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REVIEW ARTICLE

Removal of Acid Gas from Natural Gas: A Comparison of Conventional and Selective Membrane Processes

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Abstract. Natural gas often contains impurities such as nitrogen, hydrogen sulphide, carbon dioxide and water vapor. These impurities have to be removed prior to gas processing. Sometimes it is purified at the gas field. The complicated distillation and cryogenic processes are now replaced by novel membrane separation systems which offer lower costs, less maintenance and more flexibility. Membranes are widely used in a variety of industrial gas separation. They have been used since 1970 after the adaption of the first flat sheet of cellulose acetate. They were proved to be technologically and economically preferred against most of the conventional gas separation processes.

This paper reviews the use of membranes in gas separation with emphasis on the removal of acid gas from natural gas. Technological and economical comparison of the feasible gas membrane systems with conventional gas separation processes are presented.

List of Symbols

C_{i1}, C_{i2} = concentrations of specied i at feed and product side mole/cm^3
D_i = diffusivity of species i, cm^2/sec
l = Membrane thickness, cm
N_f = feed flux, mole/cm^2 sec
N_i = total flux of species i, mole/cm^2 sec
n_i, n_j = flux of species i and j, mole/cm^2 sec
$\overline{P}$ = permeability of membrane, cm^2 sec/gm
P_1, P_2 = total pressure at feed and product sides, Kpa

p_i = partial pressure of species i Kpa
p_{i1}, p_{i2} = partial pressure of species i at feed and product sides, Kpa
S_i = solubility constant in Henry's law
y_{i1}, y_{i2} = mole fractions of species i at feed and product sides
y_{j1}, y_{j2} = mole fractions of species j at feed and product sides
α_{ij} = separation factor

Introduction

Natural gas reserves in Saudi Arabia are approximately 2.6 billion cubic meters, *i.e.* about 3% of the world reserves. The annual production of natural gas is 32 billion cubic meters. Unfortunately, it contains high percentage of acid gas hydrogen sulphide, H_2S, and carbon dioxide, CO_2. The typical concentration of H_2S in some important Saudi wells are: Abqaid 20.5%, Berri 19.8%, Qatif 7.2%, Marjan 4.2%, Ghawar 3.6%, Dammam 2.0% etc. On an average, about 80 tons of sulphur are recovered per million cubic feet of gas from these wells. Table 1 shows the composition of natural gas in Ghawar field.

Table 1. Average composition of associated gas in Ghawar field

Compound	% Volume	Compound	% Volume
Methane	51.0	Hexane	0.4
Ethane	17.8	Heptane and heavier	0.2
Propane	10.8	Carbon dioxide	9.7
Butane	4.4	Hydrogen sulphide	3.6
Pentane	1.6	Nitrogen	0.5

Marketable natural gas must have low H_2S and CO_2 content. So H_2S and CO_2 have to be removed to the desirable customer specifications. Many non-selected processes have been used to separate these acidic gases from natural gas, such as monoethanolamine (MEA) process, dimethanolamine (DEA) process, and hot carbonate process. This paper will describe the adaption of the recent membrane separation processes in the removal of acid gas from natural gas in comparison with conventional amine process.

Conventional Processes

A suitable process for H_2S and CO_2 removal in natural gas industry must provide (1) high purity gas (2) handling large volume of gas (3) high pressure operation.

Many processes have been used. Such as:

a) Chemical solvent processes

1. Monoethanolamine, (MEA)
2. Diethanolamine, (DEA)
3. Triethanolamine, (TEA)
4. Hot potassium carbonate

b) Physical solvent processes

1. Selexol
2. Propylene carbonate
3. Sulfinol
4. Rectisol

c) Dry adsorbent

1. Molecular sieve
2. Activated charcoal
3. Iron sponge
4. Zinc oxide

The (MEA), (DEA) and the hot carbonate processes have widely used in natural gas industry. Figure 1 shows a simplified (MEA) process for H_2S and CO_2 removal from natural gas. It basically depends on absorption of these gases in the amine solution at 35 to 55°C according to the following overall reactions:

$$2\,RNH_2 + H_2S \rightarrow [RNH_3]_2^+\,[S]^{--}$$

$$[RNH_3]_2^+\,[S]^{--} + H_2S \rightarrow 2[RNH_3]^+\,[HS]^{--}$$

$$2\,RNH_2 + CO_2 + H_2O \rightarrow [RNH_3]_2^+\,[CO_3]^{--}$$

$$[RNH_3]_2^+\,CO_3^{--} + CO_3^{--} + CO_2 + H_2O \rightarrow 2[RNH_3]^+\,[CO_3]^-$$

where R denotes the ethanol group $-C_2H_4OH$.

At higher temperatures 100-150°C, these reactions are reversed and releasing H_2S and CO_2 at the stripping column. The (MEA) solution is then recirculated.

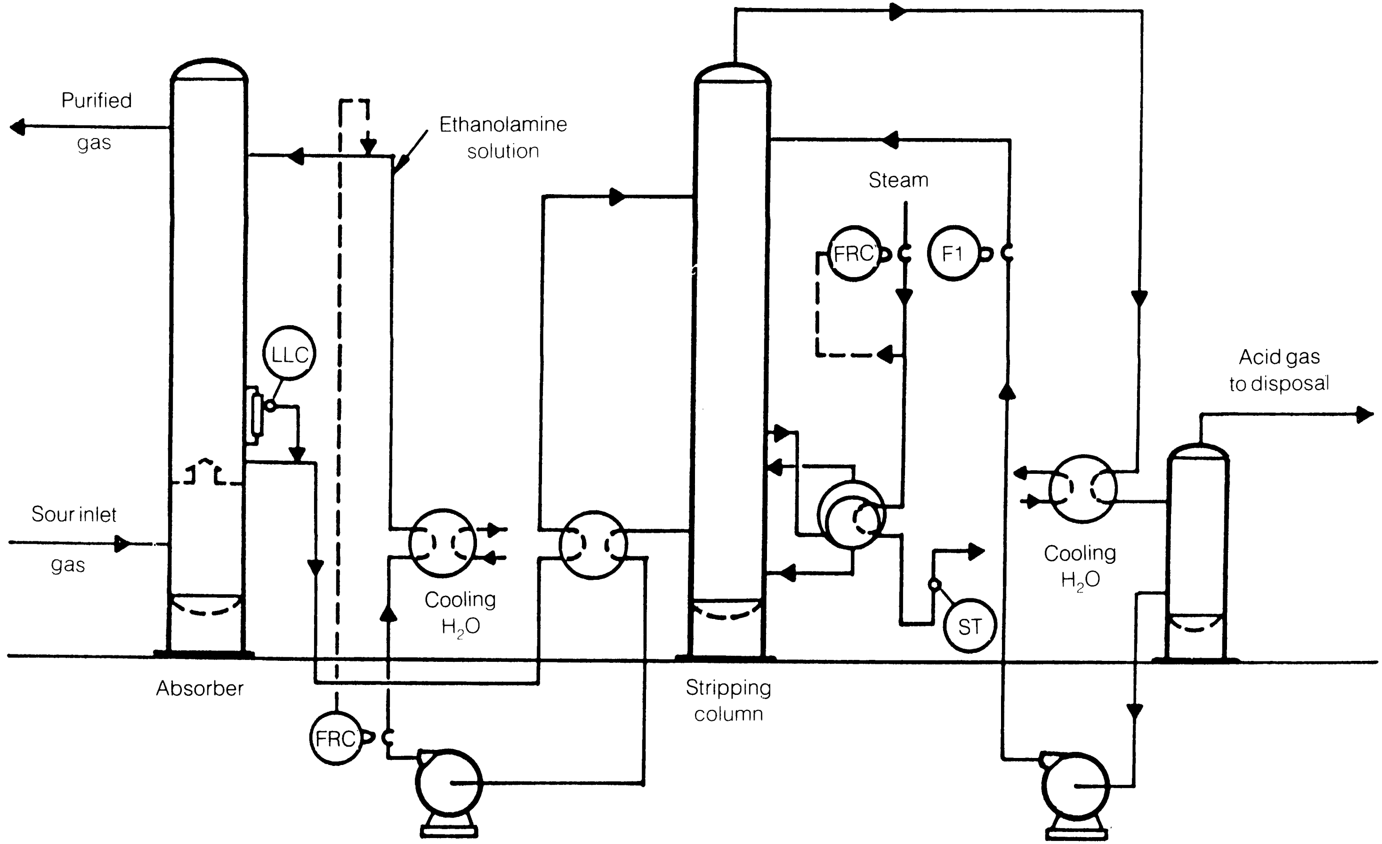


Fig. 1. Simplified MEA process

In the (DEA) process, an amine solution at 40-60°C is fed to the absorber and the following overall reactions take place.

$$2\,R_2NH + H_2S \rightarrow [R_2NH_2]_2^+\,[S]^{--}$$

$$[R_2NH_2]_2\,[S]^{--} \rightarrow 2[R_2NH_2]^+\,[HS]^-$$

$$2R_2NH + CO_2 + H_2O \rightarrow [R_2NH_2]_2^+\,[CO_3]^{--}$$

$$[R_2NH_2]_2^+\,[CO_3]^{--} + CO_2 + H_2O \rightarrow 2[R_2NH]_2] + [HCO_3]^-$$

At the higher temperature 75-130°C, H_2S and CO_2 are released and (DEA) solution is recirculated. Figure 2 shows a simplified flow diagram of (DEA) process and Table 2 lists the typical operating conditions of (MEA) and (DEA) processes.

Table 2. Typical operating conditions of (MEA) and (DEA) processes

	(MEA)	(DEA)
Amine conc. wt. %	15-20	20-30
Moles amine/mole acid gas	1.5-3.0	1.0-1.5
Liter solvent/g.mole acid gas	0.6-1.3	0.3-0.6
g.steam/liter solvent	120-140	120-180
g.steam/g.mole acid gas	70-150	40-100

The hot carbonate process is based on the following reversible reactions:

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3$$

$$K_2CO_3 + H_2S \rightleftharpoons KHCO_3 + KHS$$

A 25-40 wt.% potassium carbonate solution at 80°C is used to absorb H_2S and CO_2 in an absorber operating at 2.07 MPa (30 psig). If the pressure is reduced to 34.5 KPa (5 psig) at 120°C, the previous reactions are reversed and the potassium carbonate is freed and recirculated.

Typically 0.5 moles of acid gas per moles of K_2CO_3 and 8-110 g of steam per litre of solution are used.

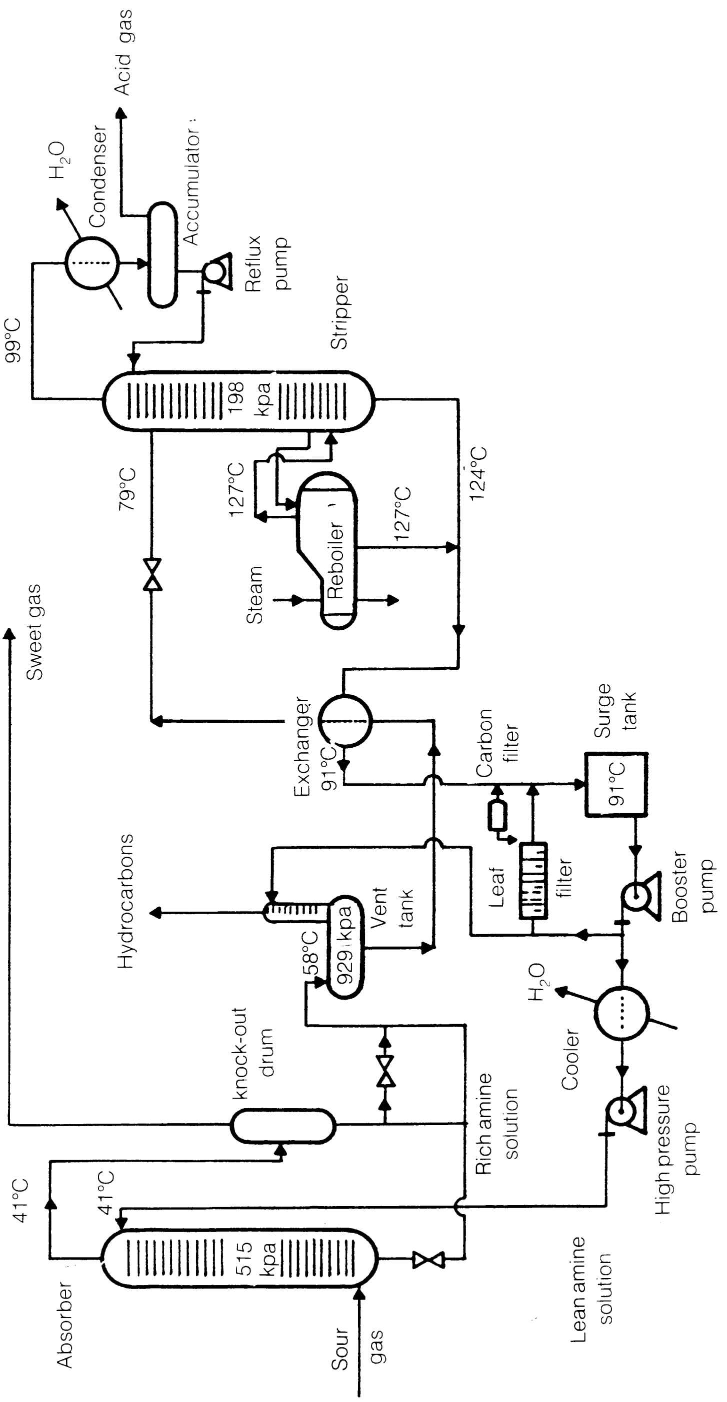


Fig. 2. Simplified DEA process

Figure 3 shows a simplified flow sheet for the hot carbonate process.

The (DEA) process has better energy efficiency than (MEA) process due to high losses in the (MEA) process. The hot carbonate process is not capable of treating acid gases rich in H_2S and lean in CO_2. Salt precipitation is a serious operational problem encountered in the hot carbonate process.

Generally absorption processes have problems of continuous loss of solvent in the stripper, high energy consumption for the separation of absorbed gas from the solvent, and relatively low recovery of absorbed gas. Absorption units are often large in volume to allow large contact area between the two contacting phases.

Fundamental of Gas Permeation

The principles of selective permeation have been well known for many years, but it did not become commercially feasible until the development of high-flut cellulose-acetate membrane for gas separation in 1970 [1;2].

The principles of membrane gas separation and basic design equations are discussed by Maclean *et al.* [3], Hogstr and Mazur [4] and Schell and Hoernschemeyer [5].

The separation of gases by membrane is based on the fact that some gases permeate more rapidly than others due to differences in their mobilities or solubilities in the membrane material. Gases flux through the membrane basically depends on diffusion and sorption of gas species. The diffusive flux through the membrane is given by Fick's law:

$$n_i = \frac{D_i (C_{i2} - C_{i1})}{l} \tag{1}$$

where,

n_i is the flux of component i, mole/cm^2 sec.

D_i is the diffusivity of component i, cm^2/sec.

l is the membrane thickness, cm.

C_{i1},C_{i2} are the concentrations of component i at the membrane sufrace, mole/cm^3.

At the membrane surface, Henry's law relates the concentration of species i with its partial pressure, p_i, according to the following relation.

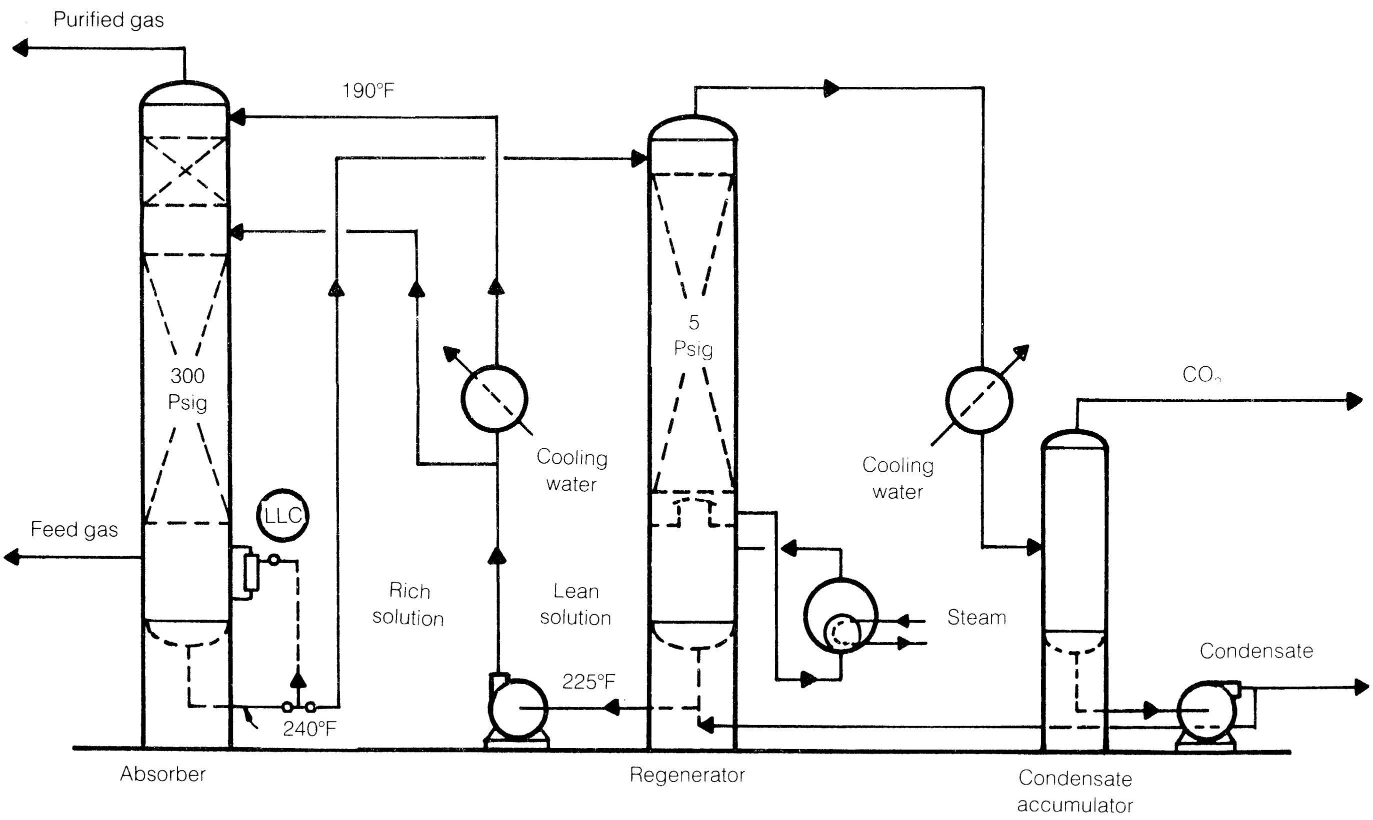


Fig. 3. Simplified hot carbonate process

$$C_i = S_i\, p_i \tag{2}$$

where, S_i is the solubility constant.

From equations (1) and (2), the local membrane flux can be given by

$$n_i = \frac{\overline{P}_i}{l}\,(P_{i2} - P_{i1}) \tag{3}$$

where $\overline{P}_i = D_i\, S_i$, is the permeability of gas i.

The total flux of species i is then evaluated by summing up all local fluxes, so

$$N_i = d_{ni} = \frac{\overline{P}_i}{l}\,(P_{i2} - P_{i1})\, dA \tag{4}$$

The membrane ability of permeating two different gas species (so called ideal separation factor) is often expressed by the ratio of their permeabilities:

$$\alpha_{ij} = \overline{P}_i \,/\, \overline{P}_j \tag{5}$$

Permeability's and separation factor are the membrane unique properties. The recovery of species i can be obtained by dividing equation (4) by the molar feed of component i, $N_f Y_{i1}$.

$$R_i = \frac{(\overline{P}/l)_i\, \Delta p_i\, dA}{N_f\, Y_{i1}} \tag{6}$$

where Δp_i is the local partial pressure difference of component i and N_f is the feed flux.

So recovery essentially depends on membrane permeability and the partial pressure difference. Increasing Δp_i will increase the recovery.

For binary gas mixture, the ratio of the permeate fluxes can be found from equation (3) noting that

$$p_i = Y_i\, p_l \quad \text{and} \quad y_j = 1 - y_i$$

So,

$$\frac{n_i}{n_j} = \frac{y_{i1}}{1 - y_{i1}} = \alpha_{ij} \frac{(P_2 / P_1)y_{i2} - y_{i1}}{(P_2 / P_1)(1 - y_{i2}) - (1 - y_{i1})} \tag{7}$$

where P_2/P_1 is the ratio of the total pressures on the high and low pressure sides of the membrane. Equation (7) is known as Weller-Stein equation. It is often used to predict permeating purity for a binary mixture. Solving equation (7) for the permeate composition, Y_{i1}, yields:

$$y_{i1} = \frac{-B + [B^2 + 4(1 - \alpha_{ij})\alpha_{ij}\,(P_2/P_1)y_{i2}]^{1/2}}{2(1 - \alpha_{ij})} \tag{8}$$

where,

$$B = (\alpha_{ij} - 1)\,(P_2 / P_1)\,Y_{i2} + (P_2 / P_1) + (\alpha_{ij} - 1)$$

So the permeate composition can be found if pressure ratio, stream composition and membrane separating factor are known.

The removal of H_2S and CO_2 from natural gas is an ideal application of membrane gas separation. CO_2 and H_2S permeate through cellulose acetate for example about 20 to 60 times faster than methane [1]. Table 3 shows the performance of an existing CO_2/H_2S recovery pilot plant [2].

Schell and Houston [6] have described three specific examples of membrane separation for natural gas purification. These are:

1) Reducing CO_2 concentration from 8-9% to 5% in order to meet the sales gas specification.
2) Removing H_2S from a gas containing 6000 ppm to produce a gas containing, 50 ppm for use on onsite fuel.
3) Reducing CO_2 concentration from about 50% to about 40% to meet the fuel heating value requirements of a gas turbine.

Commercial spiral-wound membrane were used for those three cases. Data are presented on Table 4 [1].

Table 3. Comparision of performance of CO_2 production [2]

	$CO_2/CH_4 = 10$	$CO_2/CH_4 = 23$	$CO_2/CH_4 = 23$
Residual			
% CO_2	42.0	42.0	15.0
MMscfd	(14.2)	(14.2)	(9.4)
(psia)	(985)	(985)	(965)
CH_4 Rec, %	86	86	84
Permeate			
% CO_2	95.0	95.0	95.0
MMscf	35.8	35.8	40.6
(psia)	25.0	390.0	150.0
CO_2 Rec, %	85	85.0	96.5

Feed rate = 50 MMscf, 1000 psig, 75% CO_2, 25% CH_4
Permeate min. purity 95%, 2000 psig.
1 MMscf = 26.79 Nm^3, 1 psi = 6895 Pa

Table 4. Typical membrane applications for natural gas purification [1;7]

	Case 1			Case 2			Case 3		
	Feed	Permeate	Residue	Feed	Permeate	Residue	Feed	Permeate	Residue
Flow, MMSCFD	1.13	0.13	1.00	7.41	3.71	3.70	3.00	0.66	2.34
Pressure, psig	190	10	188	745	18.2	740	215	30	210
Temp, °F	90	85	85	90	85	85	105	90	90
Composition									
N_2, %	0.8	0.6	0.8	–	–	–	0;.8	0.1	0.9
CO_2, %	8.2	32.3	5.0	3.5	6.8	0.1	53.6	94.7	42.0
HC, %	91.0	67.1	94.2	95.9	92.0	99.9	45.7	5.2	57.1
H_2S ppm	–	–	–	6.000	12.000	30	–	–	–

Membrane Process Design

Single stage membrane is often adequate for many applications. It provides the lowest capital cost. However, large processes and high recovery processes require multistage membrane design. For example, for two gas streams having different CO_2 concentrations, say 80% CO_2 in case 1 and 20% in case 2 [7]. Two membrane stages are required for case 2 to have similar specification of case 1 of 3% CO_2 in residual gas and 95% CO_2 in permeate. This increases the total capital cost in case 2 to about 2.8 times of case 1 when operating both cases at 5.3 MPa (765 psia) feed pressure, a relative CO_2 permeation rate to O_2 of 6, and a separation factor 25 [7].

The pressure differential between the feed and permeate streams has an important role on the membrane process performance. It determines the required membrane area and the volume and composition of permeate and residual streams. Also the absolute feed permeate streams pressure have important effect on the process performance.

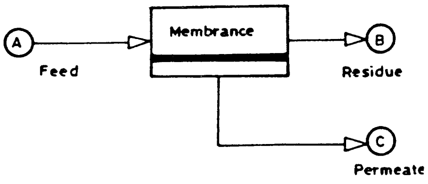
For constant differential pressure, the membrane area requirements increase as the permeation, feed flow rate and product purity increase. The membrane area requirements decrease significantly with increasing the feed pressure. On the other hand, the permeate recovery decreases with increasing the permeate pressure and increases with increasing feed pressure. Feed flow rate has little impact on the permeate recovery.

The permeate recovery cannot be used alone to judge the process economics. High recoveries have to be obtained economically. Figure 4 gives examples of treating natural gas in single stage, two stage and multistage gas separation processes [8]. Evidently, the two stage process has the higher recover for the same residual composition but it is not necessary the economically suitable process.

Membrane and Conventional Process Comparison

Amine plants for treatment of natural gas account for about 70% of natural gas treatment processes. However, these polants are large and heavy and require continuous supervision and maintenance which prohibit their use in the wellhead area. Also large amounts of gas are consumed by amine regenerator and their presence on an offshore platform represents a fire safety hazard [8].

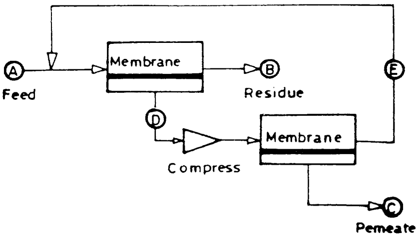
Membrane processes recently can operate up to 2000 psi (13.8 MPa) which is well above pipeline requirements. They can safely treat gas right at the wellhead to meet typical gas specification such as $< 2\%$ CO_2, < 4 ppm H_2S and < 3.2 kg per 30.000 m^3 (7 lb/MMscf) H_2O.



	Stream A	Stream B	Stream C
Composition (mole %)			
CH_4	93.0	98.0	63.4
CO_2	7.0	2.0	36.6
Flow Rate (MMSCFD)	20.00	17.11	2.89
Pressure (psig)	850	835	10

Methane Recovery = 90.2%

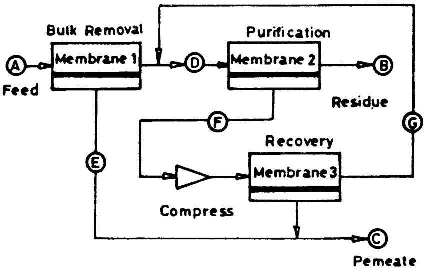
Single-stage membrane process for natural gas treating.



	Stream A	Stream B	Stream C	Stream D	Stream E
Composition (mole %)					
CH_4	93.0	98.0	18.9	63.4	93.0
CO_2	7.0	2.0	81.1	36.6	7.0
Flow Rate (MMSCFD)	20.00	18.74	1.26	3.16	1.90
Pressure (psig)	850	835	10	10	850

Methane Recovery = 98.7%

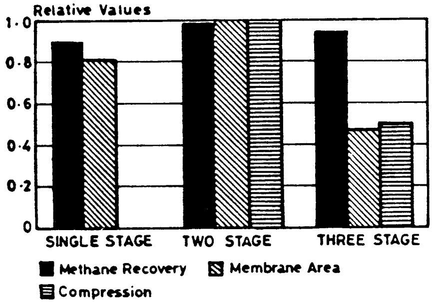
Two-stage gas separation membrane process for natural gas treating.



	Stream A	Stream B	Stream C	Stream D	Stream E	Stream F	Stream G
Composition (mole %)							
CH_4	93.0	98.0	49.2	96.1	56.1	72.1	93.0
CO_2	7.0	2.0	50.8	3.9	43.9	27.9	7.0
Flow Rate (MMSCFD)	20.00	17.95	2.05	19.39	1.62	1.44	1.01
Pressure (psig)	850	835	10	840	10	10	850

Methane Recovery = 99.7%

Multi-stage gas separation membrane process for natural gas treating.



Process comparison between single-, two-, and multi-stage membranes for natural gas treating.

Fig. 4. Different arrangements of membrane process [4]

Membrane treatment of natural gas is attractive when pressure of feed gas or product gas is high. It also provides the following advantages [9]:

1. Reduced maintenance and labor cost
2. No moving parts, no adjustments, and no solvents are used
3. Excellent flexibility in adjusting to variation in feed flow and composition
4. Significant space and weight advantages over amine plants

Table 5 shows a detailed cost comparison between the amine and the membrane processes for treatment of natural gas [9]. It includes capital costs, utilities, labor, maintenance and lost product values. The feed gas pressure is 5 MPa (725 psig) and flow rate is 1 MMm^3/day (37.2 MMSCFC).

Table 5. Cost comparison of amine and membrane processes as function of CO_2 in feed stream [9]

	5%	10%	15%	20%	30%	40%	50%	60%	70%	80%	90%
Amine											
Capital ($MM)	3.35	4.54	5.45	6.21	7.50	8.56	9.50	10.30	11.10	11.80	12.50
Expenses ($MM/yr)	1.22	1.81	2.33	2.82	3.73	4.58	5.39	6.16	6.92	7.65	8.36
Lost product [$MM/yr)	0.02	0.04	0.07	0.09	0.14	0.19	0.23	0.28	0.33	0.37	0.42
Capital charge ($MM/yr)	0.91	1.23	1.48	1.68	2.03	2.32	2.57	2.79	3.00	3.20	3.39
Processing cost ($MSCF Feed)	0.17	0.24	0.30	0.36	0.46	0.55	0.64	0.72	0.90	0.87	0.94
Membrane											
Multistage process											
Capital ($MM)	1.86	3.33	3.87	3.69	3.37	3.32	2.45	2.30	1.77	1.44	0.89
Expenses ($MM/yr)	0.53	0.85	0.97	1.00	0.98	0.96	0.85	0.79	0.67	0.56	0.42
Lost product ($MM/yr)	0.43	0.69	0.93	1.24	1.54	1.49	1.60	1.36	1.17	0.84	0.51
Capital charge ($MM/yr)	0.51	0.90	1.05	1.00	0.91	0.90	0.66	0.62	0.48	0.39	0.24
Processing cost ($MSCF Feed)	0.11	0.19	0.23	0.25	0.27	0.26	0.24	0.21	0.18	0.14	0.09
Single-stage process											
Processing cost ($MSCF Feed)	0.17	0.26	0.30	0.32	0.32	0.31	0.28	0.24	0.20	0.15	0.10

Conclusion

Membrane processes appear to offer the best promise for treatment of natural gas specially the removal of CO_2, and H_2S and the reduction in moisture content. They are flexible to obtain the desired specifications of marketable natural gas with the occasional variation in natural gas. Membrane separation can be easily installed, maintained and operated right at the gas wellhead. They provide lower processing cost as compared to amine plants. The capability of upgarding their performance and their flexibility make them superior to amine plant, even when they have comparable processing cost. The specific membrane separation system design depends on the feed and product conditions as well as the plant location and the availability of utilities.

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إزالة الغاز الحمضي من الغاز الطبيعي : مقارنة بين الطرق التقليديّة وطريقة الأغشية الانتقائيّة

إبراهيم المعتاز

قسم الهندسة الكيميائيّة ، كلية الهندسة ، جامعة الملك سعود، ص.ب ٨٠٠ ،
الرياض ١١٤٢١ ، المملكة العربية السعودية

(استلم في ٧/٦/١٩٩٣م ؛ وقبل للنشر في ٢٧/٣/١٩٩٤م)

ملخص البحث . يحتوي الغاز الطبيعي عادة على بعض الشوائب مثل النيتروجين وكبريتيد الهيدروجين وثاني أكسيد الكربون وبخار الماء . يجب إزالة هذه الشوائب قبل معالجة الغاز . وفي بعض الأحيان يَنقّى الغاز الطبيعي عند حقول الغاز . وحاليًا تحل طرق الفصل الغشائية محل عمليّات التقطير والتبريد لانخفاض تكلفتها وسهولة صيانتها والمرونة في عملها .

تستعمل الأغشية بشكل كبير في العديد من عمليّات فصل الغازات الصناعيّة . وقد تمّ استعمالها منذ ١٩٧٠م بعد تطور أول غشاء من مادة السليلوز إستيت . وقد وجد أنّها من الناحية التقنية والاقتصادية أفضل من كثير من الطرق التقليديّة لفصل الغازات .

وفي هذا البحث مراجعة لاستخدام الأغشية في عمليات فصل الغازات مع التركيز على فصل الغاز الحمضي من الغاز الطبيعي . وقد تمّ مقارنة أنظمة فصل الغازات الغشائيّة مع طرق الفصل التقليديّة من الناحية التقنية والاقتصادية .