Admission of feed gas and permeation	Reception of permeate from module A
2	Withdrawal of residue from module	Pressurization with feed gas and product release
3	Removal of residue remaining in gas line	Gas feeding stopped
4	Reception of permeate from module B	Admission of feed gas and permeation
5	Pressurization with feed gas and product release	Withdrawal of residue from module
6	Gas feeding stopped	Removal of residue remaining in gas line

3. Release of permeate product at an elevated pressure.
4. Admission of feed to carry on permeation.
5. Withdrawal of residue stream.

Clearly, step 4 is responsible for the separation, and step 2 is responsible for producing a high-pressure permeate product. Engineering designs directed to minimizing back mixing of the gas during the pressurization step are necessary to ensure product purity.

A brief description of the cycle steps is shown in Table **3** [103].

8. HYBRID PROCESS

It is well known that membrane separation processes can offer many advantages over conventional mass transfer processes. A large number of membrane separation processes are currently being practiced in various sectors of industries. Despite the advantages, membrane processes often suffer from shortcomings when used individually. To overcome such limitations, membrane-based hybrid processes have been developed to maximize the productivity of the target separation processes. Hybrid processes are thus defined as processes, in which membrane technology is combined with conventional separation equipment to perform separation more efficiently. The objective is to combine the positive characteristics of each individual technology to obtain a process which is better than the individual processes. A properly designed hybrid process will balance the drawbacks of the specific process and favorably combine their advantages. The result will be better separation, contributing to a sustainable process improvement by allowing the reduction of investment and operational cost.

A hybrid process is appropriate when it offers significant advantage (such as lower capital and production costs or reduced energy requirements) over the exclusive use of conventional processes. Moreover, membrane hybrid processes may achieve separations that are otherwise impractical or altogether impossible to achieve with either conventional process.

Lipnizki *et al*. [104] discussed two types of hybrid processes. One is a hybrid process that consists of processes which are ‘essentially performing the same function’. This would mean that all processes in the package would be separation processes. These hybrid processes are referred to as hybrid processes Type S (separation).

Another hybrid process combines a separation process with a reaction, either chemical or biochemical. These hybrid processes are referred to as hybrid processes Type R (reactor).

With regard to a Type S hybrid process, the component parts serve a common purpose (e.g. separation of A and B) and there are a maximum of two output streams (one rich in A, the other rich in B). Furthermore, the common purpose could not be achieved by either component alone.

Before the membrane technology, the removal of carbon dioxide from natural gas was amine absorption technique. Amine absorption technology achieves almost complete removal of carbon dioxide. But this process is costly and complex. The combination of membranes for removal of carbon dioxide from natural gas with amine absorption units offers a low cost alternative to all amine or all membrane plants. A block

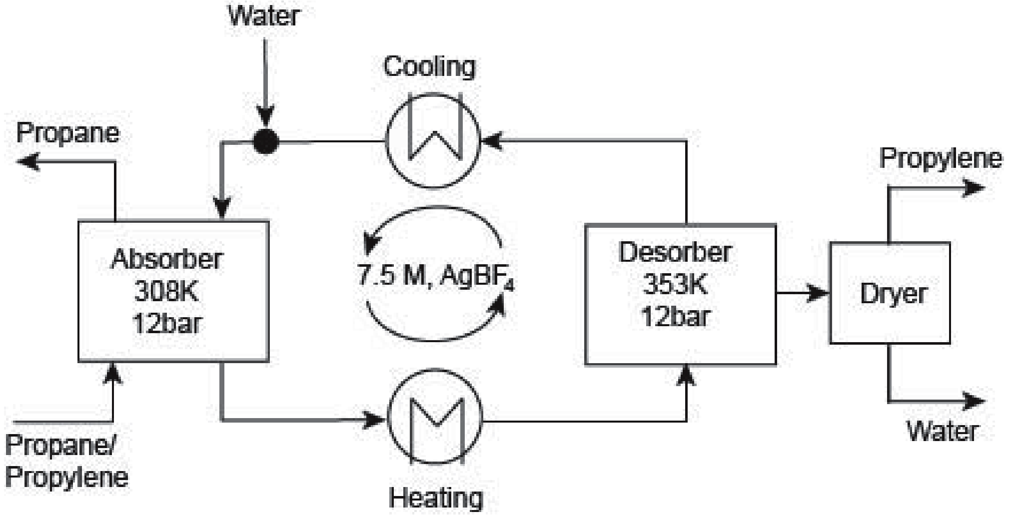

Figure 22: Typical membrane hybrid plant for the treatment of associated natural gas produced in carbon dioxide/enhanced oil projects; a portion of the membrane plant's permeate gas is used as a fuel for the amine absorption plant [104].

diagram of a membrane/amine plant is shown in Figure **22**. In this design, the membrane unit removes two-thirds of the carbon dioxide, and the amine plant removes the remainder.

8.1. Membrane / Distillation Hybrid Process

Phillips Petroleum Company [105] invented a membrane separation process incorporated in distillation cycles for efficient recovery of CO_2 from a stream containing natural gas along with carbon dioxide. In this process methane and carbon dioxide are separated from a feed stream in a first distillation to produce a stream containing essentially methane and carbon dioxide. The stream was substantially free from ethane and higher molecular weight hydrocarbons and was subjected to further distillation to produce a carbon dioxide rich product stream and a process stream enriched in methane. The methane-enriched process stream was then passed to a membrane separation unit for separating methane and carbon dioxide to obtain high purity methane.

Membrane/distillation hybrid system has the energy saving potential for the separation of ethylene from ethane, if compared to the conventional distillation [106].

8.2. Membrane/PSA

Generally, membrane permeation and pressure swing adsorption (PSA) are two methods which are widely used for gas separation and they are often considered to be alternatives or compliments to the more conventional cryogenic separation process. Membrane separation is based on the difference in the rate of permeation through a membrane. On the other hand the adsorption separation depends on the difference in either the rate or the equilibrium of adsorption on an adsorbent. Membrane gas separation is pressure driven and normally operates continuously. On the other hand, PSA is a cyclic process in which the adsorbers undergo adsorption at a high pressure and desorption at a reduced pressure alternatively, thereby making it suitable for processing a gas mixture in a continuous fashion. PSA is suitable for producing gases of higher purities. Several membrane/PSA combination schemes have been proposed in the patent literature for various applications, including helium [107].

Nikolić and Kikkinides [108] proposed a modeling and optimization framework for hybrid membrane / PSA process for gas separations. The hybrid membrane / PSA technique was applied successfully on the process of H_2 production from steam methane reformer off gas. Stoner *et al*. [109] described a hybrid membrane / PSA process which can recover helium from source streams of about 0.5 to 5 percent by volume helium and concentrate the helium to a concentration of greater than about 98 percent by volume. The process comprises a membrane separation followed by two stages of pressure swing adsorption which are used in series.

9. SUMMARY

Researchers are working on every direction of gas processing by membranes. Membrane technologies are not as well developed as other conventional gas separation techniques; however they will have a great role in future for the processing of gases. Membranes are replacing conventional methods which are costly and unfriendly to the environment. Any membrane will separate gases to some extent. However, proper selection of the polymer for the membrane material is extremely important as it determines the ultimate performance of the gas separation module. Membrane gas separation can be applied to a range of processing operations for the treatment of natural gas. In particular acidic gas removal (e.g. CO_2) and heavy hydrocarbon recovery are currently commercialized. Gas separation membranes can be applied to a range of processing steps during natural gas, biogas and syngas treatment. While membranes have been shown to be quite robust in natural gas service, long membrane life (resulting in low operating cost) is dependent upon proper feed gas pretreatment. Membranes for dehydration, nitrogen separation, sulfur dioxide removal and helium recovery are less developed. Better membranes are required to make the hybrid system economical for other applications. Liquid membranes and contact membranes are better in performance in comparison with polymeric membranes for the separation of gases, but it needs more research and development.

REFERENCES

[1] Kajama MN, Shehu H and Gobina E. Purification of gases using nanoporous inorganic membranes. Int J Sci Eng Tech 2010; 3(9): 1156-1159.

[2] Kerry F. Industrial Gas Handbook: Gas Separation and Purification, CRC Press 2007; 275-280.

[3] Sridhar S, Smitha B and Aminabhavi TM. Separation of carbon dioxide from natural gas mixtures through polymeric membranes - a review, Sep Purif Rev 2007; 36: 113-174. http://dx.doi.org/10.1080/15422110601165967

[4] Gableman A and Hwang ST. Hollow fiber membrane contactors, J Membr Sci 1999; 159: 61-106. http://dx.doi.org/10.1016/S0376-7388(99)00040-X

[5] Rongwong W, Jiraratananon R and Atchariyawut S. Experimental study of membrane wetting in gas-liquid membrane contacting process for absorption by single and mixed absorbents, Sep Purif Techno 69 (2009) 118-125. http://dx.doi.org/10.1016/j.seppur.2009.07.009

[6] Haggin J. New generations of membranes developed for industrial separations. Chem Eng News 1988: 66: 7-16. http://dx.doi.org/10.1021/cen-v066n023.p007

[7] Baker RW and Lokhandwala K. Natural gas processing with membranes: An overview. Ind Eng Chem Res 2008; 47 (7): 2109-2121. http://dx.doi.org/10.1021/ie071083w

[8] Dortmundt D, Schot M and Cnop T. Sour gas processing applications using Separex membrane technology. UOP LLC, Des Plaines, Ill., 2007.

[9] Atchariyawut S, Jiraratananon R and Wang R. Separation of CO2 from CH4 by using gas–liquid membrane contacting process. J Membr Sci 2007; 304(1-2): 163-172. http://dx.doi.org/10.1016/j.memsci.2007.07.030

[10] Scholes CA, Stevens GW and Kentish SE. Membrane gas separation applications in natural gas processing. Fuel 2012; 96: 15-28. http://dx.doi.org/10.1016/j.fuel.2011.12.074

[11] "Off shore processing plant uses membranes for CO2 removal". Oil and Gas Journal, 05/28/2007.

[12] NETL. CO2 capture membrane process for power plant flue gas. NT0005313, February 2011, Internet, June 30, 2015.

[13] H2S Removal from natural gas: SOURSEP™, internet Feb. 2015. http://www.mtrinc.com/h2s_removal.html.

[14] Cnop T, Dortmund D and Schott M. Continued development of gas separation membranes for highly sour service. UOP LLC, 25 East Algonquin Road, Des Plaines, Illinois, 60017, USA 2007.

[15] Ravanchi MT and Kargari A. New advances in membrane technology. In Advanced Technology, INTECH 2009; Chapter 21: ISBN 978-953, 009-4.

[16] Hydrogen fueling systems, available on line: http:www.protonsite.com/technology/hydrogen-fueling-systems.html. (Accessed on 16th Oct. 1212).

[17] He X and Hägg MB. Membranes for environmentally friendly energy processes. Membranes 2012; 2: 706-726. http://dx.doi.org/10.3390/membranes2040706

[18] PRISM Membrane Products. http://www.airproducts.com/products/Gases/supply-options/prism-membranes/prism-membrane-products.aspx

[19] Stocker J, Whysall M and Miller G. 30 Years of PSA technology for hydrogen purification. UOP LLC 1998.

[20] Adhikari S and Fernando S. Hydrogen membrane separation techniques. Ind Eng Chem Res 2006; 45(3): 875-881. http://dx.doi.org/10.1021/ie050644l

[21] SCA. Kluiters Status review on membrane systems for hydrogen separation Intermediate report EU project MIGREYD NNE5-2001-670.

[22] Delft YC, van JA, Hugill, van EM, Dorst HM and van Veen, Hydrogen preparation in process industry with inorganic membranes, ECN-CX-03-110 (confidential), ECN, November 2003; Petten.

[23] Norby T and Haugsrud R. Dense Ceramic Membranes for hydrogen separation,:nonporous inorganic membranes. WILEY-VCH Verlag GmbH and Co. KGaA, Weinheim 2006.

[24] Hydrogen Separation Membranes Technical Brief May 2010 http://www.undeerc.org/ncht/pdf/eercmh36028.pdf

[25] Air Products. Hydrogen Recovery and Purification. www.airproducts com/Products/Equipment/PRISMMembranes/page08.html (accessed February 2010).

[26] Kim D, Tzeng P, Barnett KJ, Yang YH, Wilhite BA and Grunlan JC. Highly size-selective ionically cross-linked multilayer polymer films for light gas separation. Adv Materials 2014; 26(5): 746-751. http://dx.doi.org/10.1002/adma.201302177

[27] Hydrogen purification in refineries (MTR) http://www.mtrinc.com/pdf_print/refinery_and_syngas/MTR_Brochure_Hydrogen_Purification.pdf, March 2015, MTR.

[28] China's gas separation by membrane technology advanced. China Chemical Reporter, April 2004.

[29] Zhu X, Sun S, Cong Y and Yang W. Operation of perovskite membrane under vacuum and elevated pressures for high-purity oxygen production. J Membr Sci 2009; 345: 47-52. http://dx.doi.org/10.1016/j.memsci.2009.08.020

[30] Buonomenna MG, Golemme G and Perrotta E. Membrane operations for industrial applications: Advances in Chemical Engineering. INTECH 2012.

[31] Feng X, Ivory J and Rajan VSV. Air Separation by integrally asymmetric hollow fiber membranes. AIChE J 1999; 45: 2142-2152. http://dx.doi.org/10.1002/aic.690451013

[32] Baker RW. Membrane technology and applications, McGraw-Hill New York. 2000.

[33] Smith AR and Klosek J. A review of air separation technologies and their integration with energy conversion processes. Fuel Proc Technol 2001; 70: 115. http://dx.doi.org/10.1016/S0378-3820(01)00131-X

[34] http://www.grasys.com/products/gas/oxygen/.

[35] PermSelect 2015, http://permselect.com/markets/oxygen-enrichment [Oxygen/Nitrogen-Enriched Air]

[36] http://www.ube-ind.co.jp/english/rd/separation_membranes.htm

[37] The Essential Chemical Industry, Department of Chemistry, University of York, UK. 18th March 2013,

[38] Faiz R and Li K. Polymer membranes for light olefin/paraffin separation. Desalination 2012; 287: 62-97. http://dx.doi.org/10.1016/j.desal.2011.11.019

[39] Semenova SI. Polymer membranes for hydrocarbon separation and removal. J Membr Sci 2004; 231: 189-207. http://dx.doi.org/10.1016/j.memsci.2003.11.022

[40] Ismail AF, Khulbe KC and Matsuura T. Gas separation membranes: Polymeric and Inorganic, Springer, New York, 2015.

[41] Ma X, Williams S, Wei X, Kniep J and Lin YS. Propylene / propane mixture separation characteristics and stability of carbon molecular sieve membranes, Ind Eng Chem Res 2015; 2(54): 9824-9831. http://dx.doi.org/10.1021/acs.iecr.5b02721

[42] Ma, Lin YS, Wei X and Kniep J. Ultrathin carbon molecular sieve membrane for propylene/propane separation, AIChE J 2016; 62: 491-499. http://dx.doi.org/10.1002/aic.15005

[43] Kwon HT, Jeong HK, Lee AS, An HS and Lee JS. Heteroepitaxially grown zeolitic imidazolate framework membranes with unprecedented propylene / propane separation performances. J Am Chem Soc 2015; 137(38): 12304-12311. http://dx.doi.org/10.1021/jacs.5b06730

[44] Rao MB, Sircar SS and Golden TC. Gas separation by adsorbent membranes. US 1992; Patent 5(104): 425.

[45] Rao MB and Sircar S. Performance and pore characterization of nanoporous carbon membranes for gas separation J Membr Sci 110 (1996); 109-118. http://dx.doi.org/10.1016/0376-7388(95)00241-3

[46] Rao MB and Sircar S. Nanoporous carbon membranes for separation of gas mixtures by selective surface flow. J Membr Sci 1993; 85: 253-264. http://dx.doi.org/10.1016/0376-7388(93)85279-6

[47] Hägg MB and He X. Carbon molecular sieve membranes for gas separation: Membrane engineering for the treatment of gases: Volume 2: Gas-separation problems combined with membrane reactors, RSC 2011.

[48] Ma X, Swaidan R, Teng B, Tan H, Salinas O and Litwiller E. Carbon molecular sieve gas separation membranes based on an intrinsically microporous polyimide precursor. Carbon 2013; 62: 88-96. http://dx.doi.org/10.1016/j.carbon.2013.05.057

[49] Brandt P. Addition compounds of olefins with metal salts, Part 2. Acta Chem Scand 1959; 13: 1639-1652. http://dx.doi.org/10.3891/acta.chem.scand.13-1639

[50] Nymeijer K, Visser T, Assen R and Wessling M. Super selective membranes in gas-liquid membrane contactors for olefin/paraffin separation. J Membr Sci 2004; 232 (1-2): 107-114. http://dx.doi.org/10.1016/j.memsci.2003.10.045

[51] http://en.wikipedia.org/wiki/Natural_gas

[52] Honeywell's UOP Introduces New Membrane Element To Improve Natural Gas Processing Capacity (Honeywell, Press Releases, 26th Feb. 2013). http://honeywell.com/News/Pages/Honeywell%E2%80%99s-UOP-Introduces-New-Membrane-Element-To-Improve-Natural-Gas-Processing-Capacity.aspx, June 2014

[53] Walter KG. Process for separating higher hydrocarbons from natural or produced gas streams. US 4857078 A, 1989.

[54] Reyes SC. Separation of methane from higher carbon number hydrocarbons utilizing zeoliticimidazolate framework materials. US 8192709 B2, 2012.

[55] Baker RW. Future direction of membrane gas separation technology. Ind Eng Chem Res 2002; 41: 1393-14. http://dx.doi.org/10.1021/ie0108088

[56] Jariwala KA, Lokhandwala K and Baker RW. Only raw sour gas for engine fuel? Proven membrane process cleans gas for engines. Presented at the Laurance Reid Conditioning Conference. University of Okhlahoma, Norman, OK, 2006.

[57] Lokhandwala KA and Jacobs ML. Membranes for fuel gas conditioning, Hydrocarbon Eng 2000; 5(5): 81-84.

[58] LPG Recovery from Associated Gas: LPG-SepTM (MTR) http://www.mtrinc.com/natural_gas_liquids_recovery.html

[59] Natural Gas Processing Plants in the United States: 2010 Update, U.S. Energy Information Administration, Natural Gas. Released date June 17, 2011.

[60] Mohamadbeigy KH. Studying of the effectiveness parameters on gas dehydration plant, Petroleum and Coal 2008; 50(2): 47-51.

[61] Advanced membrane technology for hydrocarbon separations: New membrane technology for natural gas dehydration promises improved separation efficiency, U.S. Department of Energy, Energy Efficiency and Renewable Energy, May 2009.

[62] Feng H, Zhang H and Xu L. Polymeric membranes for natural gas conditioning. Energy Sources Part A: Recovery, Utilization and Environmental Effect 2007; 29(14): 1269-1278. http://dx.doi.org/10.1080/00908310600623611

[63] Liu L, Chen Y and Kang Y. Industrial development for natural gas dehydration by membrane. Petrochem Eng 2001; 30: 302-304. (In Chinese).

[64] Lin H, Thompson MSM, Serbanescu-Martin A, Wijmans JG, Amo KD and Lokhandwala KA. Dehydration of natural gas using membranes. Part I: Composite membranes. J Membr Sci 2012; 413-414: 70-81. http://dx.doi.org/10.1016/j.memsci.2012.04.009

[65] Morgan WH, Bleikamp LK and Kalthod DG. Hollow Fiber Membrane Dryer with Internal Sweep. US Patent 5, 1996; 525: 143. 1996 Jun 11.

[66] Zhao B, Peng N, Liang C, Yong WF and hung TS. Hollow Fiber Membrane Dehumidification Device for Air Conditioning System, Membranes (Basel) 2015; 5(4): 722-738.

[67] Lin H, Thompson SM, Serbanescu-Martin A, Wijmans JG, Amo KD, Lokhandwala KA, *et al.* Dehydration of natural gas using membranes. Part II: Sweep/countercurrent design and field test, J. Membr. Sci.2013; 432:106-114. http://dx.doi.org/10.1016/j.memsci.2012.12.049

[68] Liu C, Faheem SA and Minkov R. Membrane system for natural gas upgrading, US 8575414 B2, 2013.

[69] http://www.mtrinc.com/publications/GPAATLANTA.pdf

[70] http://www.borsig-china.com June 15, 2015.

[71] RW. Baker, Vapor and gas separation by membranes: Advanced membrane technology and applications, Hoboken NJ, John Wiley and Sons. 2008. http://dx.doi.org/10.1002/9780470276280.ch21

[72] Corvini G, Stiltner J and Clark K. Mercury removal. UOP. http://www.uop.com/?document=mercury-removal-from-natural-gas-and-liquid-streams&download=1.7

[73] Echt WI and Singh M. Integration of membranes into natural gas process schemes. UOP LLC, A Honeywell Company, http://www.uop.com/?document=integration-of-membranes-into-natural-gas-process-schemes&download=1

[74] UOP Offshore Gas Processing, Proven gas treating solutions for offshore floating or fixed platforms. https://www.honeywell-uop.cn/wp-content/uploads/2011/10/UOP-Offshore-Gas-Processing-brochure.pdf

[75] Honeywell's UOP launches new membrane element to improve contaminant removal from natural gas, 2013.

[76] Rasi S, Veijanen A and Rintala J. Trace compounds of biogas from different biogas production plan. Energy 2007; 32: 1375-1380. http://dx.doi.org/10.1016/j.energy.2006.10.018

[77] He X and Hägg MB. Membranes for environmentally friendly energy processes. Membranes, 2012; 2:706-726. http://dx.doi.org/10.3390/membranes2040706

[78] CO2 Removal from Syngas (MTR). http://www.mtrinc.com/co2_removal_from_syngas.html Feb. 2015.

[79] Smith DR, Lander RJ and Quinn JA. Carrier-mediated transport in synthetic membranes; Recent Developments in Separation Science, 3, CRC Press, Cleveland, Ohio, 1977.

[80] Noble RD and Way JD. Eds. Liquid Membranes: Theory and Applications. ACS Symposium Series 347, American Chemical Society: Washington, DC 1987.

[81] Araki T and Tsukube H. Eds. Liquid Membranes: Chemical Applications. CRC Press: Boca Raton, FL, 1990.

[82] Bartsch RA and Way JD. Eds. Chemical Separations with Liquid Membranes. ACS Symposium Series 642. American Chemical Society: Washington, DC 1996.

[83] Liang L, Gan Q and Nancarrow P. Composite ionic liquid and polymer membranes for gas separation at elevated temperatures. J Membr Sci 2014; 450: 407-417. http://dx.doi.org/10.1016/j.memsci.2013.09.033

[84] Petra C and Katalin B. Application of Ionic Liquids in, Membrane Separation Processes, in Ionic Liquids: Applications and Perspectives, Edi. Alexander Kokorin, chapter 25, pp. 561-586, ISBN 978-953-307-2011.

[85] Li N. Separating hydrocarbons with liquid membranes. US 1968; 3: 410-794.

[86] Cserjési P, Nemestóthy N, Vass A, Csanádi Z and Bélafi-Bako K. Study on gas separation by supported liquid membranes applying novel ionic liquids. Desalination 2009; 246: 370-374. http://dx.doi.org/10.1016/j.desal.2009.02.046

[87] Bessarabov DG, Jacobs EP, Sanderson RD and Beckman LN. Use of nonporous polymeric flat-sheet gas separation membranes in a membrane-liquid contactor: experimental studies. J Membr Sci 1996; 113; 275-284. http://dx.doi.org/10.1016/0376-7388(95)00126-3

[88] Jiang Y, Zhou Z, Jiao Z, Li L, Wu YT and Zhang ZB. SO_2 gas separation using supported ionic liquid membranes. J Phys Chem B 2007; 111 (19): 5058-5061. http://dx.doi.org/10.1021/jp071742i

[89] Mecerreyes D. Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes. Prog Polym Sci 2011; 36: 1629-1648. http://dx.doi.org/10.1016/j.progpolymsci.2011.05.007

[90] Bara JE, Hatakeyama ES, Gin DL and Noble RD. Improving CO_2 selectivity in polymerized room-temperature ionic liquid gas separation membranes through incorporation of polar substituents. J Membr Sci 2008; 321: 3-7. http://dx.doi.org/10.1016/j.memsci.2007.12.033

[91] Carlisle TK, Wiesenauer EF, Nicodemus GD, Gin DL and Noble RD. Ideal CO2/light gas separation performance of poly (vinylimidazolium) membranes and poly (vinylimidazolium)-ionic liquid composite films. Ind Eng Chem Res 2013; 52 (3): 1023-1032. http://dx.doi.org/10.1021/ie202305m

[92] Bara JE, Gabriel CJ, Hatakeyama ES, Carlisle TK, Lessmann S and Noble RD. Improving CO_2 selectivity in polymerized room-temperature ionic liquid gas separation membranes through incorporation of polar substituents. J Membr Sci 2008; 321: 3-7. http://dx.doi.org/10.1016/j.memsci.2007.12.033

[93] Gu Y and Lodge TP. Synthesis and gas separation performance of triblock copolymer ion gels with a polymerized ionic liquid mid-block. Macromolecules 2011: 44(7): 1732-1736. http://dx.doi.org/10.1021/ma2001838

[94] Simons K, Nijmeijer K and Wessling M. Gas-liquid membrane contactors for CO2 removal. J Membr Sci 2009; 340: 214-220. http://dx.doi.org/10.1016/j.memsci.2009.05.035

[95] Chilukuri P, Rademakers K, Nymeijer K, Vabn der Ham L and Van den Berg H. Propylene/propane separation with a gas/liquid membrane contactor using a silver salt solution. Ind Eng Chem Res 2007; 46: 8701-8709. http://dx.doi.org/10.1021/ie070556w

[96] Zein R, Nassar AF and Mostafa TM. Design of a chemical absorption system for the separation of propane/propylene, Scientific Cooperation International Workshops on Engineering Branches, 9th August 2014, Koc University, Istanbul, Turkey.

[97] Stanojević M, Lazarević B and Radić D. Review of membrane contactors designs and applications of different modules in industry. FME Transactions 2003: 31: 91-98.

[98] Wankat PC and Kostroski KP. Hybrid membrane-cryogenic distillation air separation process for oxygen production. Sep Sci Technol 2011: 46; 1439-1545. http://dx.doi.org/10.1080/01496395.2011.577497

[99] Burdyny T and Struchtrup H. Hybrid membrane/cryogenic separation of oxygen from air for use in the oxy-fuel process. Energy 2010; 35(5); 1884-1897. http://dx.doi.org/10.1016/j.energy.2009.12.033

[100] Ye P, Korelskiy D, Grahn M and Hedlund J. Cryogenic air separation at low pressure using MFI membranes. J Membr Sci 2015; 487: 135-140. http://dx.doi.org/10.1016/j.memsci.2015.03.063

[101] Ye P, Sjöberg E and Hedlund J. Air separation at cryogenic temperature using MFI membranes. Micro Meso Mater 2014; 192: 14-17. http://dx.doi.org/10.1016/j.micromeso.2013.09.016

[102] Rufford TE, Chan KI, Huang SH and May EF. A Review of conventional and emerging process technologies for the recovery of helium from natural gas. Adsorption Sci Technol 2014; 32(1): 49-72. http://dx.doi.org/10.1260/0263-6174.32.1.49

[103] Feng X, Pan CY, Ivory J. Pressure swing permeation: Novel process for gas separation by membranes. AIChE J 2000; 46(4): 724-733. http://dx.doi.org/10.1002/aic.690460407

[104] Lipnizki F, Field WR and Ten PK. Pervaporation-based hybrid process: a review of process design, applications and economics. J Membr Sci 1999; 153: 183-210. http://dx.doi.org/10.1016/S0376-7388(98)00253-1

[105] Burkinshaw JR and Waldo RA. Distillation plus membrane processing of gas streams. US 4936887 A, 1998.

[106] Motelica A, Bruinsma OSL, Kreiter R, den Exter M and Vente JF. Retrofit with membrane the paraffin/olefin separation. ECN-M-12-059, October 2012.

[107] Rufford TE, Chan KI, Huang SH and May EF. A review of conventional and emerging process technologies for the recovery of helium from natural gas. Adsorption Sci Technol 2014: 32(1): 49-72. http://dx.doi.org/10.1260/0263-6174.32.1.49

[108] Nikolić DD and Kikkinides ES. Modelling and optimization of hybrid PSA / membrane separation processes. Adsorption 2015; 21(4): 283-305. http://dx.doi.org/10.1007/s10450-015-9670-z

[109] Stoner G, Reinhold HFI, D'Amico J and Knaebel KS. Enhanced helium recovery. US patent no. 5632803, 1997.

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