ACKNOWLEDGEMENT

I would like to my thesis advisor Professor Bernado RUGGERI of DISAT faculty, at Politecnico di Torino. The door to professor was always open whenever I ran into a trouble spot or had a question about my research or writing. He assisted and led me during the redaction process of my thesis and then consistently want this job to be a reference in the use of this new technology.

First, I would like to be grateful to my almighty GOD Jesus Christ for the support he gave me till now to achieve and handle this challenge.

Finally, I must express my very profound gratitude to my parents and my spouse, my friends Domenico MOTTURA, Elena SCOTTI, Federico FERRARIS, and my local church priest, padre MUTHOKA Nikolas, for providing me with unfailing support and continuously encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

Thank you

ABSTRACT

Membrane technology can be traced back to 18th century. However, during 19th and in the beginning of 20th centuries membranes were being used only on laboratory scale to develop physical and chemical theories and were not being used for industrial and commercial purpose. In the last 15 year membranes gas separation have been commercially available, their application in natural gas processing has been mostly limited to CO_2 removal. The performance of membrane depend of parameters such as pore size, porosity, tortuosity and surface hydrophobicity, which can be controlled by a number of methods. Addition of nonsolvents to spinning solution is known to be one of such methods, recent improvements in membrane technology have boosted membranes to be competitive in the natural gas area and other separations for the first time. Hydrocarbon gas liquids (HGL) are produced from crude oil and at natural gas processing plants from unprocessed natural gas at refineries. From 2010 to 2015, total HGL production increased by 42%. Natural gas processing plants accounted for all the increase, with recovered natural gas plant liquids (NGPL)—light hydrocarbon gases such as propane—rising by 58%, from 2.07 million barrels per day (b/d) in 2010 to 3.27 million b/d in 2015, in that time refinery output of HGL declined by 7%. That big rapid increase in NGPL output was the result of rapid growth in natural gas production, as production shifted to tight gas and shale gas resources, and as producers targeted formations likely to yield natural gas with high liquids content. (The Annual Energy Outlook 2016 (AEO2016) New membrane processes are focused on three separations: nitrogen, CO_2 /H_2S and natural gas liquids (NGL). Nitrogen removal from natural gas, membranes are beginning to be used to separate hydrocarbons from nitrogen because it generates enough profit for economic end use. The NitroSep™ process using these membranes will allow production from currently shut-in high-nitrogen gas reserves.

- ➔ For <u>NGL removal</u> and recovery, a membrane similar to the NitroSep membrane can be used to preferentially permeate heavy hydrocarbons, allowing conditioning of fuel gas, dew point adjustment and oil vapor recovery.
- ➔ For <u>CO_2 removal</u>, a new membrane termed Z-Top™, based on Teflon chemistry, has been extensively field-tested. Stand-alone or hybrid processes using this improved membrane can prove useful in treating gas to meet pipeline specifications and in debottlenecking existing solvent absorption plants.
- ➔ <u>An H_2S -selective membrane</u> has also been developed and tested, allowing the same hybrid

approach to be applied to sour gas. This membrane can be used for conditioning H_2S rich fuel gas, thereby reducing engine maintenance needs.

There were four main reasons which prohibited the wide use of membrane separation process, those obstacles were 1.reliability, 2.efficiency, 3.cost and 4.limited choice, however over the last three decades these obstacles have been resolved and now these days membrane separation processes are being widely used.

INTRODUCTION

Raw natural gas varies substantially in composition from source to source. Methane is always the major component, typically 75%-90% of the total, but natural gas also contains significant amounts of ethane, some propane and butane, and 1%-3% of other higher hydrocarbons. In addition, the gas contains undesirable impurities, such as water, carbon dioxide, nitrogen, and hydrogen sulfide. Although the composition of raw gas varies widely, the composition of gas delivered to commercial pipeline grids is tightly controlled. To meet pipeline specifications, all natural gas requires some treatment (if only to remove water), and ~20% requires extensive treatment, before delivery to the pipeline.1 The opportunity for membranes lies in processing raw gas to meet these specifications. Processing of natural gas is, by far, the largest industrial gas separation application. The U.S. consumption of natural gas is ~22 trillion scf/yr; total worldwide consumption is~95 trillion scf/yr. (Throughout this paper, "scf" is used to represent standard cubic feet.) This consumption drives a worldwide market for new natural gas separation equipment of ~$5 billion per year. Currently, membrane processes have <5% of this market, almost all of which is applied toward the removal of carbon dioxide Membrane technology competes most directly against absorption for carbon dioxide removal. A typical absorption process consist buy using two towers. In the first tower, the feed gas, usually at high pressure, and an absorbent liquid flow countercurrent to each other. The absorbent liquid that contains the absorbed component (carbon dioxide, water, or heavy hydrocarbon) is removed from the bottom of the tower. The liquid is then heated and sent to a low-pressure stripper tower. The combination of heat and lower pressure liberates the sorbed component, which leaves the stripper tower as a low overhead gas. The regenerated absorbent liquid is then recycled to the first tower. Heat exchangers are used to minimize the cost of heating the absorber fluid. Absorber-stripper units represent a proven, well-accepted technology in the gas processing industry, and no gas processing plant designer will be fired for recommending the installation of one of these units. Having said this, the high-pressure absorber tower in particular is an expensive, large, thick-walled, heavy vessel. The size of such a tower is proportional to the mass of the material to be absorped. In natural gas dehydration, only a few hundred parts per million (abbreviated hereafter as ppm) of water must be removed; consequently, these systems are relatively compact and low in cost. On the other hand, the removal of carbon dioxide from natural gas may require 10%20% of the gas to be removed, which means large amounts of absorbent fluid must be used in large towers. Carbon dioxide absorber-

strippers are also relatively high-maintenance units. The need to heat and cool the recirculating fluids requires careful, well-monitored operating procedures. Furthermore, corrosion is a critical maintenance issue. Amines are the most common sorbents for carbon dioxide, and the degradation of amines leads to corrosive mixtures that can destroy the system within a few days if left unchecked. Constant monitoring of the amine absorbent chemistry is needed. The need for regular maintenance and good operator care hinders the use of amine absorber-strippers in remote locations. Membrane companies first broke into the natural gas processing industry in the 1980s, offering systems for carbon dioxide removal in competition with amine absorption. Membranes could gain a foothold in locations where the operational issues previously mentioned are especially problematic. The first membrane systems to separate carbon dioxide from natural gas were introduced by Grace Membrane Systems (a division of W.R. Grace), Separex (now part of UOP), and Cynara (now part of Natco). These companies used anisotropic cellulose acetate membrane that was produced using the Loeb-Sourirajan technique.3-5 Cellulose acetate membranes are still widely used. In the last 10 years, they have begun to be challenged by newer membranes, such as the polyimide membranes (made by Medal a division of Air Liquide)6 and perfluoropolymer membranes pressure.

1. *NATURAL GAS*

Natural gas processing vary to conform to the product specifications. When hydrogen sulfides (H2S) is present in the raw gas, the processing scheme must produce a residue gas that meets the pipeline specification. This typically requires pretreatment of the feed gas prior to natural gas liquid (NGL) recovery but post-treatment of the liquid fractions is also possible. When the liquid ethane recovery is desired, some removal of carbon dioxide (CO2) from the feed gas and/or the liquid product is required Projections for natural gas consumption, production, imports, and prices differ significantly, largely as a result of different assumptions. For example, the Annual Energy Outlook 2016 Reference case Assumes that current laws and regulations generally remain unchanged from 2015 to 2040, whereas other projections may include assumptions about policy developments over the period. In particular, the AEO2016 Reference case does not incorporate any future changes in policies affecting carbon emissions or other environmental issues. A raw NGL stream may also be produced offshore when a pipeline or floating production, storage, and off-loading (FPSO) ship is made available. Several offshore applications with a combination of dehydration, CO2 removal using membranes and NGL production have been installed or are currently under construction. We will look at various process schemes and highlight where advantages may be found. Bulk CO2 removal processes using membranes onshore can also apply the process schemes discussed in this paper.[1]

2. NATURAL GAS PRODUCTION

All the outlooks shown in Table (2) (with the exception of IHSGI, which did not provide production data) project increases in natural gas production from 2015, when production totaled 27.2 trillion cubic feet (Trillion cubic feet). BP projects the largest production increase, to 42.0 Trillion cubic feet in 2035, or 54% more than the 2015 level. BP is followed closely by ExxonMobil, which projects 40.8 Trillion cubic feet of natural gas production in 2035 and 41.4 Trillion cubic feet (Tcf) in 2040, or 50% and 53% above 2015 levels, respectively.

The AEO2016 Reference case, ICF, BP, and ExxonMobil all project larger increases in natural gas production before 2025 than in the later years. In the AEO2016 Reference case, natural gas production increases by 28% from 2015–2025 and by 15% from 2025–2035.

ICF, BP, and ExxonMobil project production increases of more than 30% from 2015–2025 and less than 20% from 2025–2035.

EVA projects roughly equal growth rates for natural gas production from 2015–25 and 2025–2035. EVA projects production increases of 23% (to 33.4 Tcf) from 2015–25 and 22% (to 40.6 Tcf) from 2025–2035. **"Source (AEO2016)"** [1] [11]

3. WORLDWIDE NATURAL GAS LIQUID CONSUMPTION

In the AEO2016 Reference case, total domestic natural gas consumption increases by 19% from 2015–2035 and by 25% from 2015–2040 to a total of 34.4 Tcf in 2040. The 5.1 Tcf increase in total domestic consumption in the AEO2016 Reference case from 2020–35 is 0.8 Tcf larger than the projected increase in net natural gas exports (4.3 Tcf). The domestic consumption share of total U.S. natural gas production declines in the Reference case from 90% in 2020 to 82% in 2035 and 2040. From 2015–35, natural gas consumption in the electric power sector grows by 16%, to a total of 11.1 Tcf, as compared with a 22% increase in the industrial sector, to 9.2 Tcf, and a 10% increase in the commercial sector, to 3.6 Tcf in 2035. In the residential sector, natural gas consumption remains constant at 4.6 Tcf from 2015 to 2035 in the Reference case.

EVA, ICF, BP, and ExxonMobil provided outlooks for domestic natural gas consumption at different levels of detail, with the ICF projections being the most comprehensive. BP provided separate projections for consumption in the industrial and electric power sectors—projections of residential and commercial sector consumption are included with projections of consumption in the transportation sector, for lease and plant operations, for liquefaction to LNG for export and for pipeline fuel. BP consistently shows higher projections than those in the AEO2016 Reference case for total natural gas consumption. BP shows increasing consumption of natural gas in all domestic sectors, led by consumption in the electric power sector, with ICF showing a greater increase than BP in electric power sector consumption from 2020–35. ICF projects 63% growth in power sector natural gas use, to 16.3 Tcf in 2035, which is higher than projected in the AEO2016 Reference case and the other outlooks. The AEO2016 projection for natural gas consumption in the electric power sector is lower than the others, and its projection for industrial sector natural gas consumption in 2035 is lower than the EVA, BP, and ExxonMobil projections. **"source(AEO2016)"** [1] [11]

Annual energy outlook 2016						
2025						
projection	2015	AEO2016 reference	EVA	ICF	BP	ExxonMobil
Dry Gas Production	**27.19**	**34.81**	**33.37**	**35.70**	**36.18**	**35.51**
Net Imports	**0.95**	**-5.32**	**-2.86**	**-3.55**	**-4.42**	-
PIPELINE	0.89	-0.76	0.16	-0.37	-	-
LNG	0.06	-4.56	-3.02	-3.18	-	
consumption	**27.47**	**29.35**	**28.19**	**31.70**	**31.75**	-
Residential	4.62	4.67	4.68	5.15	-	6.82
Commercial	3.22	3.35	3.53	3.36	-	-
Industrial	7.51	8.65	10.15	8.08	11.25	10.72
Electricity Generation	9.61	9.33	9.74	12.06	12.17	10.72
Other	2.51	3.34	0.08	3.04	8.34	
2035						
projection	2015	AEO2016 reference	EVA	ICF	BP	
Dry Gas Production	**27.19**	**39.92**	**40.65**	**39.89**	**42.02**	**40.84**
Net Imports	**0.95**	**-7.18**	**-4.70**	**-3.38**	**-7.61**	-
PIPELINE	0.89	-0.99	0.51	-0.77	-	-
LNG	0.06	-6.19	-5.22	2.61	-	-
consumption	**27.47**	**32.59**	**-**	**-**	**34.41**	-
Residential	4.62	4.62	-	-	-	6.82
Commercial	3.22	3.55	-	-	-	-
Industrial	7.51	9.19	-	-	11.76	10.72
Electricity Generation	9.61	11.13	-	-	13.32	13.65
Other	2.51	4.09	0.10	3.28	9.33	1.00

Table.1: annual energy outlook showing increase in LNG supply

4. THEORIES OF FORMATION OF NATURAL GAS

Like other non-renewable fossil fuels, natural gas is essentially formed from the decomposition of living organics matters such as plants, animals and micro-organisms that lived over millions of years ago and became an inanimate mixture of gases. Although many various theories exits about the origin of fossil fuels, the widely most accepted theory states that fossil fuels come from organic matters, that are decayed and compressed under the earth's crust at high pressure and temperature for a very long time. The decomposition is the main formation process of this type of natural gas, organic matters are piled and compressed that are covered in mud, sediment and debris at high temperature beneath the crust of the earth. This kind of formation is technically referred to as thermogenic methane. In another way, natural gas can also be formed by the action of tiny methane-producing microorganisms and it is technically termed as biogenic methane. In this case, methane formation usually takes place close to the earth's surface and the methane produced is usually dissipated into the atmosphere. However, in some cases, this methane can be trapped underground and recovered as natural gas. As a third theory, abiogenic processes form natural gas where this process takes place at extremely underneath the earth's crust, where hydrogen-rich gases and carbon molecules are dominant. These gases may interact with minerals found in the underground in the absence of oxygen by the time the gases gradually rise towards the surface of the earth. In such processes reaction will take place and forms gaseous compounds such as nitrogen, carbon dioxide, oxygen, water and inert gases like argon. Hence, the condition will form methane deposits at very high pressure, similar to that of the thermogenic methane (NaturalGas.org 2010). [2]

4.1 Composition of Natural Gas

The composition of natural gas processed at the wells will have different range depending on type, depth, and location of the underground reservoirs of porous sedimentary deposit and the geology of the area. Most ot the time, oil and natural gas are found together in a reservoir.

When the natural gas is produced from oil wells, it is categorized as associated with (dissolved in oil) crude oil or non-associated. It is apparent that two gas wells producing from the same reservoir may have different compositions.

Table.2: General Chemical Composition of Natural Gas

Component	**Typical Analysis (mole %)**	**Range (mole %)**
Methane	94.9	87.0 - 96.0
Ethane	2.5	1.8 - 5.1
Propane	0.2	0.1 - 1.5
iso - Butane	0.03	0.01 - 0.3
normal - Butane	0.03	0.01 - 0.3
iso - Pentane	0.01	trace - 0.14
normal - Pentane	0.01	trace - 0.04
Hexanes plus	0.01	trace - 0.06
Nitrogen	1.6	1.3 - 5.6
Carbon Dioxide	0.7	0.1 - 1.0
Oxygen	0.02	0.01 - 0.1
Hydrogen	trace	trace - 0.02
Specific Gravity	0.585	0.57 - 0.62
Gross Heating Value (MJ/m^3), dry basis *	37.8	36.0 - 40.2

the composition of natural gas reservoirs in some part of the world is different in their component composition. Further, the composition of the gas produced from a given reservoir may differ with time as the small hydrocarbon molecules (two to eight carbons) in addition to methane that existed in a gaseous state at underground pressures will become liquid (condense) at normal atmospheric pressure in the reservoir. Generally, they are called condensates or natural gas. [4]

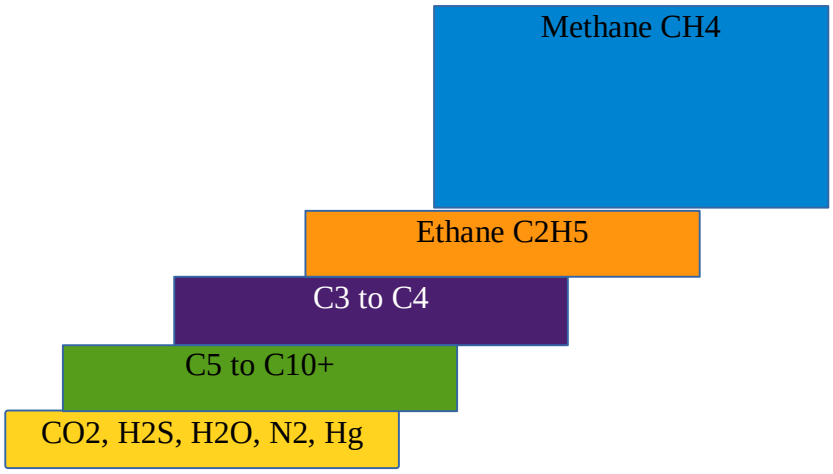


Figure 1: representation of natural gas composition

5. MEMBRANE PROCESS ASSESSMENT

The common factor in all the membrane separation processes is the physical arrangement of the process in which a membrane acts as a semi permeable barrier between two phases made up of two liquids (or two gases or a liquid and gas).The membrane prevents actual hydrodynamic flow of the two phases and the semi-permeable membrane differentiates between solutes of different sizes. Separation occurs as the membrane controls the rate of movement of various components through selective transport, allowing some components to pass through while retaining others Membrane separation can be classified into 3 main categories on the basis of the driving force, which facilitates mass transfer across the membrane.[5] [4]

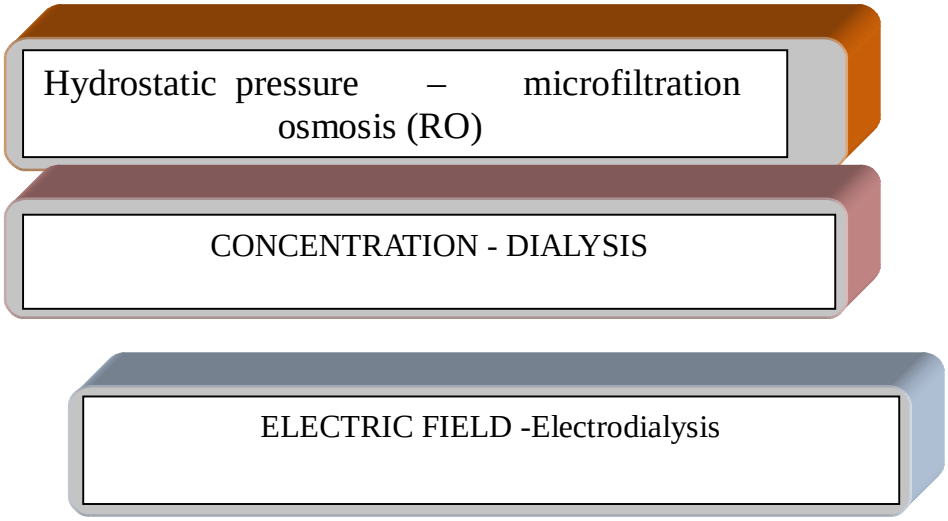
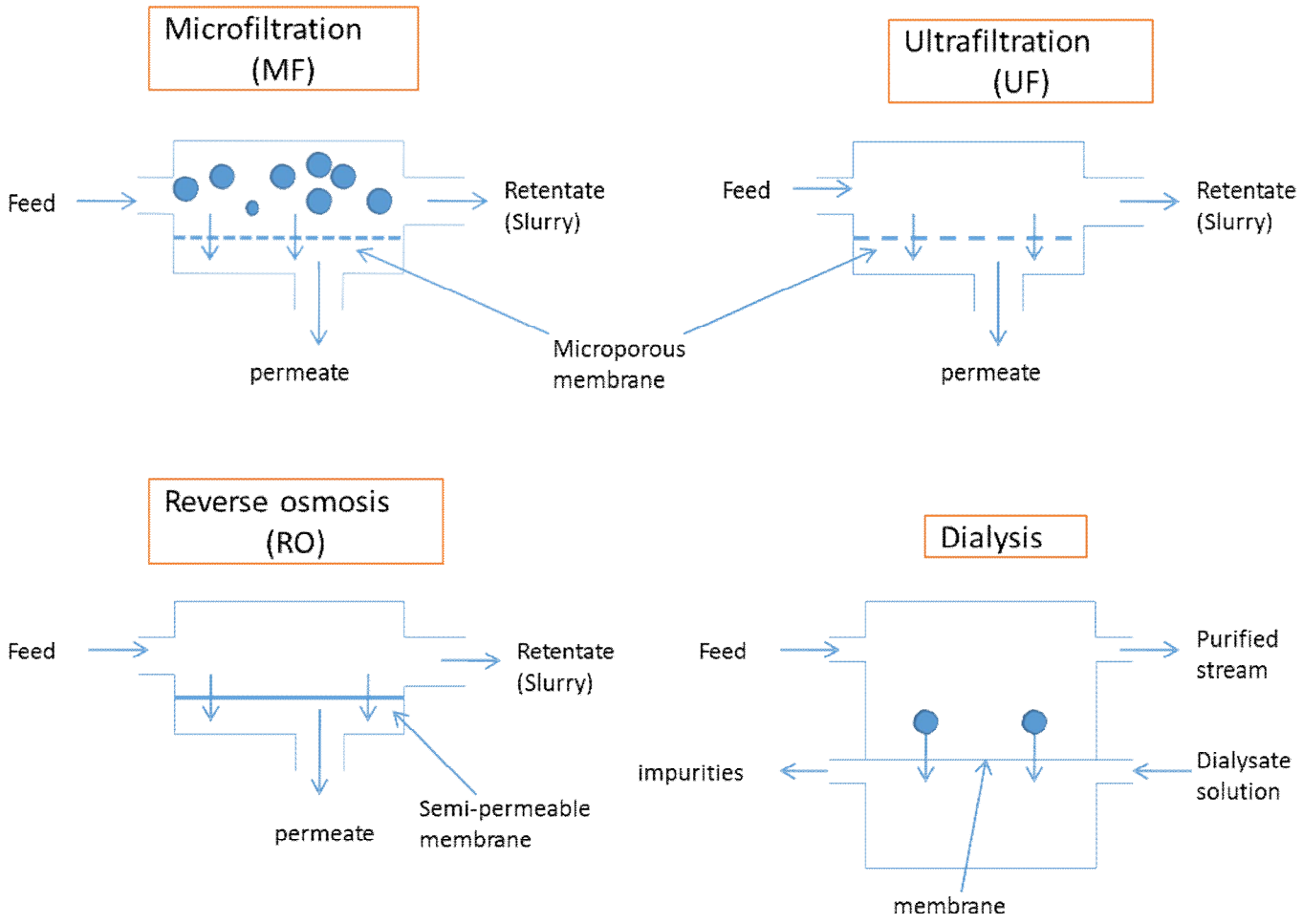


Figure 2: Membrane separation can be classified into 3 main categories on the basis of the driving force

5.2. Membrane process

The widely use membrane process are :

Figure 3: membrane process



5.2.1. Reverse Osmosis (RO)

Reverse Osmosis is a high pressure membrane process which operates at a pressure between 30 -40 bars.This is a reverse of natural osmosis which works by putting the pressure on the concentrated side of the membrane which overcome the natural osmotic pressure.

Reverse Osmosis membranes have the smallest pore size ranging from approximately 5-15 A° (0.5nm 1.5nm). Extremely small size of membrane pores only allow to pass through the smallest organic molecules and unchanged solutes.More than 95-99% inorganic salts gets rejected by the membrane due to the charge repulsion established at membrane surface.

As compare to basic membrane methods like microfiltration(MF), ultrafiltrtation(UF)and Nanofiltratiion(NF) recerse Osmosis can remove the smallest particles retaining particles smaller than 0.001 microns. Reverse Osmosis can remove the particles down to the molecular weight of 100. Rverse Osmosis(RO) can effectively remove sand, silt, clay, algae, protozoa(5-10 microns) bacteria(0.4-30 microns), viruses (0.004 -6 microns) humic acids, organic/inorganic chemicals and most of the aqueous salts and metal/non-metal ions including NO3-1, iron and manganese.[18]

Application:

1) Reverse Osmosis (RO) technique is extensively applied in the following fields
2) Conversion of sea or brackish water into potable water
3) To get the ultrapure water for food processing and electronic industries
4) To get the pharmaceutical grade water
5) For chemical, pulp and paper industry usable water
6) Usage in waste treatment

5.2.2. Ultrafiltration (UF)

Ultrafiltration is mainly used to separate a mixture which consists of desirable and undesirable components. Ultrafiltration process operates between 2-10 bars but in some cases it goes up to 25-30 bar. Ultrafiltration (UF) can retain particles from 1000 – 1000 000 molecular weight. Ultrafiltration system can be based on hollow fibre, spiral wound or plate and frame membranes. Ultrafltration by using membranes of polyether sulfone and plyvinylpyrlidone can remove the polyphenols which are responsible for browning colour and haze forming in apple juice.[19]

5.2.3.Electro dialysis (ED)

Like Reverse Osmosis, ED can remove the particles smaller than 0.001microns but the condition is that the particles must be charged ions. It can not remove non ionic dissolved species or microbes. Electrodialysis is an electrochemical process in which ions pass through an ion selective semipermeable membrane because of their attraction to the electrically charged membrane surface.

ED system consists of anion and cation membranes which place in electric field. The cation selective membrane only let pass through the cation ions, while the anion selective membrane will let only cation ions. Ions get transported through membrane from one solution to another under the influence of electrical potential.

5.2.4. Gas Separation

Gas separation technology is nearly eleven years old but has been proven one of the most important technology. Membranes made up of polymers and copolymers in the form of flat film or hollow fibre are being used in gas separation. Gas separation technology has the advantages of

- Light in weight
- Low labour
- Easy expansion
- Operatable at partial capacity
- Involves low maintenance
- Needs less energy
- Economical so for small sizes

5.2.5. Pervaporation

Pervaporation is a membrane-based process to separate miscible liquids. Pervaporation process is very effective as compare to conventional techniques to separate the mixtures of close boiling point or azeotropic mixtures. Pervaporation technique works by absorbing one of the components of the mixture by the membrane, its diffusion across the membrane and then evaporation, partial vacuum applied to the underside of the membrane makes permeate vapour. Based on this, hydrophilic membranes are used for dehydration of alcohols containing small amounts of water and hydrophobic membranes are used for removal/recovery of trace amounts of organics from aqueous solutions. Pervaporation is a very mild

process and hence very effective for separation of those mixtures which can not survive the harsh conditions of distillation.[13]

6. BASIC CONCEPT OF THE SEPARATION PROCESS

Assuming ideal gas behavior, the driving force for transport through the membrane is the difference in partial pressure, that mean that the thermodynamically correct driving force for a component moving across a membrane is the chemical potential. Partial pressure differences are equal to chemical potential differences if the gases follow the ideal gas law. By Assuming ideal gas behavior. $y_i P$, for component i on the two sides of the membrane. If component i is the diffusing component, then

$$y_{i,feed} P_{feed} > y_{i,\,permeate} P_{permeate}$$

where the materials moves from feed side to the permeate side. (gas not permeating the membrane s called the residue.) this equation shows what terms affect the driving force across the membrane. This equation can be rearranged to obtain

$$\frac{y_{i,\,permeate}}{y_{i,\,feed}} \square \frac{P_{feed}}{P_{permeate}}$$ this relation shows that the separation achieved ($y_{i,\,permaete} / y_{i,\,feed}$) can never exceed the the pressure ratio ($P_{feed} / P_{permaete}$).

Fick's law for solution-diffusion membranes in rectangular coordinates is (Echt et al., 2002)

$$J_i = \frac{S_i D_i \nabla P_i}{L}$$

where :

- the flux of component i, i.e, the molar flow of component i through the membrane per unit area of membrane is J_i
- the solubility is S_i
- the diffusion coefficient is D_i
- the partial pressure difference across the membrane ∇P_i

- the thickness of the membrane L

all mixture components have a finite permeability and the separation is based on differences in them. A term important in process design and evaluation is selectivity, α, which is the ratio of two permeabilities, P_1/P_2 α of 20 for CO_2/CH_4 means that the CO2 moves through th membrane 20 times faster than does the methane. The two components of the permeability provides two different trends with respect to molecular size and molar mass (Baker et al., 1998). For component of increasing molecular size the diffusivity decreases while the solubility tends to increase. Membrane materials are either a glassy or rubbery polymers [1]

6.1. Process Selection Factors

The processes that are used to remove acid gas are broad and the existing technologies are many that effective selection of process becomes a critical concern. This is because each of the processes has their own advantages and limitations relatives to others. Although common decisions in selecting an acid gas removal process can generally be simplified, factors such as nature and amount of contaminants in the feed gas, the amount of every contaminants present in feed gas and the targeted removal capacity, amount of hydrocarbon in the gas, pipeline specification, capital and operating cost, amount of gas to be processed, desired selectivity, conditions at which the feed gas is available for processing are the major factors that should also be considered (Dortmundt and Doshi 1999).

6.3. Membrane Process Requirements

Membranes themselves impose process requirements over and above the demands of the gas processing product streams. 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. For the feed gas described, advanced pretreatment is required for dew point control to enhance membrane life and efficiency. UOP employs a temperature-swing adsorption (TSA) unit called the UOP MemGuardTM pretreatment system for dew point control. The effect of various process parameters on the size of the TSA system will be examined.

In principle, the membrane process is simple and has no moving parts. It has three components:

- feed pretreatment

- membrane modules
- Recompression, if required

6.4. feed pretreatment

Because membrane are susceptible to degradation because of impurities, pretreatment is usually required. The impurities possibly present in natural gas that may cause damage to the membrane (Echt et al., 2002) include :

1.) liquids: the liquids may be entrained in the feed to the unit or formed by condensation within the unit. Liquids can cause the membrane to swell, which results in decrease flux rates and possible damage. Liquid can form internally in glassy membranes by two mechanisms:

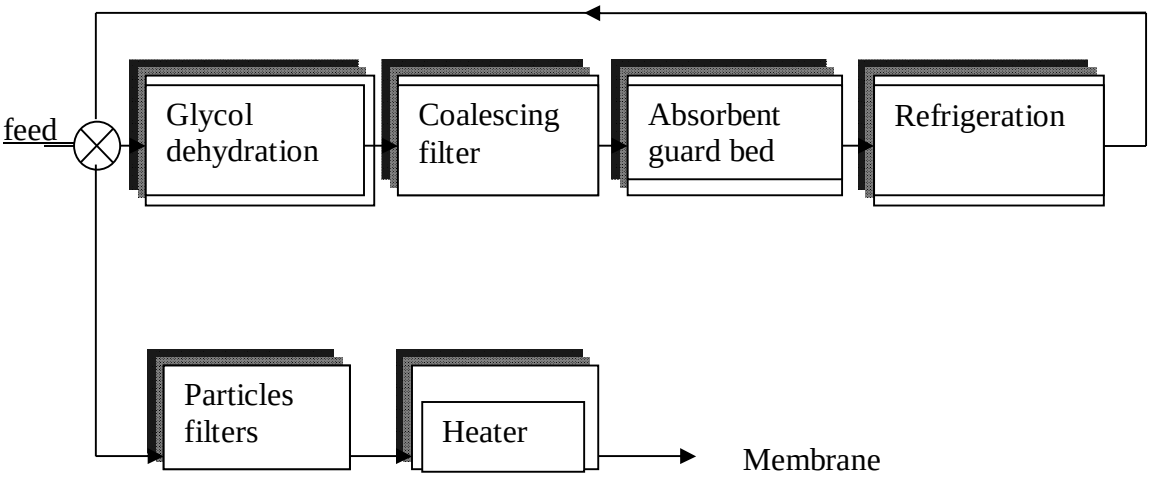
2.) because of condensation and higher molecular mass compounds caused by the cooling that occurs as the gas expends to a lower pressure (JT effect) through the membrane.

3.) because N2, CO2, and the lighter hydrocarbons diffuse more quickly than the heavier hydrocarbons, the dew point of the residue gas may increase to the point where condensation occurs. In rubbery membranes heavier components are preferentially permeated and the dew point temperature of residue High molecular mass hydrocarbons (C15+) such a compressor lube oils: These compounds coat the membrane surface surface causing a loss of performance. The concentrations of these materials are low but the effect is cumulative.

4.)Particulates: these materials block the small flow passages in the membrane element. Erosion of the membrane could also be a problem.

5.)Corrosion inhibitors and wells additives: certain of these additives are destructive to membrane or porous support material.[1]

MAXIMUM PRETREATMENT



MINIMUM PRETREATMENT

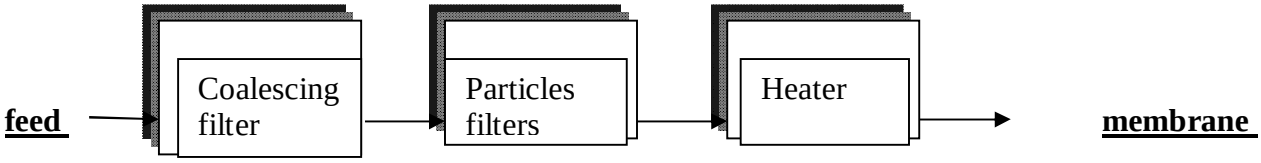


figure 4.1 and 4.2 schematic of membrane-pretreatment equipment

the common method for pretreating the feed gas to a glassy membrane system is shown in figure 1.2 the coalescing filter removes any entrained liquids; the adsorbent bed takes out trace contaminants such as volatile organic compounds (VOC); the particulate filter removes any dust from from the adsorbent bed; and the heater superheats the gas to prevent liquid formation in the membrane unit. The system shown has the following disadvantages (Echt et al., 2002).

- the adsorbent bed is the only unit that removes heavy hydrocarbons. Consequently, if the gas contain more heavy hydrocarbons than anticipated, or in th even of a slug of these materials, the adsorbent bed becomes saturated in a relatively short time and allow heavy hydrocarbons to contact the membrane.

- Only the heater provides superheat, and consequently, if this unit fails, the entire membrane system can be shut down.

Rubbery membrane system lower the dew point temperature of the residue gas but create a low steam pressure containing heavy components with the potential for condensation if the permeate is compressed. Therefore preheating may not be required for removing liquid and solid particles in the feed gas.[1]

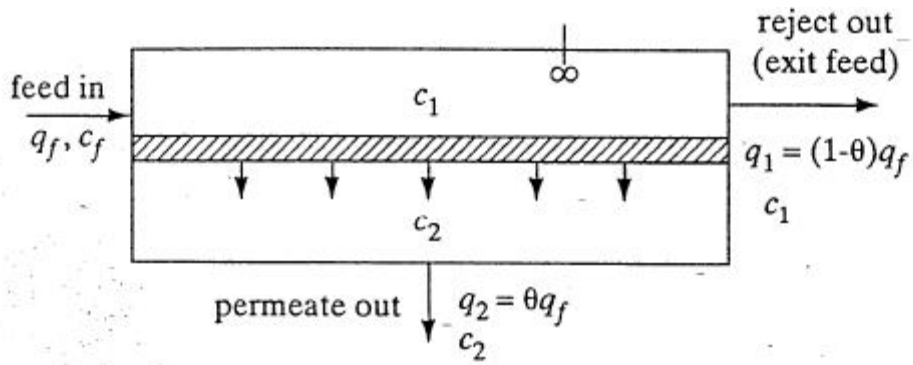
6.5. Membrane Modules

About 80% of gas-separation membranes are formed into hollow fiber modules (Baker, 2002), and the configurations of commercials membranes are also done in hollow fibers elements or flat sheets wrapped into spirally wound elements. Many of these membranes are in hydrogen service instead of gas processing. The low-pressure, bore-feed configuration is a countercurrent flow configuration similar to a shell-tube heat exchanger with the gas entering in a side tube. This more resistance to fouling had an advantage because the inlet gas flows through the inside of the hollow fibers. Therefore there is a limited pressure drop across the membrane due mechanical strength. The configuration is used in low-pressure applications, such as air separation and air dehydration (Baker, 2002). the permeates flow into the hollow fiber from the shell side, to handle the high pressure. This feature makes the membrane much more susceptible to plugging, and gas pretreatment is usually required (Baker, 2002). the gas flow is crosscurrent and provides goods feed distribution in the module. In the spiral wound element two membrane sheet are separated by a permeate spacer and glued shut at three ends to form an envelope of leaf. Many of these leaves separated by feed spacers, are wrapped around the permeate tube, with the open end of the leaves facing the tube.

Example of determination membrane permeability

Example 1.Determination of membrane permeability Experiments at 25 oC were performed to determine the permeabilities of a cellulose acetate membrane. The laboratory test section shown in Figure 3 has a membrane area A = 2□10-3 m2. The inlet feed solution concentration of NaCl is c1 = 10 g NaCl/L solution γ_1 = 1004 kg solution/m3). The water recovery is assumed low so that the concentration c1 in the entering feed solution flowing past the membrane and the concentration of the reject solution are equal. The product solution contains c2 = 0.39 g NaCl/L solution (γ2 = 997 kg

solution/m3) and its flow rate is $1.92*10^{-8}$ m3 solution/s. A pressure differential of 5514 kPa (54.42 atm) is used. Calculate the permeability constants and the solute rejection R.[1]



Solution. Since c2 is very low. cw2 can be assumed to
as the density of water. cw2 = 997 kg solution/m3.

Water flux is :

$$N_w = \frac{F\gamma_2}{A} = \frac{(1.92*10^{-8}\ m^3/s)(997 kgsolvent/m^3)}{2*10^{-3} m^2}$$

$$N_w = 9.57*10^{-3} kgsolvent/(sm^2)$$

$$N_s = \frac{N_w * c_2}{c_{w2}} = \frac{9.57*10^{-3}*0.39}{997}$$

$$N_s = 3.744*10^{-6} kg.solute.NaCl/sm^2$$

The osmotic pressure is found from Table,

Sodium Chloride Solutions			Sea Salt Solutions		Sucrose Solutions	
g mol NaCl / kg H_2O	Density (kg/m^3)	Osmotic Pressure (atm)	Wt. % Salts	Osmotic Pressure (atm)	Solute Mol. Frac. $\times 10^3$	Osmotic Pressure (atm)
0	997.0	0	0	0	0	0
0.01	997.4	0.47	1.00	7.10	1.798	2.48
0.10	1001.1	4.56	3.45*	25.02	5.375	7.48
0.50	1017.2	22.55	7.50	58.43	10.69	15.31
1.00	1036.2	45.80	10.00	82.12	17.70	26.33
2.00	1072.3	96.2				

* Value for standard seawater.

3

$\pi_1 = 7.80 atm \quad \pi_2 = 0.32 atm$

$$\Delta\pi \ = \pi_1 - \pi_2 = 7.80 - 0.32 = 7.48 atm$$

$$\Delta \mathrm{P} = 52.42 atm(given)$$

$$N_w = 9.57 * 10^{-3} kg / sm^2$$

Hence,

$$\frac{P_w}{L_m} = A_w = 2.039 * 10^{-4} kg / sm^2 * atm$$

$$N_s = 3.744 * 10^{-6} kg / sm^2$$

$$\frac{D_s K_s}{L_m} = (c_1 - c_2) = \frac{D_s K_s}{L_m} = (10 - 0.39)$$

$$\frac{D_s K_s}{L_m} = A_s = 3.896 * 10^{-7} m / s$$

$$R = (c_1 - c_2) / c_1 = \frac{10 - 0.39}{10} = 0.961$$

7. THE TRENDS OF MEMBRANE PRODUCTION MAKING MEMBRANE SEPARATIONS MORE COMPETITIVE.

Current membranes used for natural gas separation applications are produced as hollow fibers or flat sheets packaged as spiral-wound modules. Hollow-fiber modules allow large areas of membrane to be packaged into compact membrane modules. This advantage proved decisive in the choice of membranes for the separation of nitrogen from air, which was an early large-scale membrane gas separation process. Nitrogen production from air uses relatively low permeability membrane materials to process a clean, non-plasticizing gas (air) at low pressures (generally <10 bar). Essentially all membrane nitrogen-from-air separation systems use hollow-fiber modules. Natural gas streams, in contrast, contain multiple components, some of which (water, carbon dioxide, C_4+ hydrocarbons, aromatics) degrade and plasticize the membrane. Natural gas streams may also contain entrained oil mist, fine particles, and hydrocarbon vapors that can easily [21]

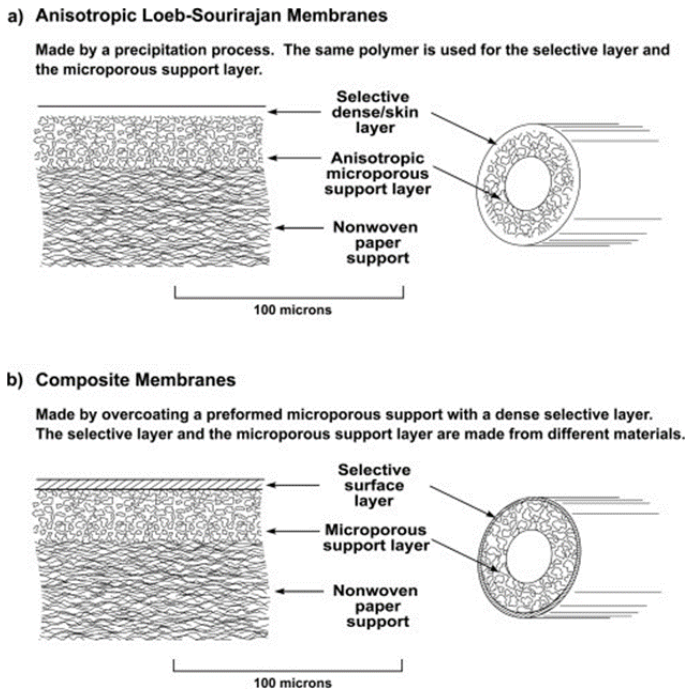


Figure 5. Structure of membranes used in membrane gas separation processes: (a) anisotropic Loeb-Sourirajan membranes and (b) composite membranes.

Collect on the membrane surface. In addition, the gas is typically treated at relatively high pressures of 30-60 bar. Under these conditions, the generally higher permeances of flat sheet membranes formed as spiral-wound modules can compensate for their higher cost (on a $/(m^2 membrane) basis), compared to hollow-fiber modules. Currently, both types of membrane modules (spiral and hollow-fiber) are produced, by different companies, and no clear winner has emerged.

One trend that has emerged in commercial gas separation membranes is a move to composite Membranes, in which a base anisotropic membrane is used as a highly porous support (to provide the mechanical strength required), and a thin layer of perm selective material (typically 0.2-1.0 μm thick) is deposited onto the support to perform the separation. Hollow-fiber membranes and flat sheet membranes can be made in this composite membrane form. Composite membranes, offer two key advantages over the conventional Loeb-Sourirajan anisotropic membrane (shown in Figure 2 a). In Loeb-Sourirajan membranes, the porous support layer that provides mechanical strength and the relatively dense surface layer that performs the separation are formed at the same time from the same

material. This limits the number of materials that can be used to make the membrane. It also means the separation properties are often compromised to make membranes with sufficient mechanical strength.

Composite membranes consist of a microporous support layer coated with one or more thin layers of a different polymer that performs the separation. Because the separation function and the mechanical support function are separated, each can be optimized separately, and the polymer best suited for each

Table 3. Principal Suppliers of Membrane Natural Gas Separation Systems

company	principal natural gas separation	membrane module type	membrane material
Medal (Air Liquide)	CO_2	hollow fiber	Polyimide
W.R. Grace	CO_2	spiral-wound	cellulose acetate
Separex (UOP)	CO_2	spiral-wound	cellulose acetate
Cynara (Natco)	CO_2	hollow fiber	cellulose acetate
ABB/MTR	CO_2, N_2, C_3+ hydrocarbons	spiral-wound	perfluoropolymers silicone rubber
Permea (Air product)	Water	hollow fiber	Polysulfone

Table 4. Typical Costs for Membranes, Membranes in 8-In.-Diameter Spiral-Wound Modules, and Module Skids

Typical cost of membrane $\$/m^2$		
t/ype of unit	gas separation (steel vessels and components)	reverse osmosis (fiberglass vessels, plastic components)
membrane	20	5
membrane in spiral-wound module form	100	10-15
membrane modules in a skid	500	30-50

Hollow-fiber reverse osmosis skids are normally less expensive on a per-square-meter-of-membrane

basis; however, lower permeances offset much of this advantage cost as much as \$1000/kg-\$10000/kg to synthesize. A Loeb-Sourirajan membrane generally uses ~50 g of polymer/ (m^2 membrane), so the material cost of membrane made from these high-cost polymers is in the \$50/m^2-500/m^2 range. Composite membranes generally use a dense layer of polymer only 0.2-0.5 μm thick, so less than one gram of polymer/m^2 of the high performance material is needed for a comparable separation. The cost of this polymer is much more affordable, at \$1/m^2-10/m^2. The micro porous support membrane for most natural gas applications can be made from conventional low cost materials.

A second emerging trend in commercial membrane separations is a move to larger membrane modules. Natural gas separations operate with high-pressure flammable gases that must be contained in code-stamped heavy steel vessels. The impact of the cost of these vessels, flanges, valves, and pipes on the system capital cost is illustrated in Table 3. Costs of module skids purchased for ultrafiltration/reverse osmosis applications are lower by a factor of 5-10. This difference reflects the higher production volumes and lower costs of the plastic components and fiberglass housings that can be used in water treatment processes.

Table 3 shows that the cost of membranes used in gas separation processes is a small fraction of the final membrane skid cost. High skid costs arise because of the many pressure vessels, pipes, flanges, and valves that are required. One way to reduce membrane skid cost is to increase the permeance of the membranes, allowing a smaller membrane area to be used to treat the same volume of gas. All membrane manufacturers pursue this approach. Increasing the feed gas pressure also reduces the membrane area required, and, hence, skid size, but at the expense of larger compressors (higher capital cost) and increased energy consumption (higher operating cost). A third approach is to develop larger membrane modules and new skid designs.

Currently, most modules, both spiral-wound or hollow fiber, are designed to fit in 8-in.-diameter housings. However, 12-in.-diameter spiral-wound modules are now being installed in some units, and some hollow-fiber module producers are also beginning to introduce very large modules, as shown in Figure 3.[10] These developments, combined with the use of lower-cost module skids,[11] are likely to significantly reduce the cost of future membrane systems and increase their long-term competitiveness.[22]

8. GENERAL FLOW SCHEME

8.1. Characteristic Of Membrane Separation

process	CHARACTERISTIC FETURES		
	Driving Force	Membrane Pore Size	Separation Mechanism
MF	Pressure 0.1-1 bar	0.02-10 µm	Sieving
UF	Pressure 2-10 bar	0.001-0.02 µm	Sieving
RO	Pressure 10-100 bar	NoN-porous	Solution diffusion
Dialysis	Concentration difference	1-3 nm	Sieving and diffusion
Electro dialysis	Electrical potential	Mol. Weight <200	Ion migration

Table 5 characteristic feature according to membrane process

The use of membranes is a very good fit for bulk removal of CO_2 from 38% in the feed gas to 22% in the product gas. When the required CO_2 removal is <50% of the inlet (42% in this application) a single-stage of membrane separation is adequate to achieve acceptable hydrocarbon recovery. Since the permeate stream will be flared, the amount of methane that co-permeates with the CO_2 needs to be monitored closely. “Assist” fuel gas will be needed to flare the CO_2 -rich permeate if its heating value is too low.

It is more efficient to design the membrane system to deliver permeate at the desired minimum heating value. However, for the small CO_2 “cut” in this case study, assist fuel is likely to be required.

Membranes are efficient in removing trace contaminants such as H_2S as long as the removal requirements are not very stringent. In this application, the pipeline specification of 50 ppmv was met.

If the inlet H_2S is higher (which has not been typical in high-CO_2 applications), or if product specification is very tight, then another technology may have to be employed. Removal of trace contaminants will be discussed later.

Membrane area requirement is strongly dependent upon feed gas pressure. Because membranes are more efficient at higher pressures, feed gas compression is indicated in order to reduce membrane size. Operating CO_2 removal membranes above 1600 psig (11,000 kPag) is not

recommended. In most applications, is it desirable to stay within the pressure that allows the use of 600# ANSI flanges. For practical purposes, this preference limits the feed gas pressure to 1275 psig (8790 kPag) for carbon steel and about 1070 psig (7400 kPag) for stainless and duplex steels.

Based on the assumptions above and the criteria for this case study, the general flow scheme options can be looked at for optimization are shown in Figure 1.

Membranes are efficient in removing trace contaminants such as H2S as long as the removal requirements are not very stringent. In this application, the pipeline specification of 50 ppmv was met. If the inlet H2S is higher (which has not been typical in high-CO2 applications), or if product specification is very tight, then another technology may have to be employed. Removal of trace contaminants will be discussed later.

Membrane area requirement is strongly dependent upon feed gas pressure. Because membranes are more efficient at higher pressures, feed gas compression is indicated in order to reduce membrane size. Operating CO2 removal membranes above 1600 psig (11,000 kPag) is not recommended. In most applications, is it desirable to stay within the pressure that allows the use of 600# ANSI flanges. For practical purposes, this preference limits the feed gas pressure to 1275 psig (8790 kPag) for carbon steel and about 1070 psig (7400 kPag) for stainless and duplex steels. [23][24]

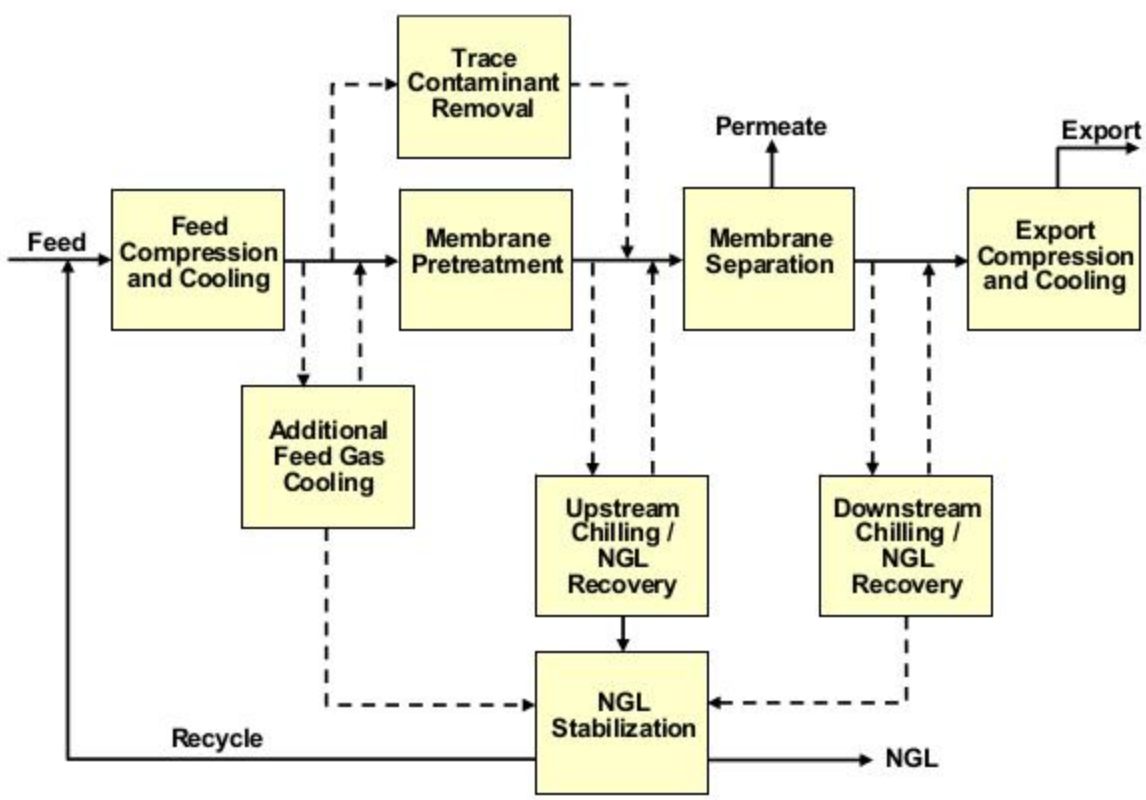


Figure 1 – General Flow Scheme Options

8.2 Feed Gas Pressure / Compression

Compressors and membranes are the highest cost equipment on the platform. Feed gas pressure is a critical parameter due to its impact on compressor and membrane cost. In all cases, compression cost is minimized by keeping the number of stages as low as possible while not exceeding the maximum discharge temperatures. With a starting pressure of 300 psig at the production separator, a single-stage feed gas compressor can reach 1200 psig (8300 kPag) and remain within 300ºF (149ºC) discharge temperature. [1]

8.3 Feed Gas Temperature / Cooling

The choice of feed compressor discharge cooling can be tied to the decision on gas chilling / NGL recovery (see the discussion below). For the case study chosen, aerial fin-fan coolers were used for all cases, which provided a temperature of 113ºF (45ºC) downstream of feed compression. Aerial coolers are low in capital and operating cost, but occupy a large plot space and are typically installed on the top deck of the platform, where space is at a premium.

Seawater cooling provides the lowest process gas temperature and can be used in direct cooling as long as corrosion issues are addressed with proper metallurgy. Direct seawater can achieve process gas temperatures of 90ºF (32ºC) in this application and lower temperatures at locations further from the equator. Closed loop cooling water circuits are sometimes employed and can achieve a process gas temperature of 97ºF (36ºC) in warm waters. This type of cooling water system uses a closed loop of treated water, which exchanges heat with seawater and is then used at various process gas coolers. Although the capital and operating cost is higher compared to aerial cooling, plot space is minimized, particularly when printed circuit exchangers or other types of compact exchangers are employed.

Feed gas cooling beyond the capability of aerial coolers can be advantageous. The level of cooling will impact the technology chosen to cool the gas. Each of these technologies has their advantages and disadvantages. Note that for the case study, the hydrate formation temperature of the raw feed gas is approximately 60ºF (15ºC). This varies slightly depending upon the feed gas pressure chosen. The lowest temperature discussed for feed gas cooling is 10ºF (5ºC) above the hydrate formation

temperature.[1]

8.2.1 Direct or Indirect Cooling Water [1]

This technology has the advantage of being incorporated into the feed gas compressor discharge cooling, eliminating the need for an additional cooler and separator by using the final discharge scrubber to remove condensed liquids.

8.2.2. Gas/Gas Cross Exchange

The membrane residue gas stream is typically a cold stream that can be used for cross exchange with the warmer raw feed gas stream to achieve a process gas temperature equal to or less than a cooling water system. This depends upon the feed gas temperature to the membrane section and the amount of CO2 being removed by the membranes. High percentage of CO2 removal results in colder residue gas stream because the permeating CO2 cools the residue via the Joules-Thompson (J-T) effect. In the case study, the membranes are operated hot to minimize membrane area and the residue gas is relatively warm for cross exchange with the raw feed gas.

8.2.3. Refrigeration System

Mechanical refrigeration systems can be employed to obtain any desired temperature. Cooling to lower temperatures can result in a significant decrease in the size of the pretreatment system. However, that advantage is countered by the addition of a new system consisting of a compressor and associated auxiliary equipment: discharge cooler, surge drum, chiller, cross exchangers, and separators required for a refrigeration system. The added cost, complexity and plot space of a refrigeration system has to be carefully weighed.

8.2.4. J-T Valve or Expander-compressor

An expander or J-T valve coupled with cross exchangers can be used to reach moderate to low process gas temperatures. If a J-T valve is used for feed gas cooling, a higher feed gas pressure and more compression power is required at the feed gas compressor. This has an advantage over mechanical refrigeration in that the horsepower in incremental and does not introduce another piece of rotating equipment that needs to be maintained. An expander-compressor reduces the amount of additional power required in the feed gas compressor, but does introduce a new unit operation. Both options require cross exchangers and additional separators.

9.3. CONTAMINANT REMOVAL

The use of a TSA unit for membrane pretreatment offers several options for the removal of trace contaminants. UOP is a world leader in adsorption technology and can offer specialty adsorbents in a "compound" or layered adsorbent bed to achieve various separations. The base design of a MemGuard pretreatment system removes only water and heavy hydrocarbons, however this system can be custom designed to remove additional contaminants.

9.3.1. Hydrogen Sulfide Removal

H2S is not harmful to Separex membranes. UOP has done extensive testing at very high levels of H2S - 1450 psig (10,000 kPag) and 20% H2S - with no ill effects reported.[3] Hydrogen sulfide and CO2 permeate at about the same rate. Membranes are a bulk removal technology and very low product specifications cannot be economically achieved. With 80 ppmv H2S in the feed gas, the case study membrane system removes H2S to about 30 ppmv, well within the export gas specification.

If required, H2S can be removed to lower export gas specifications using UOP™ GB-217™ absorbent. The most economical location for this guard bed material is the export stream where gas volumes are lowest. A slipstream can be fed to a 2-bed absorption system in lead-lag configuration. The treated gas at less than 1 ppm H2S can then be blended into the bypass stream to meet a 4 ppmv (or any other) specification.

9.3.2. Mercury Removal

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 less than 0.01 µg/Nm3. 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 MemGuard pretreatment system for moderately contaminated feed gas streams (less than about 100 µg/Nm3). High levels of mercury can also be handled, but there may be a small increase in the overall size of the TSA unit.

9.3.3. Non-regenerative mercury removal

is available using UOP™ GB-562™ absorbent. This guard bed material uses a metal oxide to react with the mercury and hold it securely. Because of the high total loadings of mercury on the absorbent, the non-regenerative guard bed can be economical for feed gas streams with low to moderate mercury contamination.

9.3.4. Mercaptan and Arsenic Removal UOP

Adsorbents can also be used to remove trace amounts of mercaptans and arsenic found in some feed gases. The heavier mercaptan species are preferentially removed, but methyl mercaptan is also adsorbed. Disposal of the mercaptan is an issue that must be solved for each individual application.

10. UPSTREAM CHILLING / NGL RECOVERY

If the design condensing temperature for NGL recovery upstream of the membranes is less than the hydrate formation temperature, the gas must be dehydrated prior to chilling. Dehydration is not

required upstream of the membrane. Cellulose acetate membranes provide very good dehydration and can meet typical water specifications when treating water-saturated feed gas. A decision to reduce the wet feed gas below the hydrate formation temperature introduces another unit operation that is not

required for more moderate feed gas cooling. Adding an adsorption system for the sole purpose of dehydration has to be carefully considered as it adds incremental cost, plot space and weight.

NGL Production, Feed Gas Rate and Membrane Area At lower condensing temperatures, more NGL is extracted from the gas stream. This contributes to "shrinkage" of the sales or export gas. Hence, higher production of NGL requires higher feed gas rates because the system requirement to meet a minimum daily delivery volume of export gas is unchanged. Cooling from 75ºF to 60ºF increases NGL production 5%. For this case study, this is an additional 1000 barrels per day of NGL. Correspondingly, the feed gas rate increases almost 6% and the membrane area requirement also increases by about 6%. At today's liquid prices, this trade off is still attractive.

At the next level, cooling to 50ºF increases NGL production by 8% (about 1500 barrels per day) relative to 75ºF. Correspondingly, the feed gas rate increases 20% and the membrane area requirement increases about 14%. Clearly this is a case of diminishing returns as the condensing temperature is lowered.

10.1. NGL Production and Recycle Compression

The effect of colder condensing temperatures is even more dramatic when looking at the condensate stabilizer recycle compressor. Cooling from 75ºF to 60ºF increases NGL production by 5% while the flash gas compression increases about 150%. At 60ºF, the recycle stream is about 10% of the feed gas.

At the next level, cooling to 50ºF increases the recycle compressor duty about 520% relative to 75ºF. At these very high recycle rates (almost 28% of the raw feed gas) the added NGL production is no longer justified due to the impact on capital and operating costs of the system.

11. NGL SABILIZATION AND VAPOR COMPRESSION

All hydrocarbon liquids produced at elevated pressures are collected in a condensate stabilizer flash drum typically at 200 psig (1380 kPag). The flashed vapors from that drum are combined with the overhead vapors from the stabilizer column and are routed to a compressor for recycling to the feed gas separator. The stabilizer is operated to produce a natural gas liquids stream with a Reid vapor pressure of 12 psia (83 kPa). A product pump transfers the NGL to a sales pipeline or FPSO.

As previously discussed, the amount of flash gas plus overhead vapors from the stabilizer is an important design point. A large recycle stream can have a profound effect on the sizing of the rest of the equipment. High vapor rates require more power consumption at the stabilizer recycle compressor, a larger stabilizer system and most significantly larger main process units.

12. RELIABILITY / TURNDOWN / EQUIPMENT REDUNDANCY

There are several ways to obtain very high reliability in gas processing operations. Sparing of key equipment is the most common method. For instance, particle filters and filter coalesces that require regular replacement of cartridges can be spared to avoid shutdowns for normal maintenance. Sparing can be in the form of 2 x 100% or 3 x 50% units and economic analysis is used to determine the preferred configuration.

Specific to the TSA unit, a blower (small single stage centrifugal compressor) is often used to route regeneration gas through the circuit and return the spent vapors upstream of the TSA. This blower is typically not spared due to its high on-stream availability. For most MemGuard systems, an alternate regeneration gas supply or routing is available which can be used during the infrequent maintenance of the blower. When there is feed gas compression the spent regeneration gas can be routed to its suction. Regeneration gas typically comprises less than 10% of the feed gas stream, so the effect on total production is minimal while maintenance of the blower takes place. If a complete gearbox and rotor assembly is kept in a warehouse, downtime for catastrophic failure of a centrifugal blower, which is very rare, would be less than 12 hours.

Spare adsorbers are not recommended for the TSA system. The technology is sufficiently mature that a TSA system will be available greater than 98.5% of the time when properly designed. Interruption of the TSA cycle has mostly been due to a bad position switch at one of the automated switching valves and not from valve failure. The control logic is designed to allow the TSA cycle to continue despite the faulty position switch. The operator can field verify the valve position and acknowledge the alarm at the control panel until the position switch is replaced. UOP adsorbents typically last three to five years prior to replacement depending on feed gas and good unit operations. Gas heating is typically provided via closed-circuit heating oil using waste heat recovery installed on the feed compressor gas turbine exhaust. Hot oil is used at the membrane preheater and the TSA regeneration gas heater. Heating oil is highly reliable and if the gas turbine shuts down, there is no feed gas to process. Hence its availability is as good as the feed compression availability.

Despite the long life of membrane elements, some customers have requested installed spares. This may seem excessive given the long life of Separex membranes. Sparing a small portion of the membrane area does not require a lot of space on the platform but it does add isolation and start-up valves. Many membrane projects have built in turn down based on customer requirements. Large projects typically end up with 20 to 25% turndown so that membrane area can be matched to gas production levels. Spare housings may be accommodated within the turndown ratio for a given project by installing another incremental percentage. Having 120% installed membrane area ensures that production will not be reduced during membrane maintenance.

Other areas considered for reliability include sparing critical valves, designing for efficient maintenance, use of highly reliable instruments such as solenoid valves and installation of redundant PLC main processors.

Some customers prefer multiple trains to provide reliability. A two-train concept ensures production will rarely fall below 60% of normal production. A two-train concept can be employed offshore and remain within reasonable plot space. For the case study discussed, added reliability for a two train configuration is obtained via cross-ties between the trains at the junctions between the main sections.

For instance, the feed compression of Train One can be routed to the pretreatment section of Train Two and then sent back to Train One membranes. The likelihood that the same sections of both trains would be down at the same time is very small.

13. ENIVIRONMENTAL IMPACT

Membranes are ideal for remote and rugged locations and are environmentally friendlier than solvent-based CO2 removal systems. Membranes are dry systems without any concern for chemical spills. There are no liquids to transport on a regular basis due to normal solvent losses, reducing logistic concerns, and there is no need for water purification units to supply clean makeup water. Membrane life is measured in years so replacements are few and far between.

Membranes are also ideally suited for CO2 capture and sequestration to reduce the harmful effects of greenhouse gases. In the case study, the CO2 stream was to be flared so the permeate pressure of the membranes was maintained at 15 psig (103 kPag). But membranes can be operated at elevated permeate pressure so that the CO2 stream can be delivered for compression and re-injection to a favorable geological formation. Operating at higher pressures of 50-100 psig (350-700 kPag) greatly reduces compression duty for re-injection. There is a small price to pay in larger membrane area requirement but significant savings in capital and operating cost of the reinjection compression. Because of the flat-sheet spiral-wound configuration of Separex elements, spare membrane capacity can be provided by installing longer horizontal tubes than required for the design separation. For instance if a project needs six membrane elements per tube, a tube length that can accommodate seven elements may be provided at minimal extra weight or cost. Six elements are loaded for flaring the permeate stream and the seventh element can be loaded later to accommodate a higher permeate pressure when a CO2 re-injection system is installed.

14. MEMBRANE BACKGROUND

14.1. Factor Affecting The Separation Processes

Two (2) factors affect the selectivity and the flux or permeation rate through the membrane severely affecting the overall performance of the separation process.

These include:

- concentration polarization at the membrane surface (short term or reversible)
- fouling of the membrane (long term & irreversible)

14.1.1. Concentration polarization:

The non-permeating species is carried towards the membrane by the convective flux of the feed but the species remains on the upstream side. Its concentration increases gradually at the membrane surface and ultimately become greater than its concentration in the bulk liquid thereby setting up concentration polarization at the membrane surface. It sets in also due to different rates of transport of various species Concentration polarization augments osmotic pressure and reduces the flux through the membrane and may affect membrane separation characteristics. The phenomenon is important especially in UF. The steady state solute concentration profile in the boundary layer close to the membrane surface.

The solute concentration at the membrane may be calculated from a mass balance on the solute :

Rate of convection towards the membrane = rate of diffusion back into the bulk liquid + rate of permeation

$$J_s C = \frac{D dC}{dx} + J_s C_p$$

$$\frac{dC}{C - C_p} = \frac{J_s}{D} dx$$

Integrating from x=0 and C = Cb to x = σ (thickness of the bound layer) and C =C_m; and substituting for (D/ σ) by k', a mass transfer coeffcient, the concentration of the solute in the membrane surface is given by

$$C_m = C_p + (C_b - C_p)exp\left(\frac{J_s}{k'}\right)$$

$$J_s = k' ln\left(\frac{C_m - C_p}{C_b - C_p}\right)$$

If a negligible amount of solute passes through the membrane, C_p can taken as zero, giving:

or

$$C_m = C_b exp\left(\frac{J_s}{k'}\right) \qquad J_s = k' ln\left(\frac{C_m}{C_b}\right)$$

The ratio C_m/Cb increases if the flux, J_s is high or the mass transfer coefficient, k' is low. Low k' values may be due to low values of the diffusivity, D which is due to high molecular weight or due to high viscosity of the solution, or large values of the thickness of the boundary layer σ due to low turbulence.

The value of k' has to be determined empirically

<u>14.1.2. Fouling</u>

The flux through the membrane decreases slowly with time in all the membrane process due to fouling caused by a variety of factors such as ; slime formation microbial growth deposition of macromolecules (particularly in UF) colloid deposition physical compaction of the membrane (esp : in RO due to high pressure operation) Fouling is irreversible and necessitates the replacement of the membrane. It can inhibited by:

A) Careful selection of membrane material (eq hydrophilic surface is less prone to fouling by proteins)

B) pretreatment of feed (such as pH adjustment or precipitation to remove salt)

C) frequent cleaning of the membrane with chemicals and back flushing permeate The problems associated with concentration polarization and fouling is overcome by cross-flow filtration

instead of the conventional dead-end filtration.

In the conventional filtration, the feed is pumped perpendicularly to the filter medium. As the fluid passes through the filter, a concentration solution or gel of non- permeating species is formed on the upstream side of the filter resulting in concentration polarization Increasing the velocity at the membrane surface creates turbulence thereby decreasing the thickness of the concentration boundary layer and delaying the onset of concentration polarization However, a better strategy is to adopt cross flow filtration (see figure) instead of the conventional dead-end filtration. In cross flow filtration, the feed fluid is pumped tangentially across the filter medium (and perpendicular to the flux through the membrane) to avoid concentration polarization. Other advantages of this technique are that the membrane separation characteristics are not affected and the flux is not reduced with filtration time.

14.2. Background Of Membrane

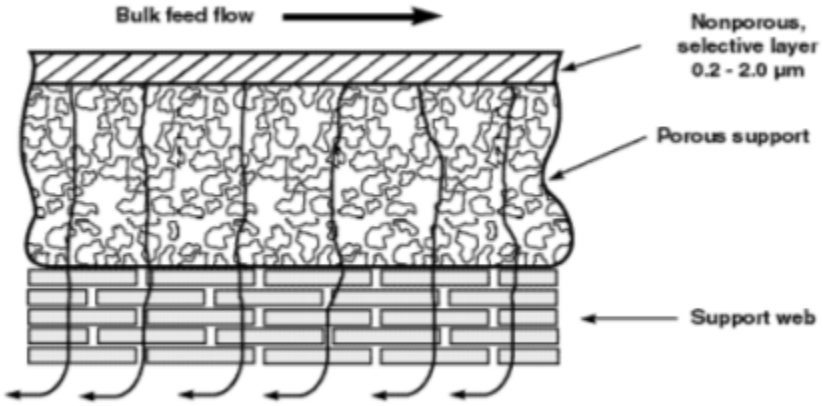


Figure 7: Cross-section of an MTR composite membrane.

Traditional membranes used for CO 2 removal are made from a single polymer, such as cellulose acetate, cellulose triacetate or polyimide. These membranes, known as asymmetric membranes, are cast in such a way as to form a thin, dense skin on a sponge-like porous substructure. The underlying porous layer provides mechanical strength; the thin skin layer is responsible for the separation properties.

Polymers that exhibit good separation performance may not be ideally suited for providing mechanical support and long term chemical stability. Therefore, a compromise has to be made, and usually results in a membrane that is neither a very good separation membrane nor sufficiently robust.

Better membranes can be made if the performance and strength properties are uncoupled. MTR has developed composite membranes with this capability and specifically geared to the natural gas market. The cross section of one of these membranes is shown in Figure 3.

The membrane consists of three layers: a non woven fabric that serves as the membrane substrate (the support web); a tough, durable, solvent-resistant microporous layer that provides mechanical support without mass transfer resistance; and a nonporous, defect-free selective layer that performs the separation. Figure 3. This configuration allows each of the layers to be independently chosen to optimize their function: the selective layer for high flux and selectivity, and the support layers for mechanical and chemical stability without influencing the separation. Specific selective layers may be chosen for specific separations, opening up exciting new applications, such as separation of heavy hydrocarbons from light hydrocarbons and nitrogen, separation of CO 2 and H 2 S from methane, and dehydration.

15. DIFFERENTS TYPES OF MEMBRANE

15.1. Micro-Porous Membrane

These membranes are usually made up of materials like ceramics, graphite, metal oxides and polymers etc. The pore size of these membranes varies from 1 nm-20 microns. Membrane works like a fibre filter and separates by sieving mechanism (Srikanth 2005). In structure and function microporous membranes are similar to conventional filters, however, the pore size is very smaller as compared to conventional filter. Microporous membranes pores sizes range from 0.01 to 10 μm

15.2. Homogeneous membranes

Homogeneous membranes are dense membranes through which molecules pass by pressure, concentration or electrical potential gradient. These membranes are used to separate the chemical species of similar size and diffusivity when their concentration difference significant

15.3. Electrically charged membrane

These membranes consist of highly swollen gels, which carry fixed positive or negative charged. Their main potential is in electro dialysis.

15.4. Asymmetric membrane

Asymmetric membranes consist of two parts; thin skin layer (0.1-1.0 micron) lay on highly porous (100-200 micron) thick substructure. The thin layer acts as a separator and its separation characteristics depends on the membrane material and its pore size. Porous sub layer has a little impact on separation its main purpose is to give support to the thin layer

15.5. Liquid membranes

These membranes utilize the carrier to transport the components selectively like metal ions “at relatively high rate across the membrane interface” There are, in fact, two basic types of liquid membranes, an Emulsion Liquid Membrane (ELM), and an Immobilized Liquid Membrane (ILM), also called a Supported Liquid Membrane. An ELM can be thought of as a bubble inside a bubble inside a bubble, and so on; the inner most bubble being the one recieving phase, all the others acting as separation skins with carriers inside, and anything outside the bubble being the source phase. In an ELM setup, there would be huge quantities of these bubbles, of course, all doing the same thing.

15.6. Dialysis (liquid permeation)

In this case the small solutes in one liquid phase diffuse through a porous membrane to the second liquid phase where the permeants are diluted by means of a so-called sweeping solvent. The driving force is a concentration gradient so the flux rates are low. If the boiling point of the permeants is much lower than that of the sweeping liquid, the permeants can be separated by flashing from the

sweeping liquid, the dialysis process is called pertraction. In practice dialysis is used to separate species that differ appreciably in size, which have a large difference in diffusion rates. Applications include recovery of sodium hydroxide in cellulose processing, recovery of acids from metallurgical liquors, removal of products from a culture solution in fermentation, and reduction of alcohol content of beer

15.7 Series resistances in membrane processes

In dialysis, the solute molecules must first be transported or diffuse through the liquid film of the first liquid phase on one side of the solid membrane, through the membrane itself, and then through the film of the second liquid phase. This is shown in Figure below, where c1 is the bulk liquid phase concentration of the diffusing solute A in kg mol A/m3, c1i is the concentration of A in the fluid just adjacent to the solid, and c1iS is the concentration of A in the solid at the surface and is in equilibrium with c1i. The mass transfer coefficients are kc1 and
kc2 in m/s. The Equilibrium distribution coefficient K' is defined as:

$$K' = \frac{C_S}{C_L} = \frac{C_{1iS}}{C_{1i}} = \frac{C_{2iS}}{C_{2i}}$$

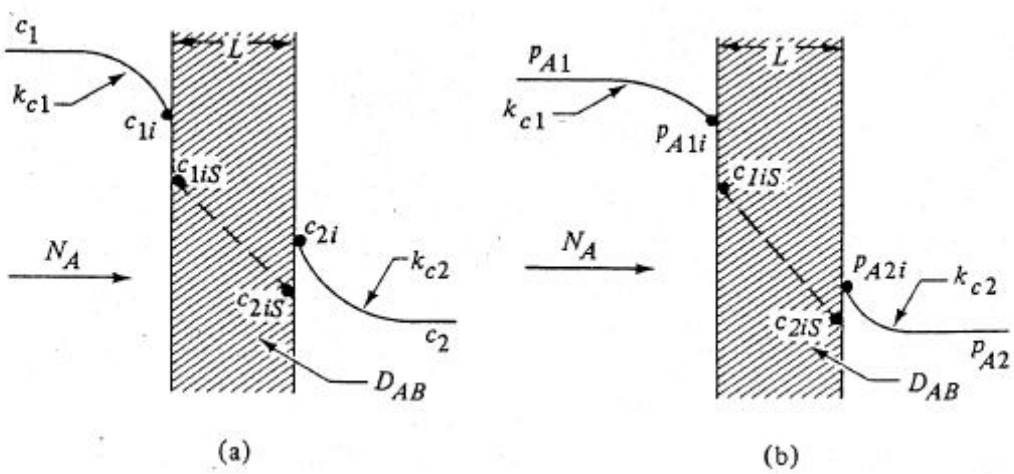


Figure 8: Concentration profile for membrane process. a) two liquid films and a solid. B) two gas films and a solid.

Example 1: Membrane diffusion and liquid film resistances

A liquid containing dilute solute A at a concentration c1=0.030 kg mol/m3 is flowing rapidly by a membrane of thickness L=3.0x10^-5 m. The

distribution coefficient K'=1.5 and DAB=7.0x10^-11 m2/s in the membrane. The solute diffuses through the membrane and its concentration on the other side

is c2=0.0050 kg mol/m3. The mass transfer coefficient kc1 is large and can be considered as infinite and kc2 =2.02x10^-5 m/s.

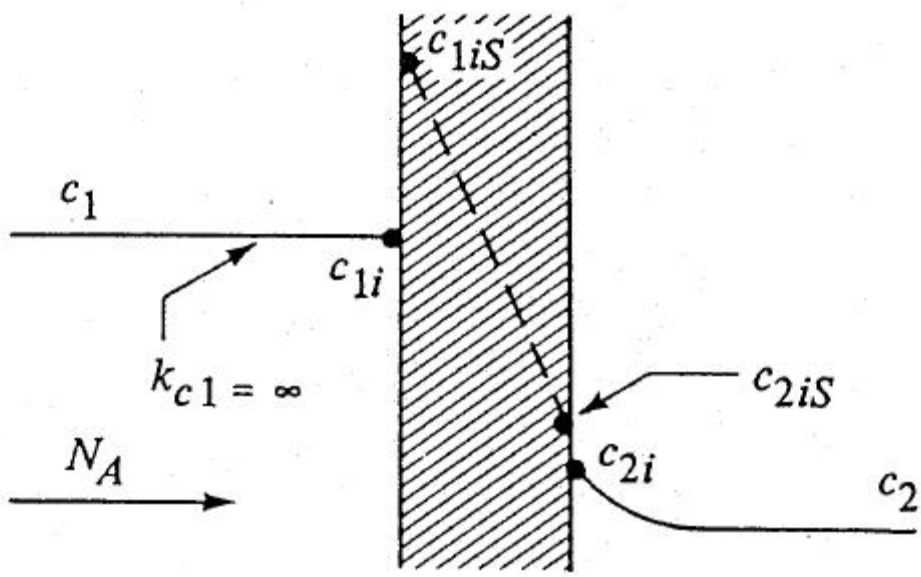
(a) Derive the equation to calculate the steady-state flux NA and make a sketch.

(b) Calculate the flux and the concentrations at the membrane interfaces.

Solution: For part (a) the sketch is shown in schema..

Note that the concentration on the left side is flat (kc1=∞) and c1 = c1i. The derivation is the same as for the internal concentrations drop out, the final equation is $N_A = \dfrac{C_1 - C_2}{1/K_{c1} + 1/P_M + 1/K_{c2}}$

but 1/kc1 = 0 to give $N_A = \dfrac{C_1 - C_2}{1/K_{c1} + 1/P_M}$



For part (b),

$$P_M = \frac{D_{AB}K'}{L} = \frac{7*10^{-11}*(1.5)}{3*10^{-5}} = 3.5*10^{-6} m/s$$

$$N_A = \frac{C_1 - C_2}{1/K_{c1} + 1/P_M} = \frac{0.030 - 0.005}{1/3.5*10^{-6} + 1/2.02*10^{-5}}$$

$$N_A = 7.458*10^{-8} kg.mol/sm^2$$

To calculate c_{i2}

$$N_A = K_{c2}(C_{2i} - C_2) = 7.458*10^{-8} = 2.02*10^{-5}(C_{2i} - 0.005) = 0.00869 kg.mol/m^3$$
$$C_{i2s} = K'*C_{i2} = 1.5*0.00869 = 0.01304 kg.mol/m^3$$
$$C_{i1s} = K'*C_{1i} = 1.5*0.03 = 0.045 kg.mol/m^3$$

16. COMMON GAS CONTAMINANTS

16.1. Effects on new and traditional membranes

When traditional membranes for CO 2 removal are used, heavy components, such as aromatics, BTEX, and heavy aliphatic hydrocarbons do not permeate the membrane. As the CO 2 is removed, the concentration of these components can build up in flowing along the feed channel. If the concentration reaches a level such that the phase envelope is crossed, hydrocarbons can condense out of the gas on the surface of the membrane. Since these organic liquids are often solvents for the membrane materials, such condensation can be potentially devastating, by literally dissolving the membranes. Significant pretreatment of the feed gas is usually required to prevent hydrocarbon condensation. The simplest treatment is to heat the gas above the highest expected dewpoint, but in many cases adsorption beds or refrigeration are required upstream to lower the hydrocarbon content.

The composite membranes developed by MTR use materials that fare much better when exposed to hydrocarbons. The new custom membranes for NGL recovery, nitrogen separation and H 2 S removal are essentially unaffected by aromatics and other condensable hydrocarbons, even under saturation conditions. Further, these components do not build up on the feed side; rather they permeate the membranes preferentially. Asthe high pressure feed gas passes across the membrane, these condensable components are the first to be stripped from the gas and are collected as a low pressure, vapor phase

permeate stream. The result is that the dewpoint of the gas decreases, not increases, as the gas travels along the feed channel. Therefore any possibility of condensation on the membrane surface is avoided.

The new membrane developed by MTR for CO 2 removal behaves in the same manner as traditional membranes insofar as it selectively permeates CO 2 and rejects hydrocarbons.

However, the chemistry of the membrane has been carefully designed so that aromatics and other hydrocarbons are not solvents for the membrane materials. Therefore, even if briefly exposed to liquid

hydrocarbon condensates, the membranes are not permanently affected. After removal of the liquids, the membranes continue to function normally.

Further, the chemical structure of the new membrane materials, and their packaging configuration as spiral wound elements, allows them to be cleaned and reused. This results in lowered operating costs and reduced disruption to production.[17][1]

17. MEMBRANE PACKAGING

MTR makes composite membranes in flat-sheet form and packages them in a spiral-wound module configuration, as shown in Figure 2. Spacers on the feed and permeate sides of the membrane create flow channels. The feed gas enters the module and flows between the membrane sheets. The faster permeating component permeate the membrane preferentially, and flow inward to a central collection pipe. Slower permeating components are rejected and exit as the high pressure residue stream.

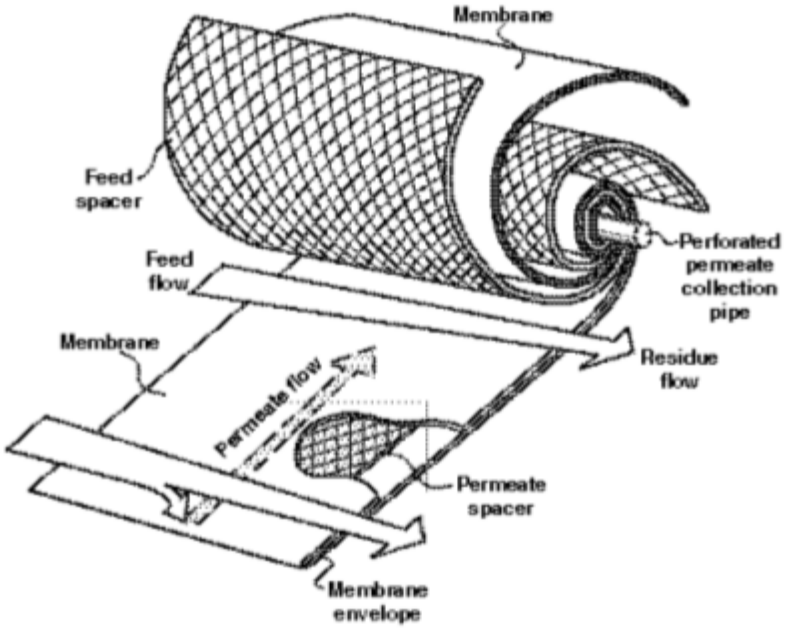


Figure 9: Schematic diagram showing components and gas flow patterns of a spiral-wound module

The spiral-wound modules are manifolded and placed in pressure vessels made from commercial steel pipe. The membrane elements are configured in series and parallel flow combinations to meet the requirements of the particular application. A picture of a typical skid-mounted membrane system showing two pressure tubes is shown in Figure 10.

Figure 10. A typical membrane skid, showing two steel pressure tubes housing the membrane modules. [12-13]

18. DESCRIPTION OF NEW APPLICATIONS AND PROCESSES

18.1 Nitrogen Removal Process

Nitrogen separation from natural gas has traditionally been performed using cryogenic processing. In the past decade, membrane and PSA processes have been introduced. Table 6 shows a general comparison of these technologies and their applicability ranges.

Table 6. A Comparison of Nitrogen/Methane Separation Processes

process	Flow range	N2 content (Mol%)	complexity	Hydrocarbon recovery	Development stage
Cryogenic processing	>15	>15	complex	Heavy hydrocarbon in product gas	Early commercialization
PSA	2-15	4-25	Simple. Batch operation requires bed swicthing	Heavy hydrocarbon in tail gas	Early commercialization
Membrane	0.5-25	4-25	Simple continuous operation	Heavy hydrocarbon in product gas	Early commercialization

When a feed gas containing nitrogen is introduced to a NitroSep membrane stage, a nitrogen rich stream will be rejected from the membrane and a hydrocarbon rich stream will pass through the membrane to the permeate outlet. By connecting two or more membrane stages, a well-defined separation can be achieved without resorting to cryogenic temperatures or collecting liquid hydrocarbons. By utilizing the nitrogen-rich stream as fuel, maximum overall efficiency can be realized. The NitroSep system can be designed to recover condensate for resale if the incoming gas is saturated with heavy hydrocarbons.

NitroSep systems can be as simple as a single stage unit, to treat streams that are only slightly out of specification in nitrogen, or can have two or more steps or stages to achieve high hydrocarbon recovery and nitrogen levels less than 2%. The flexibility of the membrane system allow for significant variations in inlet gas compositions and flow rate while achieving desired product specification.

Figure 4 shows a typical flow scheme of a NitroSep process. The low pressure inlet gas is compressed and introduced into the membrane inserts. Pipeline quality gas is generated in the first step, which includes recovery of most of the heavy hydrocarbons.

The second step allows increased recovery of methane, which is recycled to the inlet compressor for further processing. The composition of the nitrogen-rich reject gas from the second step is adjusted by

that step to be usable as compressor fuel.

The membrane system is delivered in a single compact skid, which can be placed directly on gravel. To treat raw gas of high nitrogen content, additional membrane stages may be added to treat the first stage permeate.[12-13]

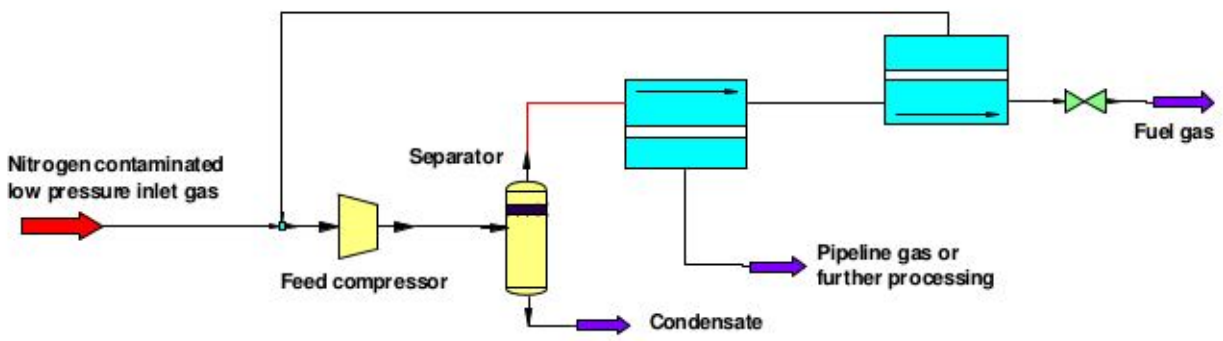


Figure 11. Flow scheme of a typical NitroSep © process for nitrogen removal from natural gas.

The membrane unit is simple to operate and control. The system can reach steady state performance within minutes of startup, and can be fully automated and remotely monitored.

The economics of the NitroSep process are affected by the nitrogen content in the feed gas, the value of the product gas, and the maximum allowable nitrogen content in the product gas. For upto about 30 mol-% N2 in the feed the membrane process can provide a solution that is economically very attractive. The membrane process is especially suited to process smaller flow rates of gas allowing smaller wells to be produced economically.

The membrane process is flexible and can be designed to maximize hydrocarbon utilization and revenues. The BTU value of the nitrogen reject stream can be tailored to match the fuel specification of compression sets used in the NitroSep process, or any can be used to produce electric power in a Gen-set for electrically driven compressors. In addition, virtually all ethane and heavier components are recovered in the product gas sent to the pipeline. This maximizes the BTU value sent to product thereby increasing the total generated revenues. The overall membrane process can be designed to not only recover pipeline spec natural gas, but also NGL as a separate product. In addition, if required the

overall process including a Gen Set can provide electrical power for the sale to the grid.

NitroSep can be used as a stand-alone operation to process gas from as low as 0.5 MMscfd to 20-30 MMscfd or higher. The membranes operate at near ambient temperatures, and in most cases no separate dehydration or hydrate control is required.

There is no accumulated liquid in the system, so no risk of pool fires or need to dispose of or store liquids. If desired, however, the system design does offer the flexibility to recover hydrocarbon liquids to increase total revenues.

Figure 6 shows a picture of a membrane skid installed In Omaha processing natural gas containing about 6.5 mol-% N2 down to less then 2.5 mol-%. The system has been operational since November 2002 and provided constant performance for the client. The system has been designed to allow upto 50% turndown “on the fly”, to accommodate the changing needs of the customer in the plant.

Figure 12. System Photograph of Unit installed in Omaha, Nebraska, reducing 6.5mol-% N2 in Natural gas to 2.5 mol-%.[12-13]

19. NGL SEPARATION PROCESS

The hydrocarbon-selective membranes used in the nitrogen separation process described above are also very suitable for removing condensible hydrocarbons to lower the dew point of the gas, or to control the Btu value of engine or turbine fuel streams.

MTR has three references in this area, including one in Brazil for conditioning turbine fuel gas, and others in offshore locations for conditioning gas engine fuel.

A schematic flow diagram for this application as applied to conditioning gas for gas engines is shown in Figure 7. A low-pressure natural gas stream is compressed to a high pressure in a pipeline compressor. The compressor is driven by a direct-drive gas engine, which is fueled by raw compressed natural gas. A small side stream is diverted from the raw compressed gas pipeline and enters the membrane system. The membrane separation step removes the heavy hydrocarbons, as well as other contaminants, such as CO_2, H_2S and water vapor, to produce a lighter, sweeter, drier conditioned residue stream, and a heavy-hydrocarbon-enriched permeate stream, which is recycled to the compressor inlet.

The conditioned residue stream has a lower Btu value and a higher methane number, and is fed to the engine fuel intake. The membrane system can be designed to meet methane numbers specified by engine manufacturers. The performance results for this system are discussed below. [12-13]

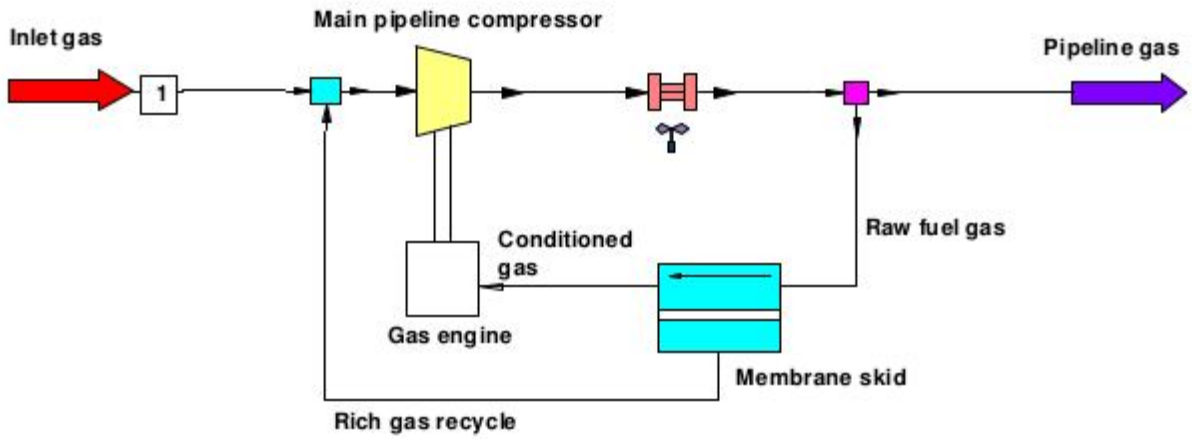


Figure 13: Schematic process flow diagram for a membrane fuel gas conditioner fora gas engine application.

The composition and conditions of the main streams in the process shown in Figure 7 are given in Table 3.

Process conditions	membrane	conditioned
	feed	Fuel gas
Temperature °C	35	10.5
Pressure (bar)	65	65
Total mass flow	110.1	58
Total volume flow	0.95	0.5
Component mol %		
Carbon dioxide	1.3	0.6
Methane	72.8	81.2
Ethane	9.6	9.0
Propane	9.9	7.1
I-butane	2.4	0.8
n-Butane	2.5	0.9
n-Pentane	1.3	0.4
Water	0.11	0.00
Hydrocarbon dew point	35	3.5

Table 7. Feed and Conditioned Fuel Gas Compositions and Important Process Variables.

The data in Table 3 show that the membrane process selectively removes the C 3+ hydrocarbon components from the feed gas. The conditioned fuel gas meets both the Btu value and methane number specifications for the gas engine. The dew point of the gas is reduced from 35 o C to 3.5 o C in the process. The system is compact (6 ft x 6ft x 6 ft), has no utility requirements, no moving parts, and requires no operator attention.[12-13]

19.1. CO2 Removal Process

The removal of CO 2 has been the predominant traditional application of membranes in the natural gas industry. Numerous small plants and several larger plants processing up to 500 MMSCFD of gas or more have been installed using cellulose acetate, cellulose triacetate or polyimide membranes. These polymer materials show good separation performance but are known to be susceptible to damage due to exposure to aromatics, other organics liquids or water, any of which can cause irreversible damage to the membranes. To mitigate the risk of damage, membrane processes utilize significant pretreatment steps to remove offending components down to acceptable levels. This increases capital and operating costs, and adds complexity to an otherwise simple process. Additionally, any upsets in the pretreatment train may still expose the membranes to harmful contaminants, resulting in the need to replace the membrane inserts.

To address this issue, MTR has focused on developing more intrinsically robust membranes. These membranes can operate safely with minimal pretreatment of the feed gas, and are more forgiving of accidental exposure to high levels of contaminants. The membranes are based on polymer chemistry similar to that of Teflon®, the well known non-stick material. These polymers do not dissolve or disintegrate in aromatics like other conventional polymers, and retain performance even after a limited accidental exposure to such components.

Table 1 above shows the various common contaminants of natural gas and how they can affect membrane performance. The Z-Top membrane shows superior chemical stability for CO 2 removal applications.

An additional benefit is that the Z-Top membranes exhibit gas fluxes an order of magnitude higher than membranes made from traditional polymers, so that smaller membrane area is required to perform a given separation, resulting in a smaller skid size, and in some cases lowering costs. The membrane process can be used as a stand-alone or a hybrid process. In a typical hybrid flow arrangement, shown in Figure 9, the membrane separation step is followed by an amine absorption step. This process configuration is useful for bulk CO 2 separation and for debottlenecking existing CO 2 removal plants. The membrane system is used to remove a significant portion of the acid gases (as much as half or more) from the gas entering the amine contactor. This allows additional flow to enter the amine plant, while significantly reducing the load on the amine regeneration section.

A combination of membranes described in this paper can be used to effectively reduce CO2 and

conditioned gas for the amine system.[12-13]

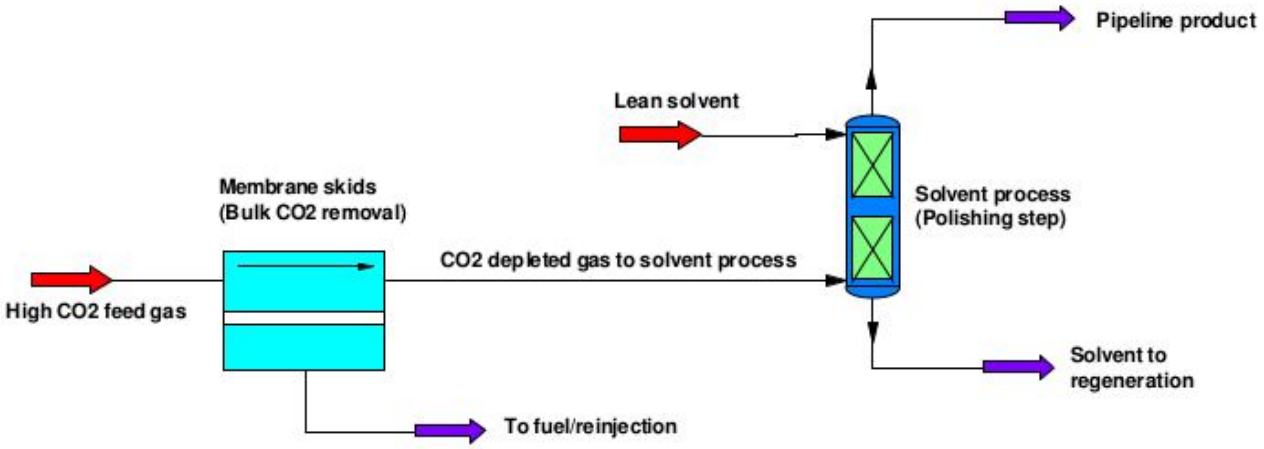


Figure 14. A hybrid process for CO 2 removal from natural gas, using a membrane separation step followed by a solvent absorption step.

The membrane step can cut the acid gas content of the feed to the amine plant by half.

19.2. H2S Removal Process

MTR has also developed a membrane process for H 2 S removal from natural gas. The applications of this membrane process include bulk separation of H 2 S from sour natural gas, and removal of H 2 S from fuel gas streams used in gas engines and turbines.The chemistry of the membrane results in preferential permeation of H 2 S and other sulfur-bearing components over hydrocarbons. A simple process scheme illustrating how this membrane can be applied for fuel gas conditioning is shown in Figure 10.

A slip stream of raw fuel gas is taken from the main gas line, cooled as required and fed to the inlet of the membrane separation unit. A separator removes condensed heavy hydrocarbons from the membrane process loop. The membrane permeate, enriched in acid gas, is returned to the main gas line. The residue stream is sufficiently reduced in acid gas content, and heavy hydrocarbons, to meet fuel specifications for a gas engine or turbine.

Figure 15: Membrane Separation Performance for Removal of H 2 S from Fuel Gas

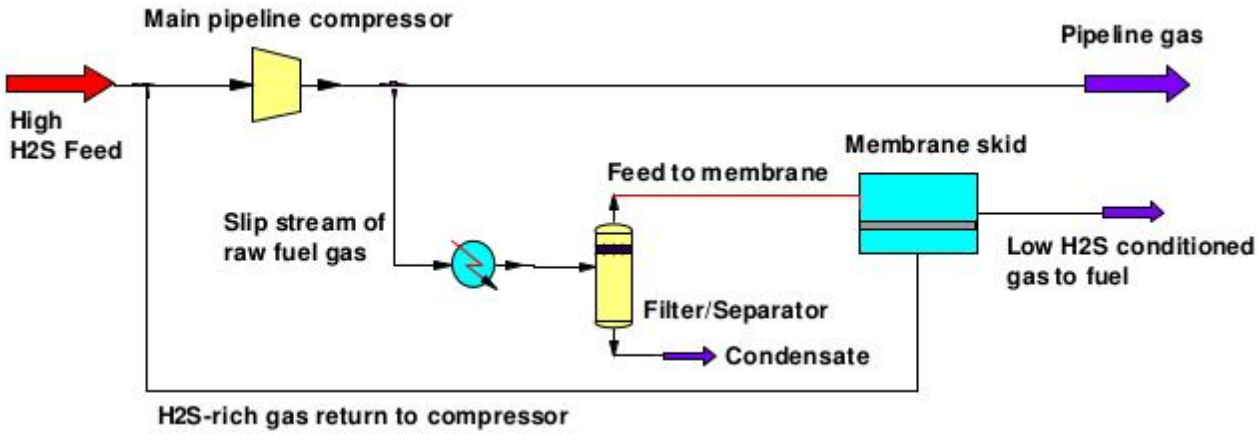


Table 6 shows the mass balance for the membrane separation step.

Stream Name	Feed to Membrane System	Conditioned Gas to Fuel	Return Gas to Compressor
Temperature (^{o}F)	90	35	62
Pressure (psia)	1015	1013	45
Total Flow Rate (MMscfd)	1.72	0.76	0.96
Component mole %			
Helium-4	0.07	0.11	0.04
Nitrogen	0.40	0.76	0.12
Carbon Dioxide	1.91	0.19	3.25
Hydrogen Sulfide	**0.34**	**0.004**	**0.60**
Methane	85.92	95.24	78.62
Ethane	6.92	2.88	10.09
Propane	2.72	0.62	4.36
I-Butane	0.37	0.05	0.62
N-Butane	0.67	0.09	1.13
I-Pentane	0.18	0.02	0.31
N-Pentane	0.19	0.02	0.32
N-Hexane	0.16	0.01	0.28
N-Heptane	0.10	0.01	0.17
N-Octane	0.04	0.00	0.07
Water	0.01	0.00	0.02

Table 8 shows that the membrane unit can reduce the H_2S content in the fuel from about 3,400 ppm to about 40 ppm.

In this way, engine or turbine components are protected, corrosion is reduced, and a significant reduction in maintenance needs can be achieved.

Use of the process also minimizes the need to buy higher priced sweet gas, which can result in significant cost savings. As an on-site treatment, membrane separation is preferred over liquid or solid scavengers because of the very low operating cost of the system.

Thus, the membrane system combines low capital and operating costs with a good technical solution to a processing problem for which conventional technologies are not attractive. As with the CO_2 removal process described previously, H_2S removal may be carried out in a stand-alone operation, as shown in Figure 10, or in a hybrid arrangement.

In a hybrid process, the membrane separation step is best suited for a first bulk H_2S separation, and can be followed by conventional amine treating or other H_2S removal technology, in a manner similar to that shown in Figure 9 for CO_2 removal. Such a configuration can debottleneck existing gas processing facilities, especially when the H_2S-rich gas can be re-injected. The membrane step can reduce the load on the regeneration columns and Claus plants downstream.

The availability of the membrane bulk removal step also allows producers the flexibility to improve the quality of acid gas that is to be sent by pipeline to remote treatment facilities.

20. ADVANTAGES AND DISADVANTAGES OF MEMBRANE USES

20.1. Advantages

- Low capital investment when compared to the solvent systems.
- Ease of operation: process can run unattended.
- Ease of installation: units are normally skids mounted.
- Simplicity: no moving parts for single-stage units.

- High turndown: the modular nature of the system means very high turndown ratios be achieved.
- High reliability and on-stream time.
- No chemicals needed.
- Good weight and space efficiency.

20.2. Disadvantages

- No economy of scale: because of their modular nature, they offer very little economy of scale.
- Clean feed: pretreatment of the feed to the membrane to remove particulates and liquids is generally required.
- Gas compression: because pressure difference is a driving force for membrane separation, considerable recompression may be required for either or both the residues and permeates streams.
  - ✓ For natural gas systems, the following disadvantages also apply:
- Generally higher hydrocarbon losses than solvents systems.

  H_2S removal: H_2S and CO_2 permeations rates are roughly the same, so H_2S specifications can be difficult to meet.
- Bulk removal: best for bulk removal of acid gases; membranes alone cannot be used to meet ppmv specifications.
  - ✓ For offshore applications, membranes are attractive because of unattended operation, no chemicals needed or generated, and good weight and space efficiency.

21. CONCLUSION

The use of membranes to process natural gas is a rapidly growing area of technology. More than 20 large (>100 million scfd) carbon dioxide membrane removal plants have now been built, as well as many smaller systems. As the technology matures, it seems likely that the membrane market share for carbon dioxide separations will grow from the present low level, especially for gases that have high carbon dioxide contents (20% or higher).

Cellulose acetate, which was the first material developed for carbon dioxide separation applications, is still the industry standard, but alternatives are now commercially available. Membranes are the technology of choice for carbon dioxide removal systems on offshore platforms, and they are beginning to compete head-to-head with amine systems at onshore plants. Another growing application is the removal of heavy hydro-carbons. Thus far, the most important use of membranes has been in small (0.2-2.0 million scfd) streams to produce clean gas for field engines and turbines. Over time, these new materials will increase the competitiveness of membranes in the realm of carbon dioxide/natural gas separations. This application is growing, but a much larger market exists for units to recover heavy hydrocarbons as natural gas liquids from associated gas streams produced on offshore platforms or at remote wells. These streams are large and not uncommon, and the value of the liquids recovered by the membrane process can lead to short payback times.

The development of better, more-selective membranes would accelerate the development of these applications. Membranes offer a modest separation selectivity of methane from nitrogen; however, the separation is difficult using any other technology, so membranes are still the low-cost solution in these applications. Nitrogen removal with membranes has also experienced development over the past two years. The dehydration of natural gas, which is a very common natural gas treatment process, has proved disappointing as an application for membrane technology. A handful of systems that are based on membranes and process designs developed for air dehydration have been installed; however, current membrane technology cannot compete with glycol absorption, except in a few offshore operations where size and weight considerations favor a membrane solution. Therefore, the dehydration of natural gas with membranes is likely to remain a niche application. Natural gas treatment and export is a well-established yet energy demanding industry.

The typical process units encountered in a gas treatment plant are elaborated along with the multiple

options and their associated advantages and drawbacks. The development of energy efficient, ecofriendly and reliable natural gas treatment technologies becomes crucial, providing the forecasted increase in the natural gas demand worldwide. In summary, membrane-based removal of natural gas contaminants is the most rapidly growing segment of the membrane gas separation industry, especially in applications for the separation of carbon dioxide, nitrogen, and heavy hydrocarbons. Improvements in polymer performance, membrane structure, module fabrication, and process design have all contributed to increasing the potential range of applications for membranes in natural gas treatment. Membranes now give natural gas producers an additional tool for upgrading the quality of the gas streams that they can deliver to the natural gas market.

References

[1] ARTHUR J.Kindnay,William R. Parrish, Daniel G. McCartney Fundament of natural gas processing second edition (major work base on)*

[2] Bakar, W. A. W. A. and R. Ali. (2010). Natural Gas, In: natural gas, Primož Potočnik, pp. (1616), Sciyo, Retrieved from http://www.intechopen.com/articles/show/title/natural-gas

[3] Adom, E., Zahidul Islam, S., Ji, X., 2015. Modelling of boil-off gas in LNG tanks: a case study. Int. J. Eng. Technol. 2, 292e296.

[4] Oilfield Processing of Petroleum: Crude oil Par Francis S. Manning, Richard E. Thompson

[5] Arnold, K., Stewart, M., 2008. Surface Production Operations. Elsevier, Amsterdam.

[6] Atwood, T., Hughes, H., 1990. Refrigerants and energy efficiency. Int. J. Refrig. 13 (4), 270e273.

[7] Baliban, R., Elia, J., Weekman, V., Floudas, C., 2012. Process synthesis of hybrid coal, biomass, And natural gas to liquids via FischereTropsch synthesis, ZSM-5 catalytic

[8] conversion, methanol synthesis, methanol-to-gasoline, and methanol-toolefins/ distillate technologies. Comput. Chem. Eng. 47, 29e56.

[9] Centre for Energy Economics at Bureau of Economic Geology, 2004. Interstate Natural GasdQuality Specifications & Interchangeability. Texas.

[10] Eiagov, 2015. U.S. Crude Oil, Natural Gas, and Natural Gas Liquids Proved Reserves

[11] [Online]. Available: http://www.eia.gov/naturalgas/crudeoilreserves/ [Accessed: 16- Nov- 2016].

[12] Parro, D.; Blizzard, G.; Hornback, K. CO2 Separation Membraness A Critical Part of the Mallat CO2 Removal Facility. Presented at the Laurance Reid Gas Conditioning Conference, University of Oklahoma, Norman, OK, 2005.

[13] Anderson, C.; Siahaan, A. Case Study: Membrane CO2 Removal from Natural Gas, Grissik Gas Plant, Sumatra, Indonesia. Presented at the Laurance Reid Gas Conditioning Conference, University of Oklahoma, Norman, OK, 2005.

[14] Anyadiegwu, C., Kerunwa, A., Oviawele, P., 2014. Natural gas dehydration using triethylene glycol (TEG). Petroleum Coal 56 (4), 409.

[15] J.A. Veil, M.G. Puder, D. Eleock, J. Robert, J. Redweik, A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane,

[16] Argonne National Laboratory, 2004

http://www.circleofblue.org/waternews/wpcontent/uploads/2010/08/prodwaterpaper1.pdf.

[17] H. Ozgun, M.E. Ersahin, S. Erdem, B. Atay, B. Kose, R. Kaya, M. Altinbas, S. Sayili, P. Hoshan, D. Atay, E. Eren, C. Kinaci, I. Koyuncu, Effects of the pre-treatment alternatives on the treatment of oil-gas field produced water by nanofiltration and reverse osmosis membranes, J. Chem. Technol. Biotechnol. 88 (2013) 1576–1583.

[18] P. Xu, J.E. Drewes, Viability of nanofiltration and ultra-low pressure reverse osmosis membranes for multi-beneficial use ofmethane produced water, Sep. Purif. Technol. 52 (2006) 67–76.

[19] D.L. Shaffer, L.H.A. Chavez, M. Ben-Sasson, S.R.-V. Castrillón, N.Y. Yip, M. Elimelech, Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions, environ. Sci. Technol. 47 (2013) 9569–9583.

[20] C.E. Clark, J.A. Veil, Produced Water Volumes andManagement Practices in the United

States, Environmental Science Division, Argonne National Laboratory,

[21]. W.I. Echt, D.D. Dortmundt and H.M. Malino, “Fundamentals of Membrane Technology for CO2 Removal from Natural Gas”, Laurance Reid Gas Conditioning Conference, 2002.

[22]. D.R. Koch, W.R. Buchan and T. Cnop, “Proper Pretreatment Systems Reduce Membrane Replacement Element Cost and Improve Reliability”, Gas Processors Association, 84th Annual Proceedings, 2005.

[23]. T. Cnop, D.D Dortmundt and M.E. Schott, “Continued Development of Gas Separation Membranes for Highly Sour Service”, Sour Oil and Gas Advanced Technology Conference, 2007.

[24]. J. Stiltner, K. Clark and G. Corvini, “Mercury Removal from Natural Gas and Liquid Streams”, Gas Processors Association, 81st Annual Proceedings, 2002

[25] Annual Proceedings, 2002 INTEGRATION OF MEMBRANES INTO NATURAL GAS PROCESS SCHEMES William I. Echt and Mander Singh UOP LLC, A Honeywell Company Des Plaines, IL

[26] The AEO2016 Reference, ANNUAL ENERGY OUTLOOK Reference 2016

[27] Andress, D., 1996. The Phillips optimized Cascade LNG Process, a Quarter Century of Improvements. Phillips Petroleum Company, Alaska.

Table of Contents

ACKNOWLEDGEMENT 1
ABSTRACT 2
INTRODUCTION 4
1. *NATURAL GAS* 6
2. NATURAL GAS PRODUCTION 6
3. WORLDWIDE NATURAL GAS LIQUID CONSUMPTION 7
4. THEORIES OF FORMATION OF NATURAL GAS 9
4.1 Composition of Natural Gas 9
5. MEMBRANE PROCESS ASSESSMENT 11
5.2. Membrane process 12
5.2.1. Reverse Osmosis (RO) 13
5.2.2. Ultrafiltration (UF) 13
5.2.3.Electro dialysis (ED) 14
5.2.4. Gas Separation 14
5.2.5. Pervaporation 14
6. BASIC CONCEPT OF THE SEPARATION PROCESS 15
6.1. Process Selection Factors 16
6.3. Membrane Process Requirements 16
6.4. feed pretreatment 17
6.5. Membrane Modules 19
7. THE TRENDS OF MEMBRANE PRODUCTION MAKING MEMBRANE SEPARATIONS MORE COMPETITIVE 21
8. GENERAL FLOW SCHEME 25
8.1. Characteristic Of Membrane Separation 25
8.2 Feed Gas Pressure / Compression 27
8.3 Feed Gas Temperature / Cooling 27
8.2.1 Direct or Indirect Cooling Water [1] 28
8.2.2. Gas/Gas Cross Exchange 28
8.2.3. Refrigeration System 28
8.2.4. J-T Valve or Expander-compressor 29
9.3. CONTAMINANT REMOVAL 29
9.3.1. Hydrogen Sulfide Removal 29
9.3.3. Non-regenerative mercury removal 30
9.3.4. Mercaptan and Arsenic Removal UOP 30
10. UPSTREAM CHILLING / NGL RECOVERY 30
11. NGL SABILIZATION AND VAPOR COMPRESSION 32
12. RELIABILITY / TURNDOWN / EQUIPMENT REDUNDANCY 32
13. ENIVIRONMENTAL IMPACT 34
14. MEMBRANE BACKGROUND 35

14.1. Factor Affecting The Separation Processes 35
14.1.1. Concentration polarization: 35
14.1.2. Fouling 36
14.2. Background Of Membrane 37
15. DIFFERENTS TYPES OF MEMBRANE 38
15.1. Micro-Porous Membrane 38
15.2. Homogeneous membranes 38
15.3. Electrically charged membrane 39
15.4. Asymmetric membrane 39
15.5. Liquid membranes 39
15.6. Dialysis (liquid permeation) 39
15.7 Series resistances in membrane processes 40
16. COMMON GAS CONTAMINANTS 42
16.1. Effects on new and traditional membranes 42
17. MEMBRANE PACKAGING 43
18. DESCRIPTION OF NEW APPLICATIONS AND PROCESSES 44
18.1 Nitrogen Removal Process 44
19. NGL SEPARATION PROCESS 48
19.1. CO2 Removal Process 50
19.2. H2S Removal Process 51
20. ADVANTAGES AND DISADVANTAGES OF MEMBRANE USES 53
20.1. Advantages 53
20.2. Disadvantages 54
21. CONCLUSION 55
References 57
Table of Contents 60
List of tables 62
List of figures 62
List of schemes 63

List of tables

Table.1: annual energy outlook showing increase in LNG supply……8

Table.2: General Chemical Composition of Natural Gas ……10

Table 3. Principal Suppliers of Membrane Natural Gas Separation Systems.....23

Table 4.Typical Costs for Membranes, Membranes in 8-In.-Diameter Spiral-Wound Modules, and Module kids.....……..23

Table 5 characteristic feature according to membrane process……25

Table 6. A Comparison of Nitrogen/Methane Separation Processes……...….45

Table 7. Feed and Conditioned Fuel Gas Compositions and Important Process Variables…….49

Table 8 shows that the membrane unit can reduce the H 2 S content in the fuel from about 3,400 ppm to about 40 ppm…….……..53

List of figures

Figure 1: representation of natural gas composition……11

Figure 2: Membrane separation can be classified into 3 main categories on the basis of the driving force ……11

Figure 3: membrane process……...……12

figure 4.1: schematic of membrane-pretreatment equipment……..……..…..18

figure 4.2: schematic of membrane-pretreatment equipment……..……..…..18

Figure 5: Structure of membranes used in membrane gas separation processes: (a) anisotropic Loeb-Sourirajan membranes and (b) composite membranes……22

Figure 6: generals flow scheme of membrane operation…….26

Figure 7: Cross-section of an MTR composite membrane……..37

Figure 8: Concentration profile for membrane process. a) two liquid films and a solid. B) two gas films and a solid……40
Figure 9: Schematic diagram showing components and gas flow patterns of a spiral-wound module...43
Figure 10: A typical membrane skid, showing two steel pressure tubes housing the membrane modules……44
Figure 11: Flow scheme of a typical NitroSep © process for nitrogen removal from natural gas…..…46
Figure 12. System Photograph of Unit installed in Omaha, Nebraska, reducing 6.5mol-% N2 in Natural gas to 2.5 mol-%.....47
Figure 13: Schematic process flow diagram for a membrane fuel gas conditioner fora gas engine application……48
Figure 14. A hybrid process for CO 2 removal from natural gas, using a membrane separation step followed by a solvent absorption step……..51
Figure 15: Membrane Separation Performance for Removal of H 2 S from Fuel Gas……52

List of schemes

Scheme1……20
Scheme2……20
Scheme3……41