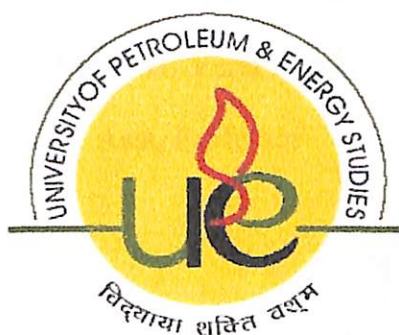
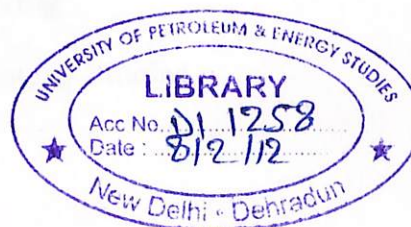


**MAJOR PROJECT**  
**ON**  
**NATURAL GAS TREATMENT: CO<sub>2</sub> REMOVAL**

Submitted By:  
Daljeet Singh (R270307013)



College Of Engineering  
University of Petroleum & Energy Studies  
Dehradun  
May, 2011



# **NATURAL GAS TREATMENT: CO<sub>2</sub> REMOVAL**

A thesis submitted in partial fulfilment of the requirements for the Degree of Bachelor in Technology.

**Intt. B.Tech (Applied Petroleum Engineering) + MBA(Upstream Asset Management)**

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**Submitted to University of Petroleum & Energy Studies, Bidholi, Dehradun**

**Submitted by**

**Daljeet Singh**

**Under the guidance of**

**Mr. C.H. VaraPrasad**

**Asst. Professor**

**Approved By:**

**Dr. Shrihari**

**Dean**

**College Of Engineering**

**University of Petroleum & Energy Studies**

**Dehradun**

**May, 2011**

## CERTIFICATE



This is to certify that the work contained in this thesis titled "Natural Gas Treatment: CO<sub>2</sub> Removal" has been carried out by Daljeet Singh under my supervision and has not been submitted elsewhere for a degree.

  
C.H. Vara Prasad

Asst. Professor

C.O.E.S.

UPES, Dehradun

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**Daljeet Singh**

**Intt. B.Tech (Applied Petroleum Engineering) + MBA (Upstream Asset Management)**

**University of Petroleum & Energy Studies Dehradun**

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## ABSTRACT

Field treatment and processing operations of natural gas and other associated products .These include dehydration, acidic gas removal ( $H_2S$  and  $CO_2$ ), and the separation and fractionation of NGL's.

Field treatment of a gas project could be divided into two main stages:

1. Stage I, known as gas treatment or gas conditioning.
2. Stage II, known as gas processing.

The major problem arises due to existence of carbon dioxide in natural gas are as follows:

- i) It reacts with  $H_2O$  to form carbonic acid which enhance corrosion of pipelines.
- ii) It decreases the heating value of natural gas(hydrocarbons).
- iii) Since it is greenhouse gas, its volume should be low as possible, etc.

**Various  $CO_2$  removing processes are:**

- i) **Reactive solvents:** MEA, DEA, DGA (diglycol amine), DIPA (di-isopropanol amine), hot potassium carbonate, and mixed solvents. These solutions are used to remove significant amounts of  $CO_2$  and the solvents are regenerated.
- ii) **Physical solvents:** Selexol, Rectisol, Purisol, and Fluor solvent. They are mostly used to remove  $CO_2$  and are regenerated.
- iii) **Membranes:** This is used for very high  $CO_2$  concentrations.

Both above processes are usually done by methods of absorption or adsorption or by chemical scrubbing using techniques such as chemical chelation. The disadvantages of lies mainly in their heavy features that require the replenishment of consumable chemical absorbent, adsorbent or complexing agents. This limits these techniques less than optimal for remote applications to the wellhead.

The technique which comes out of these problems are methanation and water wash processes as explained in this project briefly.



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## CHAPTER 1

### INTRODUCTION:

As demand for natural gas continues to rise, new areas previously ignored or deliveries of gas are being reviewed. Many of these "new" supplies of gas have been ignored in gas quality due to poor past and / or prohibitive costs associated with treating the gas to make it marketable. However, as gas prices continued to increase and new gas processing technologies have been developed, the prospect of treatment and sale of these volumes of gas has become viable. These new sources include methane gas from coal beds, landfill gas and bio-gas digester, to name a few. Each of these gas streams can contain up to 50% carbon dioxide (CO<sub>2</sub>), up to 6% oxygen (O<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S) and nitrogen, which must be removed meet pipeline specifications. Many of these gas streams are enter in the plants at a relatively low pressure, requiring an input compression. Current sources of gas that have been shut in or reduced in production because of poor quality include vacuum gathering systems and gas wells with high levels of contaminants. Despite the improving economy, the producer still wants to treat their needs gas flow in the most efficient and cost effective manner possible. Unfortunately, time constraints often take the producer to choose what they think is the best option without considering all available technologies or to make a detailed assessment of these alternatives. This project will provide several basic rules that can be applied when selecting treatment gases (CO<sub>2</sub> removal) and illustrate, through examples, how you can make the best decision for your needs gas processing. It will focus on using amine gas treatment, membranes and their application to the removal of CO<sub>2</sub> from the raw gas stream.

### IMPURITIES PRESENT IN NATURAL GAS:

Before natural gas to be transported through pipeline and to be sold in market, the various impurities shown in table 1 should be removed from hydrocarbon mixture of natural gas.



**Table 1**  
**Principal Gas Phase Impurities**

1. Hydrogen sulfide
2. Carbon dioxide
3. Water vapor
4. Sulfur dioxide
5. Nitrogen oxides
6. Volatile organic compounds (VOCs)
7. Volatile chlorine compounds (e.g., HCl, Cl<sub>2</sub>)
8. Volatile fluorine compounds (e.g., HF, SiF<sub>4</sub>)
9. Basic nitrogen compounds
10. Carbon monoxide
11. Carbonyl sulfide
12. Carbon disulfide
13. Organic sulfur compounds
14. Hydrogen cyanide

#### **GAS TREATING:**

This is reducing the level of "sour gas" carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S) and sulfur impurities, at levels sufficiently low to meet the contract specifications or permit further processing plant without problems of corrosion and plugging. This project focuses on the elimination of carbon dioxide because it is one of the most common impurities. If the gas sweetening is required at offshore, both the size and weight are additional factors that must be considered.

Whereas the elimination of CO<sub>2</sub> is performed offshore, H<sub>2</sub>S is rarely done unless absolutely necessary due to constraints such as limited space, poor handling of elemental sulfur.

Acid gas removal processes can be grouped into the seven types indicated in Table 2, which also suggests the preferred areas of application for each process type.



**Table 2**  
**Guidelines for Selection of H<sub>2</sub>S and CO<sub>2</sub> Removal Processes**

| Type of Process                 | Acid Gas         |                 | Plant Size | Partial Pressure | Sulfur Capacity |
|---------------------------------|------------------|-----------------|------------|------------------|-----------------|
|                                 | H <sub>2</sub> S | CO <sub>2</sub> |            |                  |                 |
| Absorption in Alkaline Solution | A                | A               | H          | L                | H               |
| Physical Absorption             | A                | A               | H          | H                | H               |
| Absorption/Oxidation            | A                | —               | H          | L                | L               |
| Dry Sorption/Reaction           | A                | —               | L          | L                | L               |
| Membrane Permeation             | A                | A               | L          | H                | L               |
| Adsorption                      | A                | A               | L          | L                | L               |
| Methanation                     | —                | A               | L          | L                | —               |

*Notes: A = Applicable, H = High, L = Low; dividing line between high and low is roughly 20 MMscfd for plant size, 100 psia for partial pressure, and 10 tons/day for sulfur capacity.*

Permeation membrane is specially done of carbon dioxide gas from high pressure. The process is based on the use of relatively small modules, and an increase in plant capacity is achieved by simply using proportionally more modules. Consequently, the process does not realize economies of scale and become less competitive with the absorption process that plant size is increased. McKee et al. (1991) compared diethanolamine (DEA) and membrane processes for a plant of 1000 psi gas treatment. For its reference scenario, the plant amine was generally considered more economical units for more than about 20 MMSCFD. However, at concentrations very high acid gas (carbon dioxide over about 15%), a hybrid process is more economical than either type alone. The hybrid process, which is not shown in Table 2, using the membrane process for removing bulk carbon dioxide and amine process for final cleaning.

For adsorption to be the preferred process for carbon dioxide removal there must be a high CO<sub>2</sub> partial pressure in the feed, the need for a very low concentration of carbon dioxide in the product, and the presence of other gaseous impurities that can also be removed by the adsorbent.

#### PROBLEMS ASSOCIATED WITH CO<sub>2</sub>:



- 1: Presence of  $H_2S$  and  $CO_2$  promotes hydrate formation because both these acid gases are more soluble in water than the hydrocarbons.
- 2:  $CO_2$  in natural gas reduce the heat capacity of it.
- 3:  $CO_2$  react with water molecule for the formation of carbonic acid which is corrosive to carbon-steel pipelines through which transmission of natural gas is usually done.
- 4: Because of global warming problems, since it is greenhouse gas, its volume should be low to meet environment norms.
- 5:  $CO_2$  will displace oxygen and can create an oxygen-deficient atmosphere resulting in suffocation. The principal hazard of  $CO_2$  is exposure to elevated concentrations. The atmospheric concentration immediately hazardous to life is 10% (volume). Because  $CO_2$  is heavier than air, its hazard potential is increased, especially when entering tanks and vessels.

#### PURIFICATION LEVELS:

The inlet conditions to a treatment plant are generally gases and temperatures near ambient pressures of about 300 to 1000 psi (20 to 70 bar), such that the partial pressures of acid gases entering will be very high. If the gas must be purified to a level suitable for transportation in a pipeline and used as residential or industrial fuel, the concentration of  $CO_2$  must be reduced to a maximum of 3 to 4% mol. However, if the gas must be processed for recovery or disposal of NGL nitrogen in a process of cryogenic turboexpander, the  $CO_2$  can be removed to avoid formation of solids. If the gas is fed into a liquefaction plant, LNG  $CO_2$  level maximum is about 50 ppmv due to the potential solid formation.

#### $CO_2$ DISPOSAL:

For  $CO_2$ , if the quantities are large, it is sometimes used as an injection fluid in Miscible EOR (enhanced oil recovery) projects. Several gas plants exist to support  $CO_2$  flooding projects; the natural gas and NGL are valuable by-products. If this option is unavailable, then the gas can be vented, provided it satisfies environmental regulations for impurities.

#### PURIFICATION PROCESSES:



Two scenarios are possible for CO<sub>2</sub> gas removal from natural gas:

- i) CO<sub>2</sub> removal from a gas that contains no H<sub>2</sub>S.
- ii) Simultaneous removal of both CO<sub>2</sub> and H<sub>2</sub>S.

Because the concentrations of CO<sub>2</sub> and H<sub>2</sub>S in the raw gas to be processed and the allowable acid gas levels in the final product vary substantially, no single process is markedly superior in all circumstances, and, consequently, many processes are presently in use.

Some of the more important items that must be considered before a process is selected are summarized from the Engineering Data Book (2004b):

- The type and concentration of impurities and hydrocarbon composition of the sour gas. For example, COS, CS<sub>2</sub>, and mercaptans can affect the design of both gas and liquid treating facilities. Physical solvents tend to dissolve heavier hydrocarbons, and the presence of these heavier compounds in significant quantities tends to favor the selection of a chemical solvent.
- The temperature and pressure at which the sour gas is available. High partial pressures (50 psi or higher) of the acid gases in the feed favour physical solvents, whereas low partial pressures favor the amines.
- The specifications of the outlet gas (low outlet specifications favor the amines).
- The volume of gas to be processed.
- The specifications for the residue gas, the acid gas, and liquid products.
- The selectivity required for the acid gas removal.
- The capital, operating, and royalty costs for the process.
- The environmental constraints, including air pollution regulations and disposal of byproducts considered hazardous chemicals.

Selection criteria for the solvent-based processes are discussed by Tennyson and Schaaf (1977) and Figure 1 and Figure 2 are based on their recommendations. The guidelines in these figures are naturally approximate and should be treated as such. These figures are for solvent-based



processes only. Thus, they exclude some commonly used processes such as adsorption and membranes. We slightly modified their recommendations to make it more current, but these guidelines, established in 1977, still are useful. Note that “hybrid” in the figures denotes mixed-solvent systems that contain both amine and a physical solvent.

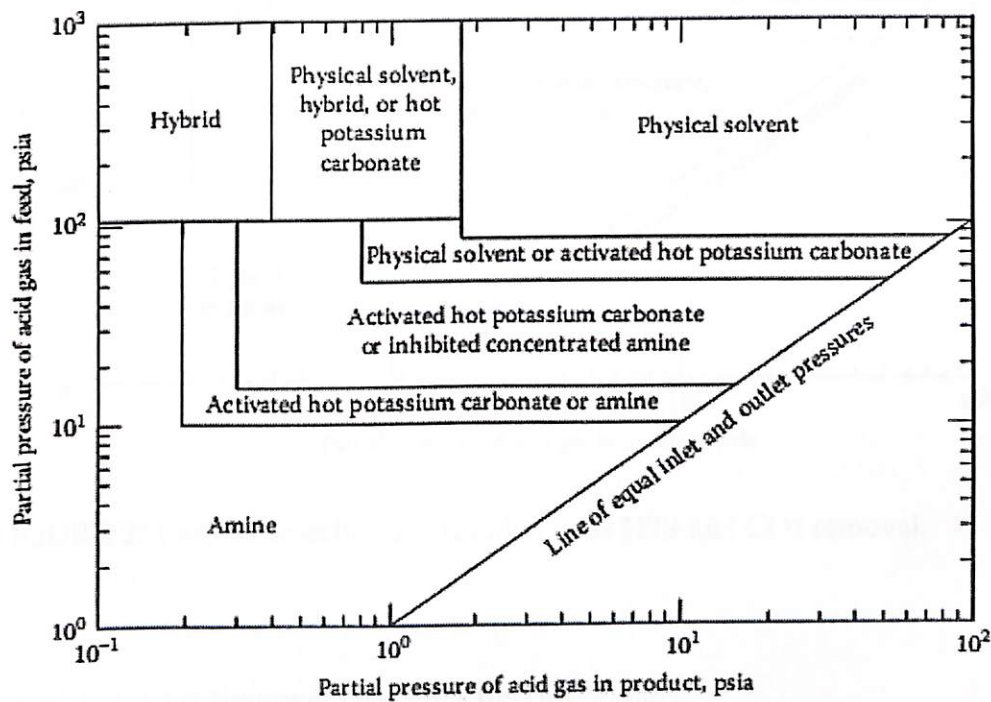


FIGURE 1: Process selection chart for CO<sub>2</sub> removal with no H<sub>2</sub>S.

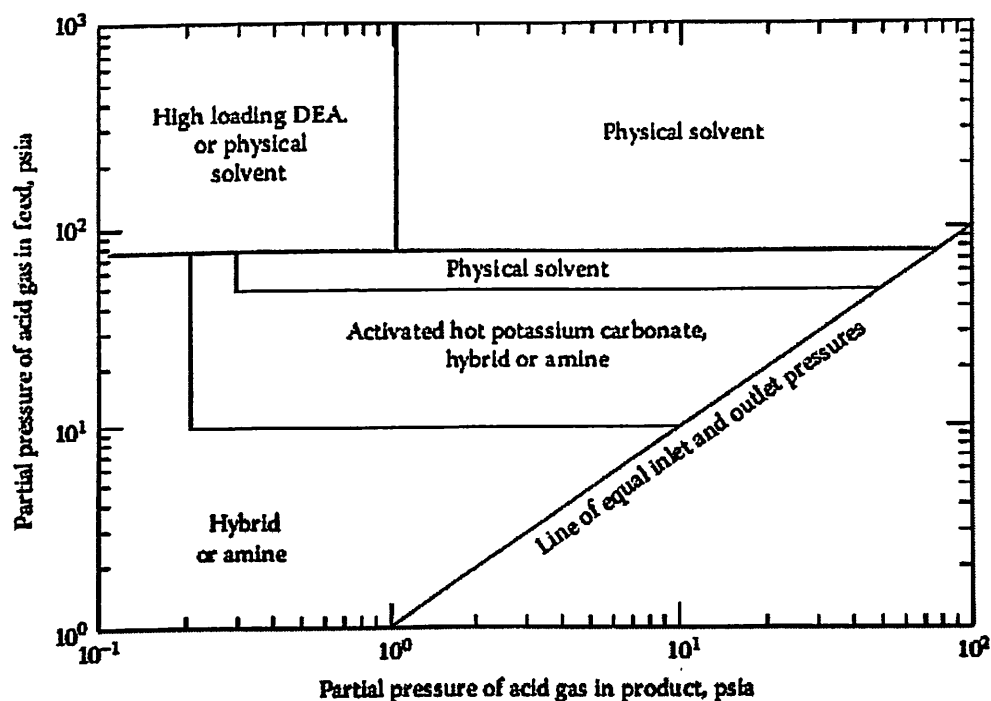


FIGURE 2: Process selection for simultaneous H<sub>2</sub>S and CO<sub>2</sub> removal.

TABLE 3: CO<sub>2</sub> Removal Processes for Gas Streams:

| PROCESS                | MINIMUM CO <sub>2</sub> LEVEL OBTAINABLE     | SOLUTION SUBJECT TO DEGRADATION? (DEGRADING SPECIES)                                            |
|------------------------|----------------------------------------------|-------------------------------------------------------------------------------------------------|
| Monoethanolamine (MEA) | 100 ppmv at low to moderate Pressures        | Yes (COS, CO <sub>2</sub> , CS <sub>2</sub> , SO <sub>2</sub> , SO <sub>3</sub> and mercaptans) |
| Diethanol amine (DEA)  | 50 ppmv in SNEA/DEA Process                  | Some (COS, CO <sub>2</sub> , CS <sub>2</sub> , HCN and mercaptans)                              |
| Triethanol amine (TEA) | Minimum partial pressure of 0.5 psia (3 kPa) | Slight (COS, CS <sub>2</sub> and mercaptans)                                                    |



|                             |                                                                            |                                                   |
|-----------------------------|----------------------------------------------------------------------------|---------------------------------------------------|
| Methyldiethanolamine (MDEA) | Bulk removal Only                                                          | No                                                |
| Diglycol amine (DGA)        | 100 ppmv at moderate to high Pressures                                     | Yes (COS, CO <sub>2</sub> , and CS <sub>2</sub> ) |
| Sulfinol                    | 50 ppmv, 50% slippage While meeting H <sub>2</sub> S Product spec          | Some (CO <sub>2</sub> and CS <sub>2</sub> )       |
| Selexol                     | Can be slipped or Absorbed                                                 | No                                                |
| Rectisol                    | 1 ppmv                                                                     | Not reported                                      |
| Molecular sieves            | Can meet cryogenic spec when CO <sub>2</sub> feed content is less than ~2% | Not applicable                                    |
| Membranes                   | Feed concentration dependent                                               | Not applicable                                    |

**SOLVENTS SWEETENERS:** Desirable characteristics of a solvent sweeteners used in the process just mentioned, are described below:

- mandatory withdrawal of H<sub>2</sub>S and other sulfur compounds to be achieved.
- Collection of oil must be low.
- The vapor pressure of the solvent must be low to minimize losses of solvent.
- Reactions between gas and solvent effect must be reversible acid to prevent degradation of solvents.
- No solvent should be thermally stable.
- Removal of degradation products should be simple.



- The acid gas sensor per unit distributed solvent must be high.
- The heat requirement for solvent regeneration or extraction should be low.
- The solvent should be non-corrosive.
- The solvent should not foam in the contactor or more.
- Selective removal of acid gases is desirable.
- The solvent should be inexpensive and readily available.

Unfortunately, there is not a solvent that has all the desirable characteristics. It is therefore necessary to choose the most suitable solvent for treating the mixture of acid gases in particular different solvents that are available. The sour natural gas mixtures vary H<sub>2</sub>S and CO<sub>2</sub> content and reporting; aromatic content heavy, and the content of COS, CS<sub>2</sub> and mercaptans.

Although most of the sour gas is sweetened with a solvent regeneration, to the gas a little sour, it may be more economical to use solvents or solid agents treasure. In such processes, the compound chemically reacts with the H<sub>2</sub>S and is consumed in the softening process, requiring the softening agent to be replaced periodically.



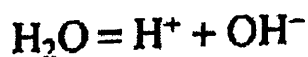
## CHAPTER 2

### AMINE PROCESS:

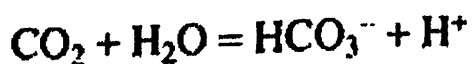
Amines those have proved to be of commercial interest for the main gas purification are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). Triethanolamine was replaced largely due to its low capacity (resulting from higher equivalent weight), low reactivity (such as a tertiary amine) and its relatively poor stability. Diisopropanolamine (DIPA) is used to some extent in the process ADIP process and Sulfinol process, as well as in the SCOT process for Claw plant tail gas purification. However, methyldiethanolamine (MDEA) is gradually replaced by DIPA in these applications.

### Base Chemicals:

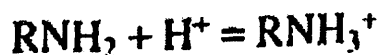
Monoethanolamine (MEA) and 2 - (2-aminoethoxy) ethanol (DGA), are known as primary amines and are generally more alkaline. Diethanolamine (DEA) and Diisopropanolamine (DIPA) have one hydrogen atom directly attached to the nitrogen atom and are called secondary amines. Triethanolamine (TEA) and methyldiethanolamine (MDEA) are completely substituted ammonia molecules without hydrogen atoms bonded to nitrogen, and are called tertiary amines. The main reactions occur when solutions of a primary amine such as monoethanolamine, are used to absorb CO<sub>2</sub> and H<sub>2</sub>S can be represented as follows: Ionization of water:



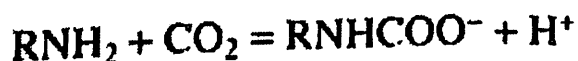
Hydrolysis and ionization of dissolved CO<sub>2</sub>:



Protonation of alkanolamine:



Carbamate formation:





Although all the above reactions are specific to primary amines such as MEA, they can also be applied to secondary amines such as DEA, by suitably modifying the formula amine. Solutions of tertiary amines undergo all the reactions above, but can not directly react with  $\text{CO}_2$  to form carbamates by reaction last.

The equilibrium concentrations of molecular  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in solution are proportional to their partial pressures in the gas phase (Henry's Law applies) so all reactions except first are driven to the right by increased acid gas partial pressure. The equilibrium reaction is also sensitive to temperature, which causes the vapor pressures of acid gas absorbed to rapidly increase the temperature is increased. Therefore, it is possible to strip gases absorbed from amine solutions by application of heat.

The effectiveness of an amine to the absorption of both acid gas is mainly due to its alkalinity. The magnitude of this factor is illustrated in Figure 3, which shows the values of pH on the titration curves for about 2N solutions of several amines when they are neutralized with  $\text{CO}_2$ . The curves were obtained by bubbling pure  $\text{CO}_2$  through the various solutions and periodically determine the solution concentration and pH. Curve equivalent KOH solution is included for comparison. The relatively smooth curves for the amines, as compared to the sharp breaks in the KOH curve, may be interpreted as an indication of the presence of non-ionized species during neutralization of the former compounds.

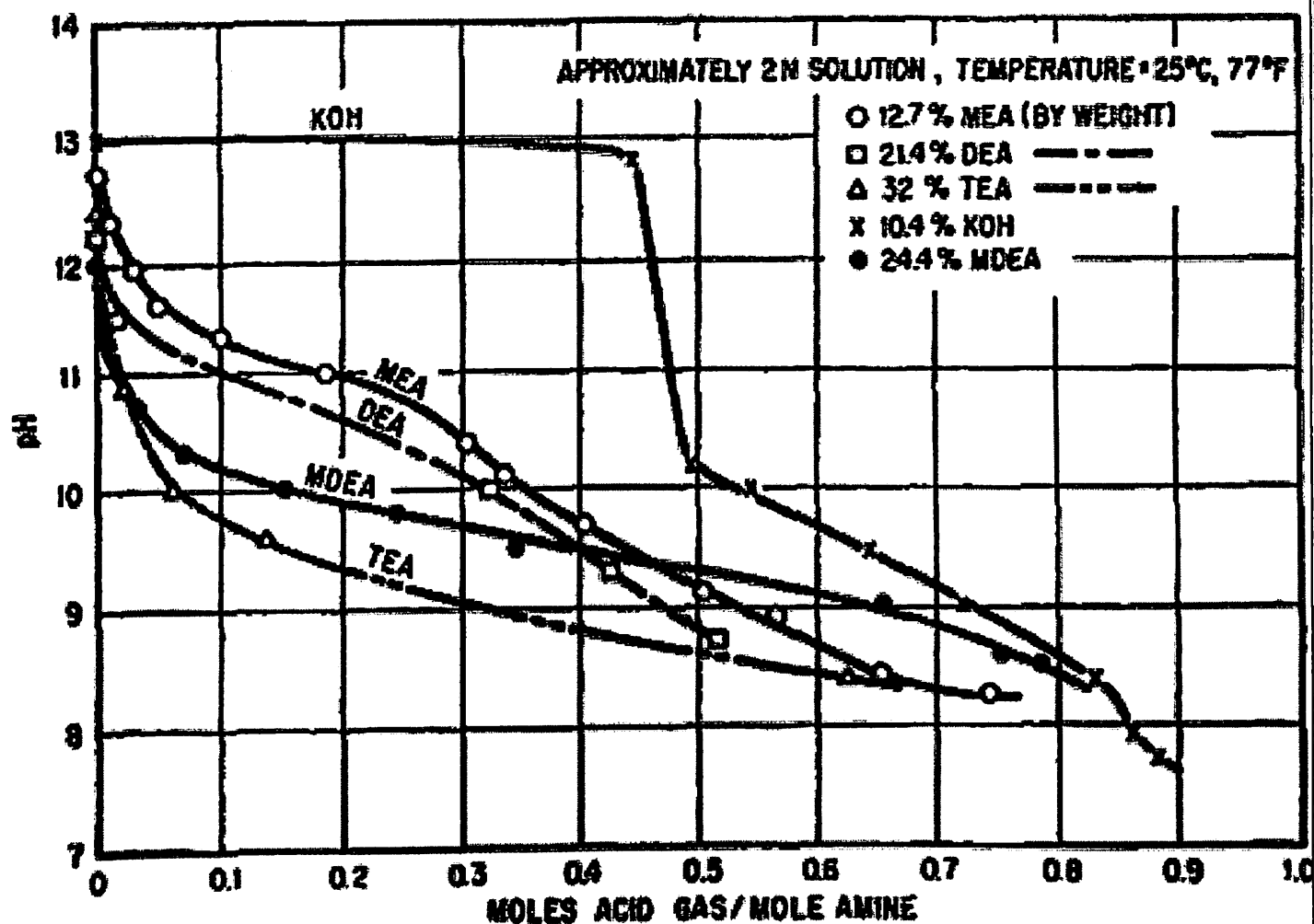


Figure 3: Titration curves showing pH during neutralization of ethanolamine and solutions with CO<sub>2</sub> and KOH.

The key concept of absorption of CO<sub>2</sub> by amines such as, for control of molecular structure, amines can be synthesized to form either a stable carbamate ion, an ion unstable carbamate, no carbamate ion. For example, through proper configuration molecular unstable carbamate is formed with the CO<sub>2</sub> that is easily hydrolyzed, leading to the formation of bicarbonate as the final product. This would result in a theoretical ratio of one mole of CO<sub>2</sub> per mole of amine.

#### Physical Properties Of Alkaloamines:



| Property                                    | MEA*     | DEA*                    | TEA*     | MDEA*    | DIPA*               | DGA**    |
|---------------------------------------------|----------|-------------------------|----------|----------|---------------------|----------|
| Mol. weight                                 | 61.09    | 105.14                  | 149.19   | 119.17   | 133.19              | 105.14   |
| Specific gravity,<br>20/20°C                | 1.0179   | 1.0919<br>(30/20°C)     | 1.1258   | 1.0418   | 0.9890<br>(45/20°C) | 1.0550   |
| Boiling point, °C                           |          |                         |          |          |                     |          |
| 760 mmHg                                    | 171      | decomp.                 | 360      | 247.2    | 248.7               | 221      |
| 50 mmHg                                     | 100      | 187                     | 244      | 164      | 167                 | —        |
| 10 mmHg                                     | 69       | 150                     | 208      | 128      | 133                 | —        |
| Vapor pressure,<br>mmHg at 20°C             | 0.36     | 0.01                    | 0.01     | 0.01     | 0.01                | 0.01     |
| Freezing point, °C                          | 10.5     | 28.0                    | 21.2     | -21.0    | -42                 | -9.5     |
| Solubility in water,<br>% by weight at 20°C | Complete | 96.4                    | Complete | Complete | 87                  | Complete |
| Absolute viscosity,<br>cps at 20°C          | 24.1     | 380(30°C)               | 1,013    | 101      | 198(45°C)           | 26(24°C) |
| Heat of vaporization,<br>Btu/lb at 1 atm    | 355      | 288(23 mm)<br>(168.5°C) | 230      | 223      | 184.5               | 219.1    |
| Approximate cost,<br>\$/lb***               | 0.59     | 0.60                    | 0.61     | 1.40     | —                   | 0.93     |

**Notes:**

\*Data of Union Carbide Chemicals Company (1957) except for pricing.

\*\*Data of Jefferson Chemical Company, Inc. (1969) except for pricing.

\*\*\*Kenney (1993). Prices are for bulk sales. Add \$0.10 per pound for drum sales.

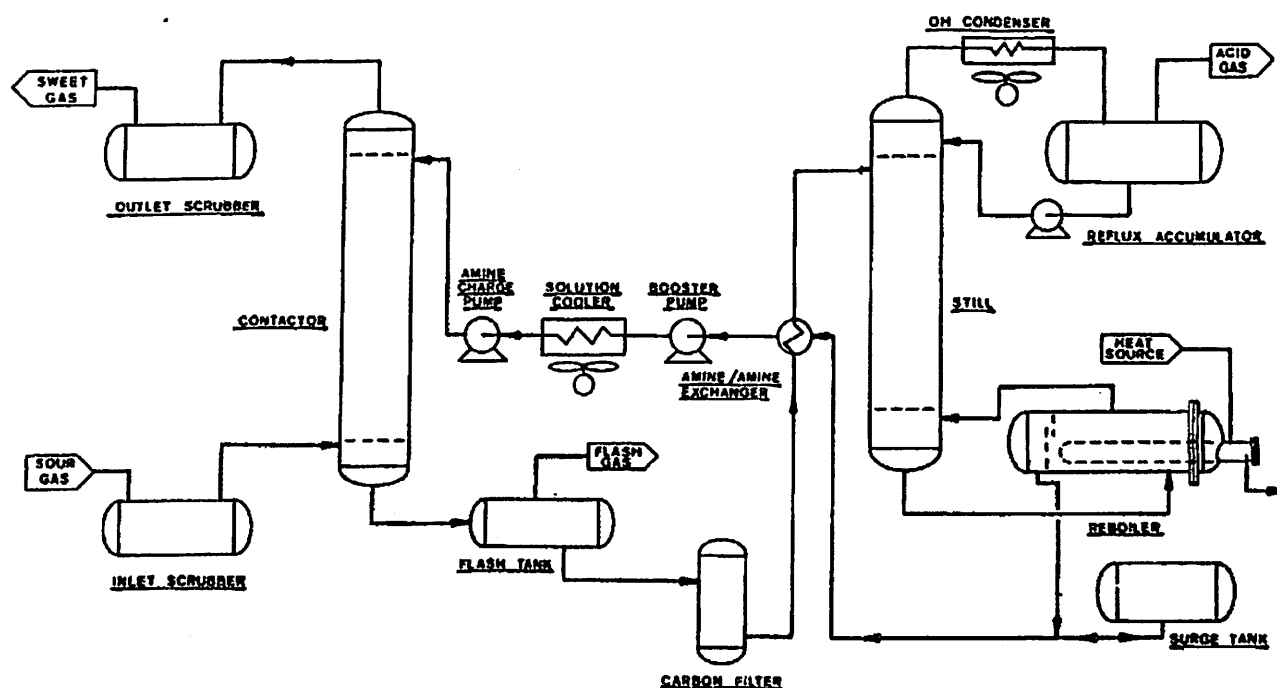


Figure 4: Process flow for typical ethanolamine sweetening unit.

### MONOETHANOLAMINE:

Monoethanolamine (MEA) is the most basic amines used in the treatment of acid and therefore more reactive toward acid gases. aqueous solutions of monoethanolamine, which were used almost exclusively for many years for the removal of  $H_2S$  and  $CO_2$  from synthesis gas natural and some are quickly replaced by other systems more efficient, especially for the treatment of high pressure natural gas. However, monoethanolamine is always the preferred solvent for gas streams containing relatively low concentrations of  $H_2S$  and  $CO_2$  and almost no minor contaminants such as COS and  $CS_2$ . This is particularly true when the gas must be processed at low pressures, and maximum suppression of  $H_2S$  and  $CO_2$  is needed. The low molecular weight of monoethanolamine, resulting from the solution's ability high to moderate levels (on a weight basis), its high alkality, and the relative ease with which it can be recovered from contaminated solutions are benefits that in many cases more than offset inherent disadvantages. Among these, the most serious is the formation of irreversible reaction products with COS and  $CS_2$ , resulting in



excessive chemical losses if the gas contains significant amounts of these compounds. In addition, the solutions of monoethanolamine are significantly more corrosive than solutions of most other amines, especially if concentrations exceed 20% amine and the solutions are heavily loaded with acid gases. This feature limits the ability of monoethanolamine solutions in cases where high partial pressures of acid gases would charge substantially higher.

It has the advantage of high capacity solution at reasonable concentrations, and is generally used for gas streams with moderate levels of CO<sub>2</sub> and H<sub>2</sub>S when complete removal of both impurities is required.

Monoethanolamine has a number of drawbacks, including:

- A relatively high vapor pressure resulting in high evaporation losses
- The formation of reaction products irreversibly with COS and CS<sub>2</sub>
- A high heat of reaction with acid gases resulting from high energy prices.
- The inability to selectively remove H<sub>2</sub>S in the presence of CO<sub>2</sub>
- Corrosion rate higher than most other amines at concentrations above 20% MEA at high levels of acid gas loading.
- The creation of thiosulfate corrosive when it reacts with oxygen requirements for regeneration.

A slow production of "heat stable salts" in all forms alkanolamine solutions, mainly by reaction with CO<sub>2</sub>. The oxygen promotes the formation of salts. In addition regenerator reboiler fouling, high concentrations of salts can be transferred to the contactor and cause foaming, which degrades the efficiency contactor. An "advantage" of the MEA (and DGA) other amines is that "reclaimers" are installed in line for the removal of these salts intermittently, and the reaction products formed irreversibly from COS and CS<sub>2</sub>.

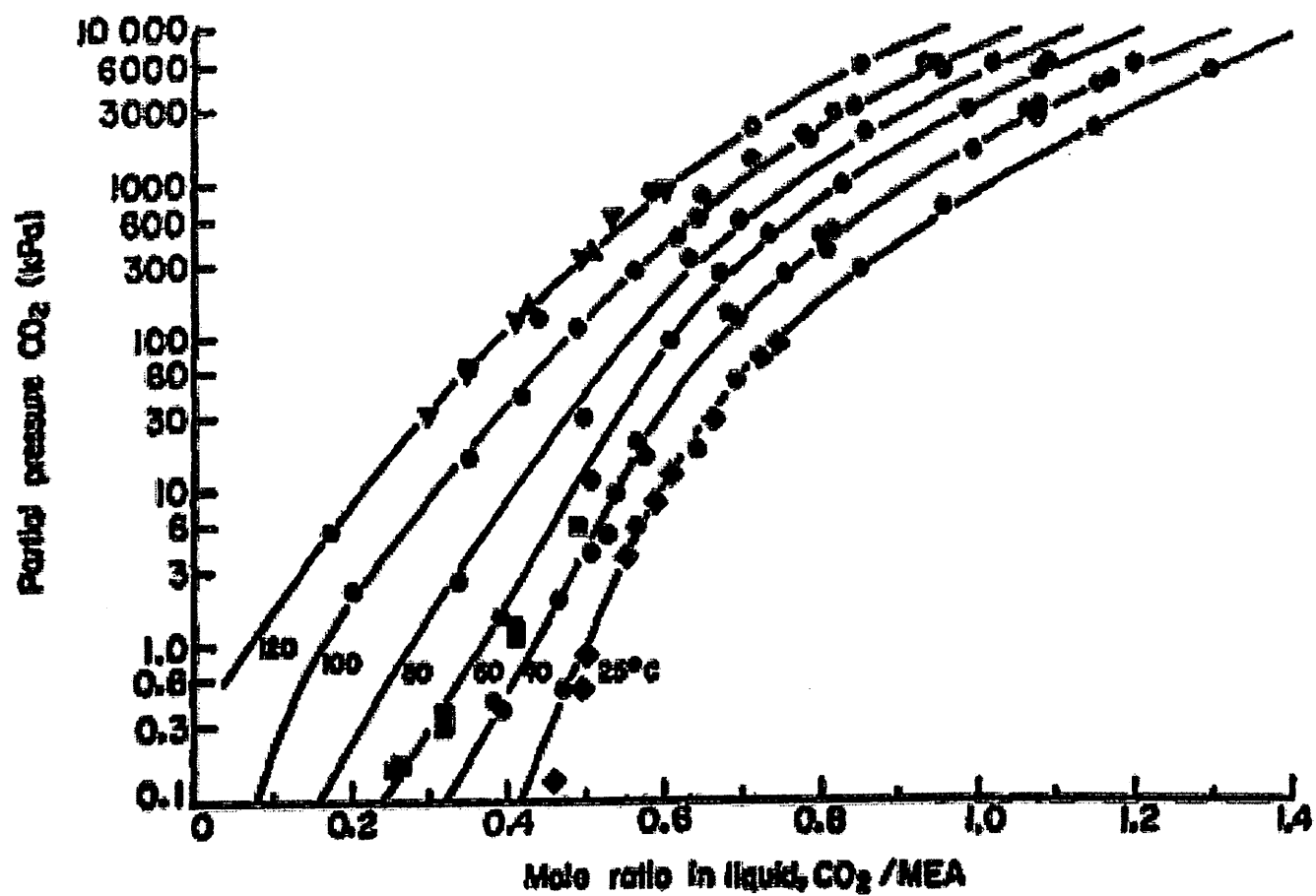


Figure 5: Solubility of CO<sub>2</sub> in 2.5 N MEA solution.

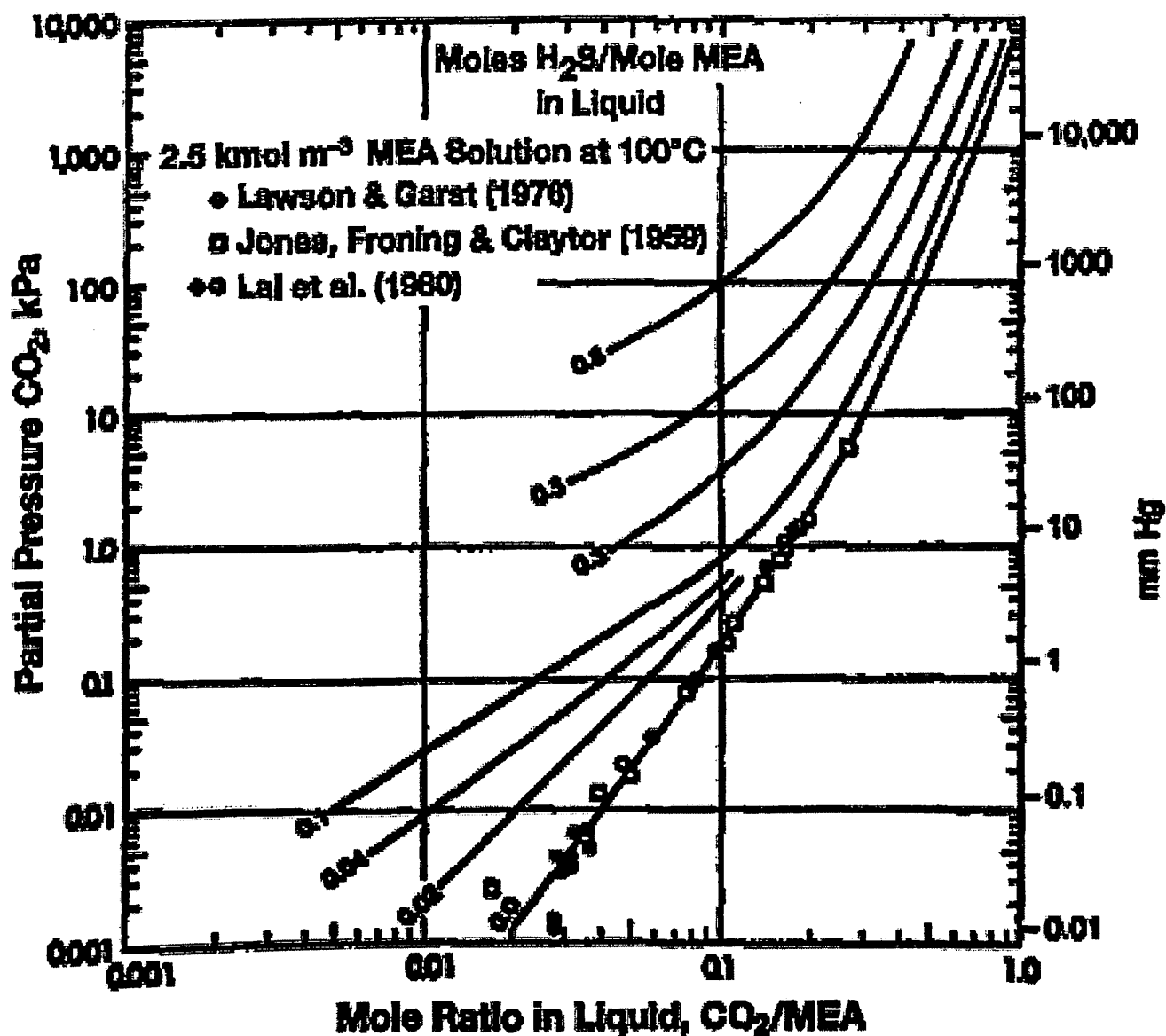


Figure 6: Effect of H<sub>2</sub>S on the solubility of CO<sub>2</sub> in 2.5 kmol/m<sup>3</sup> MEA solution at 100°C. (Lal et al, 1980).

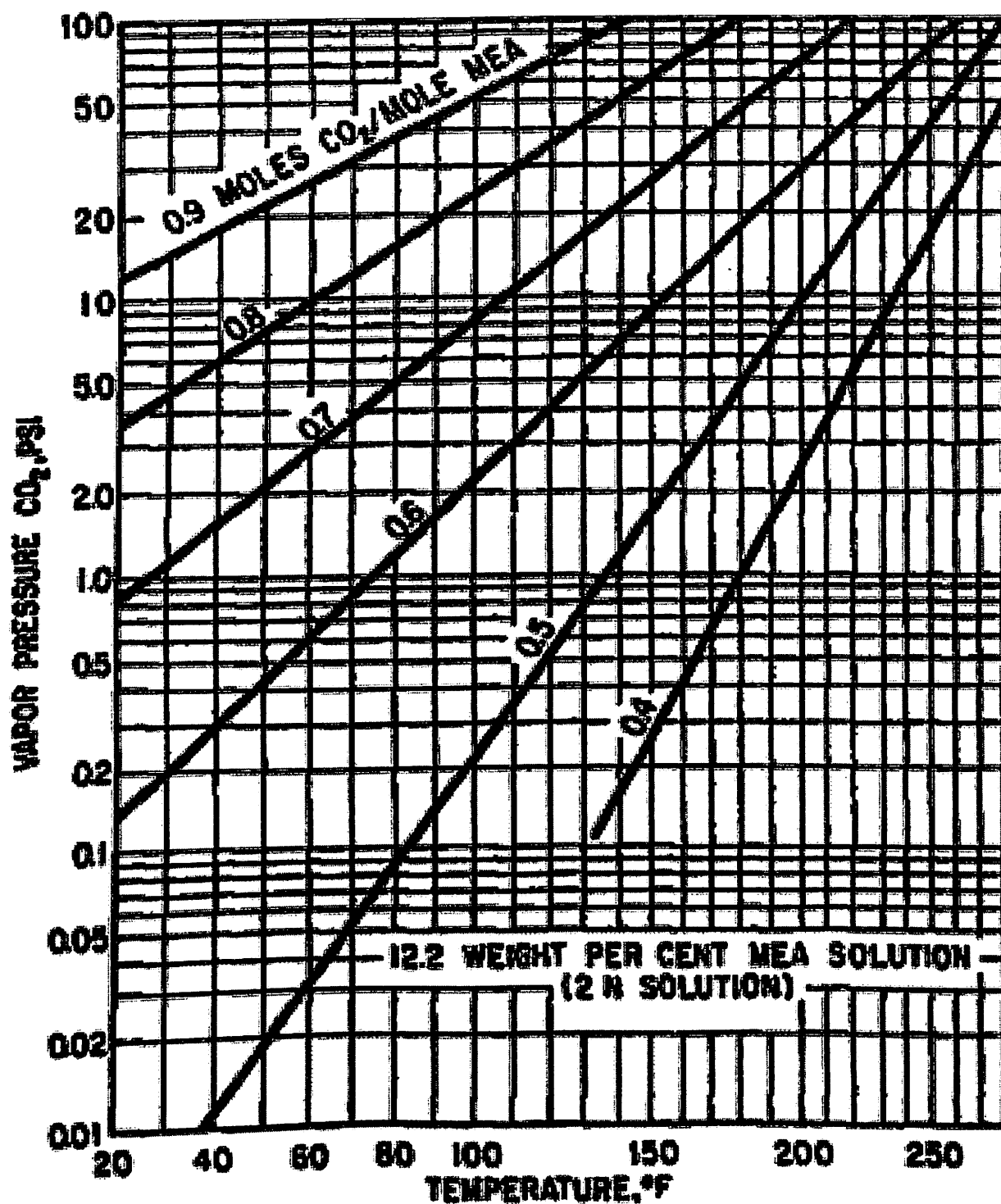


Figure 7: Effect of temperature on CO<sub>2</sub> vapor pressure for various CO<sub>2</sub> concentrations in 2N monoethanolamine solution.

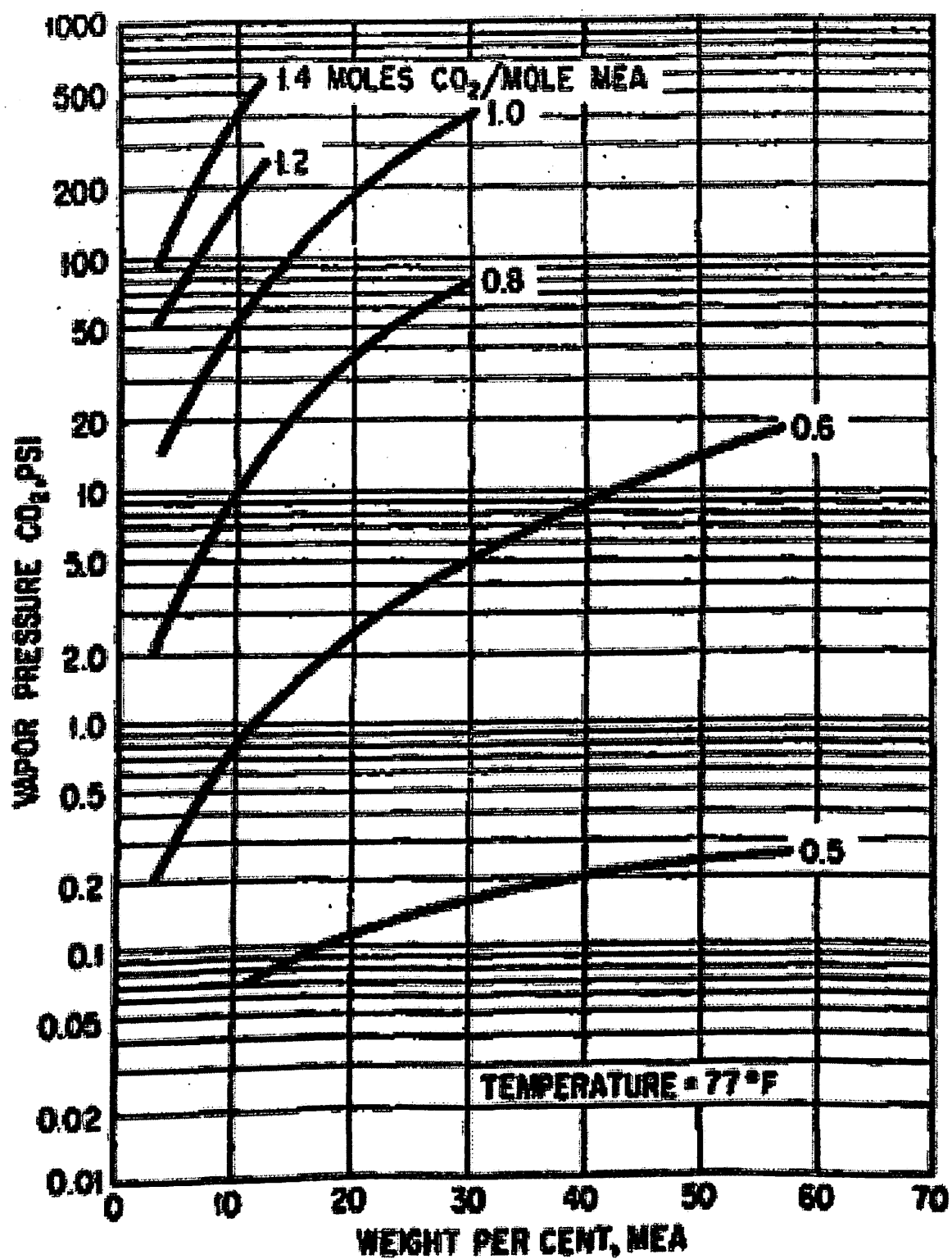


FIGURE 8: Effect of amine concentration on CO<sub>2</sub> vapor pressure.



## DIETHANOLAMINE:

Aqueous solutions of diethanolamine (DEA) have been used for many years for the treatment of refinery gases containing significant amounts of COS and CS<sub>2</sub>, H<sub>2</sub>S and CO<sub>2</sub>. Secondary amines are less reactive with COS and CS<sub>2</sub> as primary amines, and reaction products are not particularly corrosive. Therefore, diethanolamine and other secondary amines are the best choice for treating gas streams containing COS and CS<sub>2</sub>. The low vapor pressure of diethanolamine makes it suitable for operations of low pressure that evaporation losses are quite negligible. A disadvantage is that solutions of diethanolamine recovery from contaminated solutions may require vacuum distillation. Another drawback is that DEA undergoes many irreversible reactions with CO<sub>2</sub>, forming corrosive degradation products, and for this reason, DEA can not be the best choice of treatment of gas high in CO<sub>2</sub>.

Compared to the MEA, it has a low vapor pressure and therefore lower evaporation losses, it can operate at higher loads of acid gases, typically from 0.35 to 0.8 mole acid gas / mole amine from 0.3 to 0.4 mol acid-gas/mole, and it also has a lower energy need for reactivation. DEA concentration ranges are 30 to 50% by weight and are limited mainly by corrosion. DEA regenerable forms compounds with COS and CS<sub>2</sub> and therefore can be used for partial removal without significant loss solution. DEA has the disadvantage of undergoing irreversible side reactions with CO<sub>2</sub> and forming corrosive degradation products, so it may not be the best choice for high CO<sub>2</sub> gas. The elimination of these degradation products as well as heat stable salts must be done by using the vacuum distillation or ion exchange. Recovery can be performed off site or in portable equipment on the site.

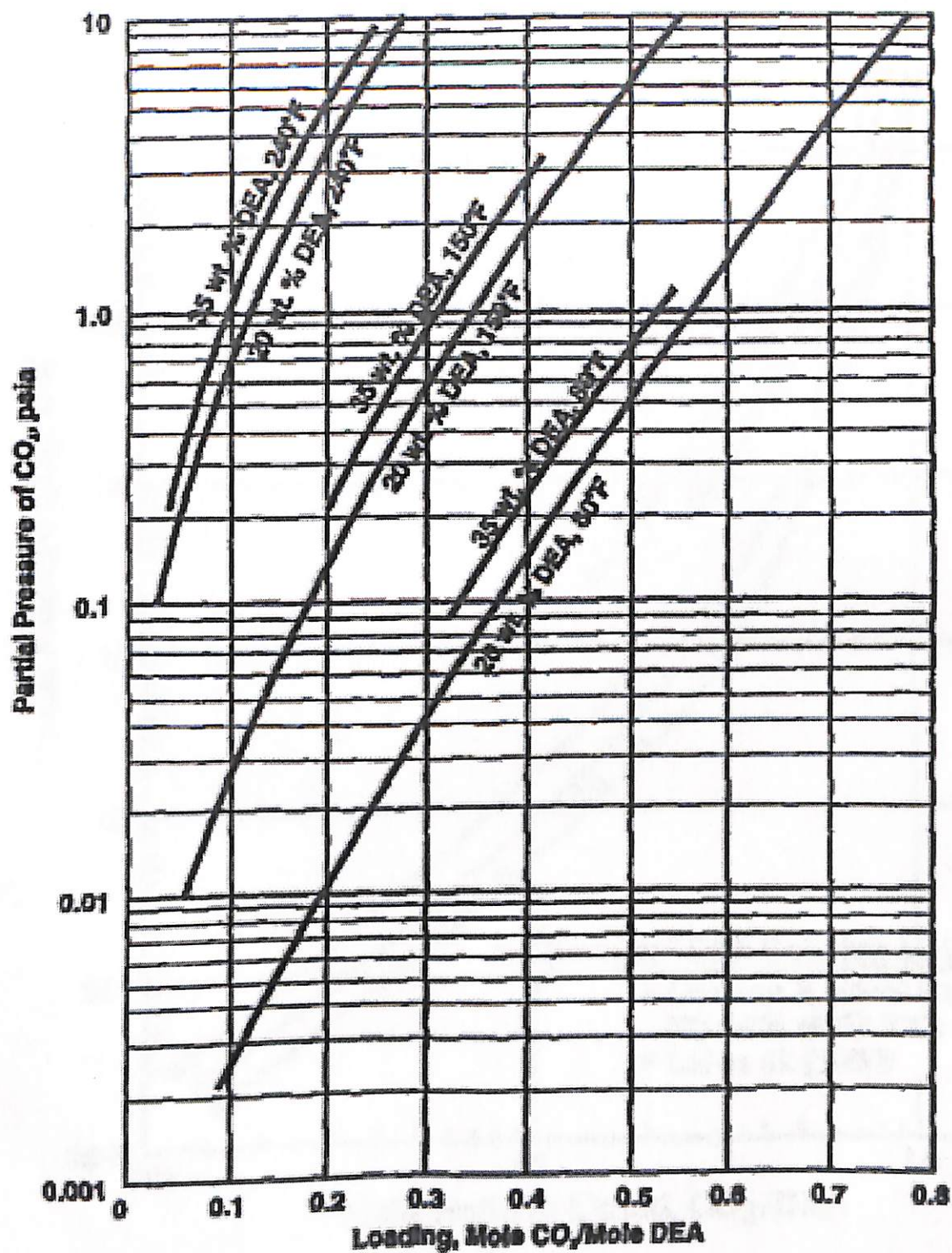


Figure 9: Solubility of CO<sub>2</sub> in aqueous DEA solutions. Data of Maddox and Elizondo (1989)

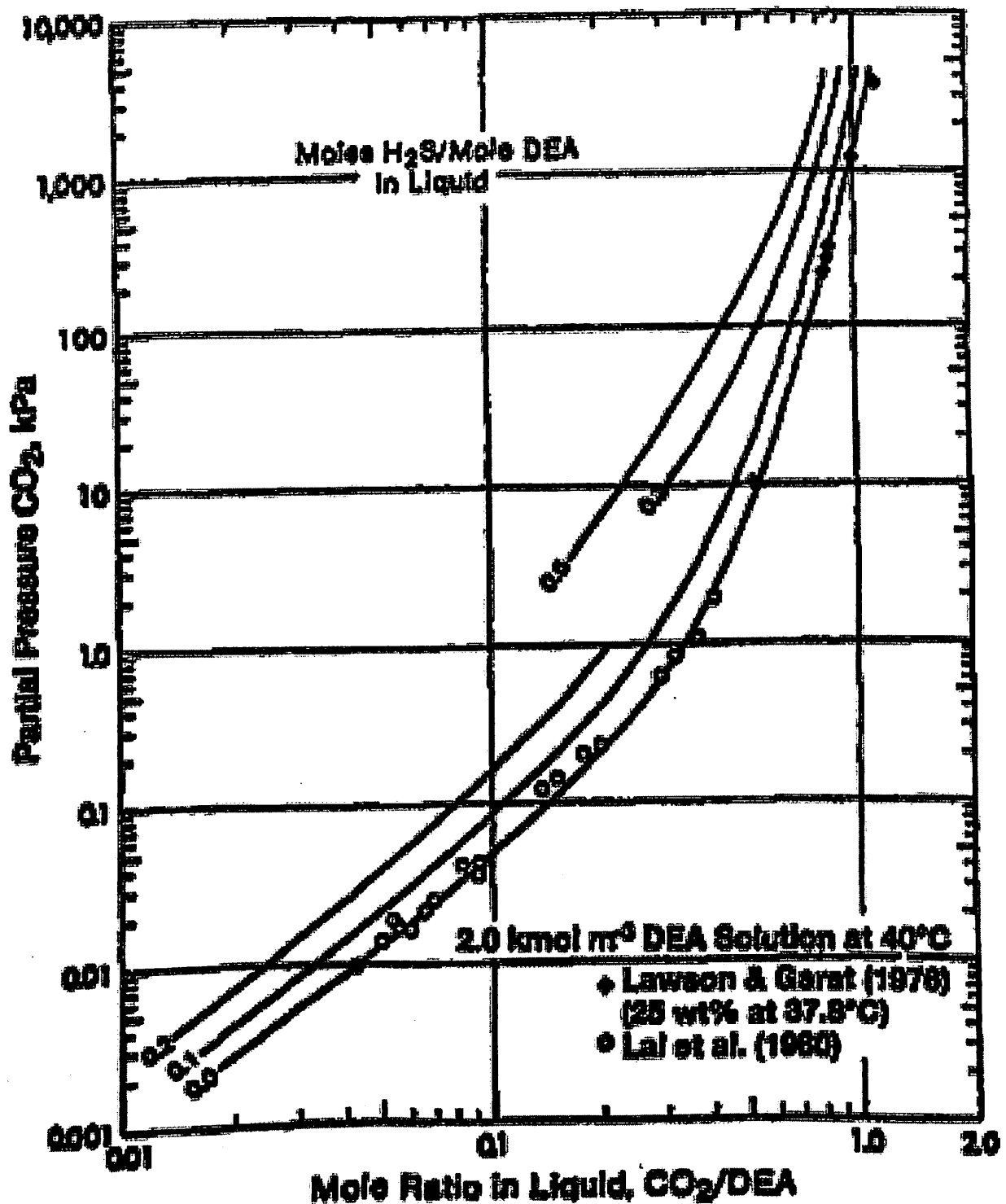


Figure 10: Effect of H<sub>2</sub>S on the solubility of CO<sub>2</sub> in 2.0 kmol/m<sup>3</sup> DEA solution at 40°C.



### DIGLYCOLAMINE:

Compared with MEA, low vapor pressure allows Diglycolamine [2-(2-aminoethoxy) ethanol] (DGA) to be used in relatively high concentrations (50 to 70%), which results in lower circulation rates. It is reclaimed onsite to remove heat stable salts and reaction products with COS and CS<sub>2</sub>.

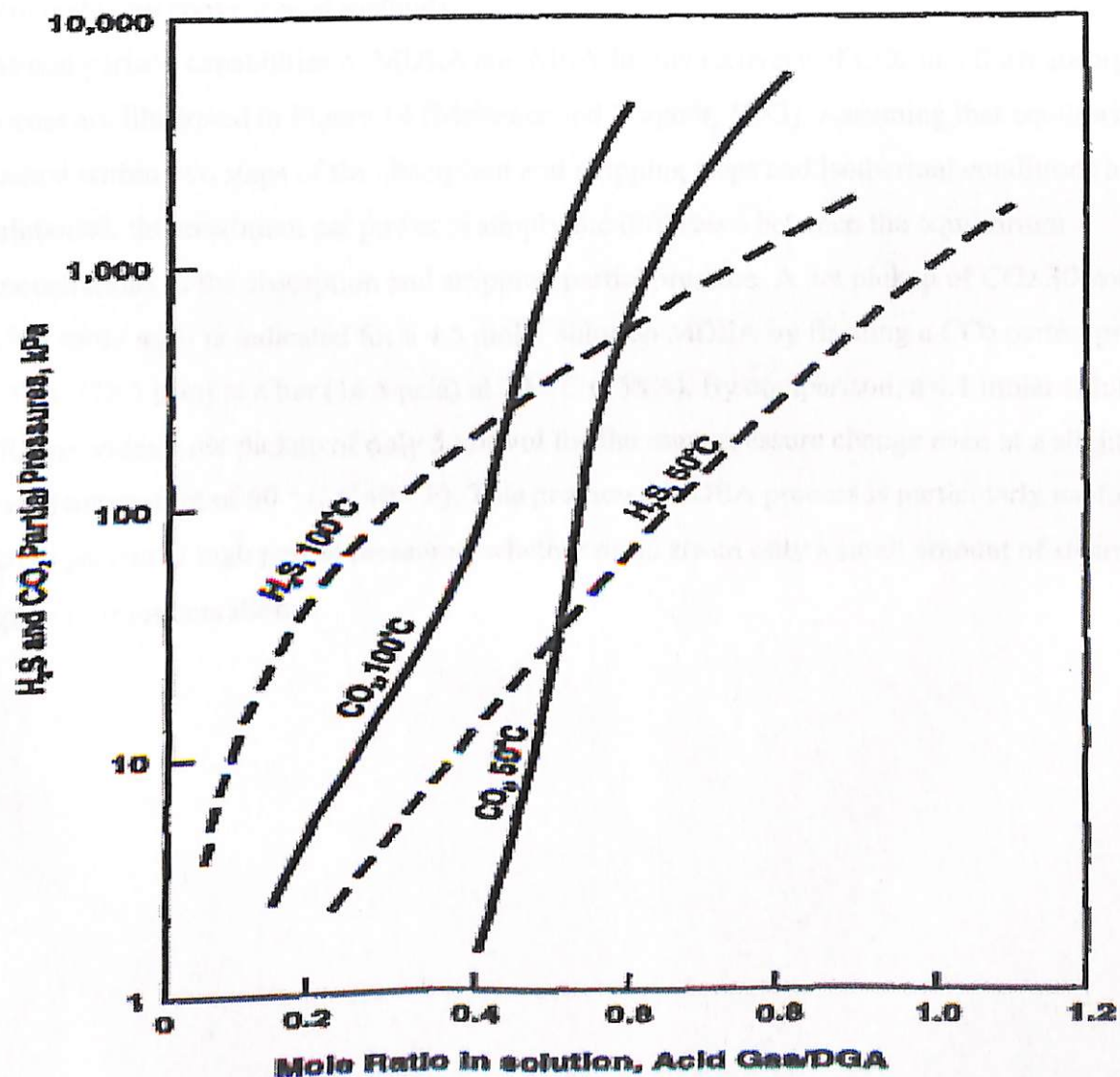


Figure 11: Solubility of CO<sub>2</sub> and H<sub>2</sub>S in 60 wt% DGA.



## METHYLDIETHANOLAMINE:

Methyldiethanolamine (MDEA), a tertiary amine, selectively removes H<sub>2</sub>S pipeline specifications while “slipping” some of the CO<sub>2</sub>. As mentioned previously, the slippage occurs because H<sub>2</sub>S hydrolysis is much faster than CO<sub>2</sub>, and the reaction of carbamate formation does not occur with a tertiary amine. Therefore, short contact time in the absorber are used to obtain selectivity. MDEA has a low vapor pressure and therefore can be used at concentrations up to 60% by weight without appreciable loss due to vaporization. Even with its relatively slow kinetics with CO<sub>2</sub>, MDEA is used for bulk removal of CO<sub>2</sub> gas in high concentration, because the energy requirements for regeneration are lower than those of other amines. It is not recoverable by conventional methods.

The comparison capabilities of MDEA and MEA for the recovery of CO<sub>2</sub> in a flash absorption process are illustrated in Figure 14 (Meissner and Wagner, 1983). Assuming that equilibrium is reached within two steps of the absorption and stripping steps and isothermal conditions are maintained, the maximum net power is simply the difference between the equilibrium concentrations in the absorption and stripping partial pressure. A net pickup of CO<sub>2</sub> 30 vol / vol (0.297 mol / mol) is indicated for a 4.5 molar solution MDEA by flashing a CO<sub>2</sub> partial pressure of 5 bar (72.5 psia) at a bar (14.5 psia) at 70 ° C (158 ° F). By comparison, a 4.1 molar solution MEA provides a net pickup of only 5 vol/vol for the same pressure change even at a slightly lower temperature of 60 ° C (140 ° F). This promoted MDEA process is particularly useful when CO<sub>2</sub> is present at high partial pressures, whether or no steam only a small amount of steam is required for regeneration.

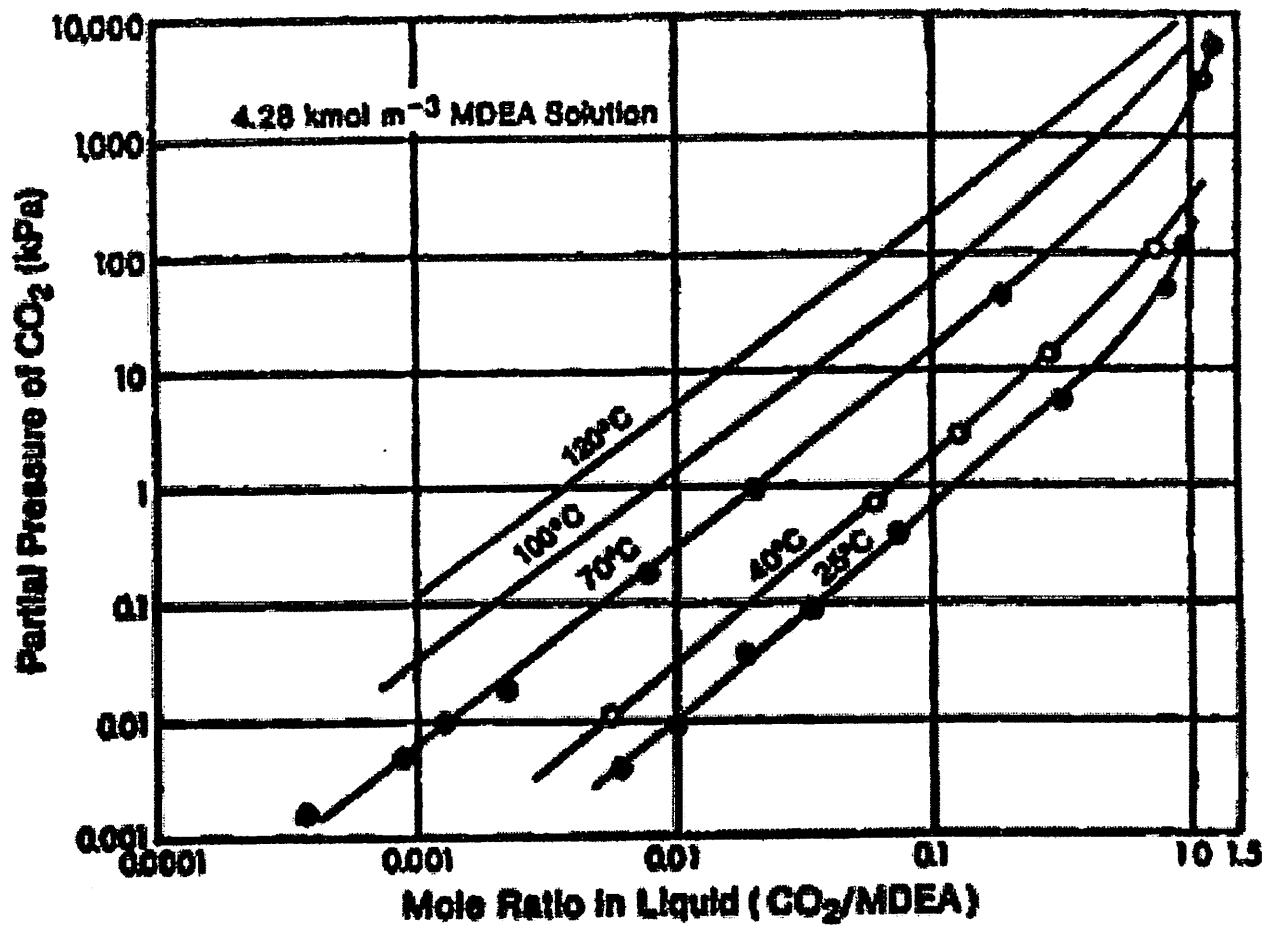


Figure 12: Effect of temperature on the solubility of CO<sub>2</sub> in 4.28 kmol/m<sup>3</sup> MDEA solution.

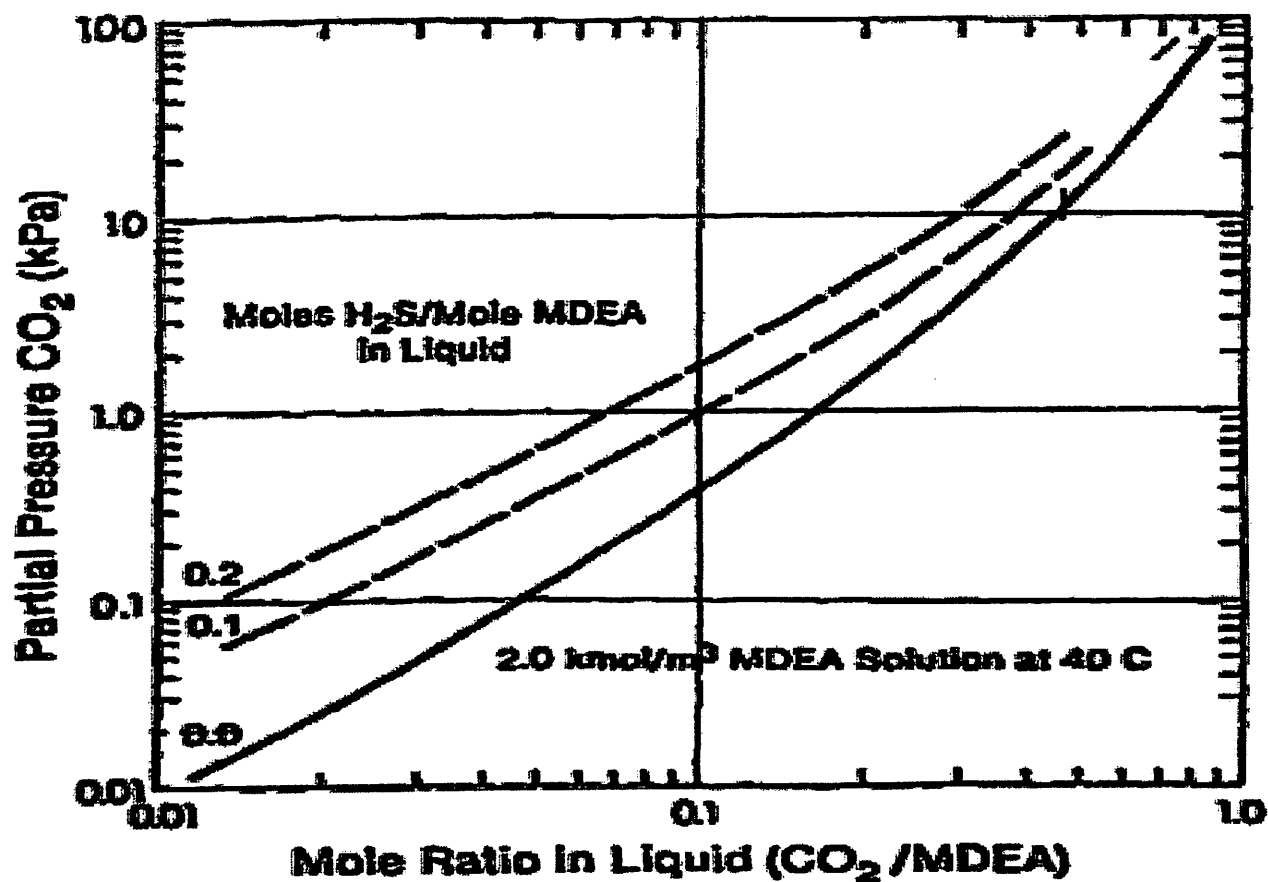


Figure 13: Effect of H<sub>2</sub>S on the solubility of CO<sub>2</sub> in 2.0 mol/m<sup>3</sup> MDEA solution at 40°C. (Jou et al, 1981)

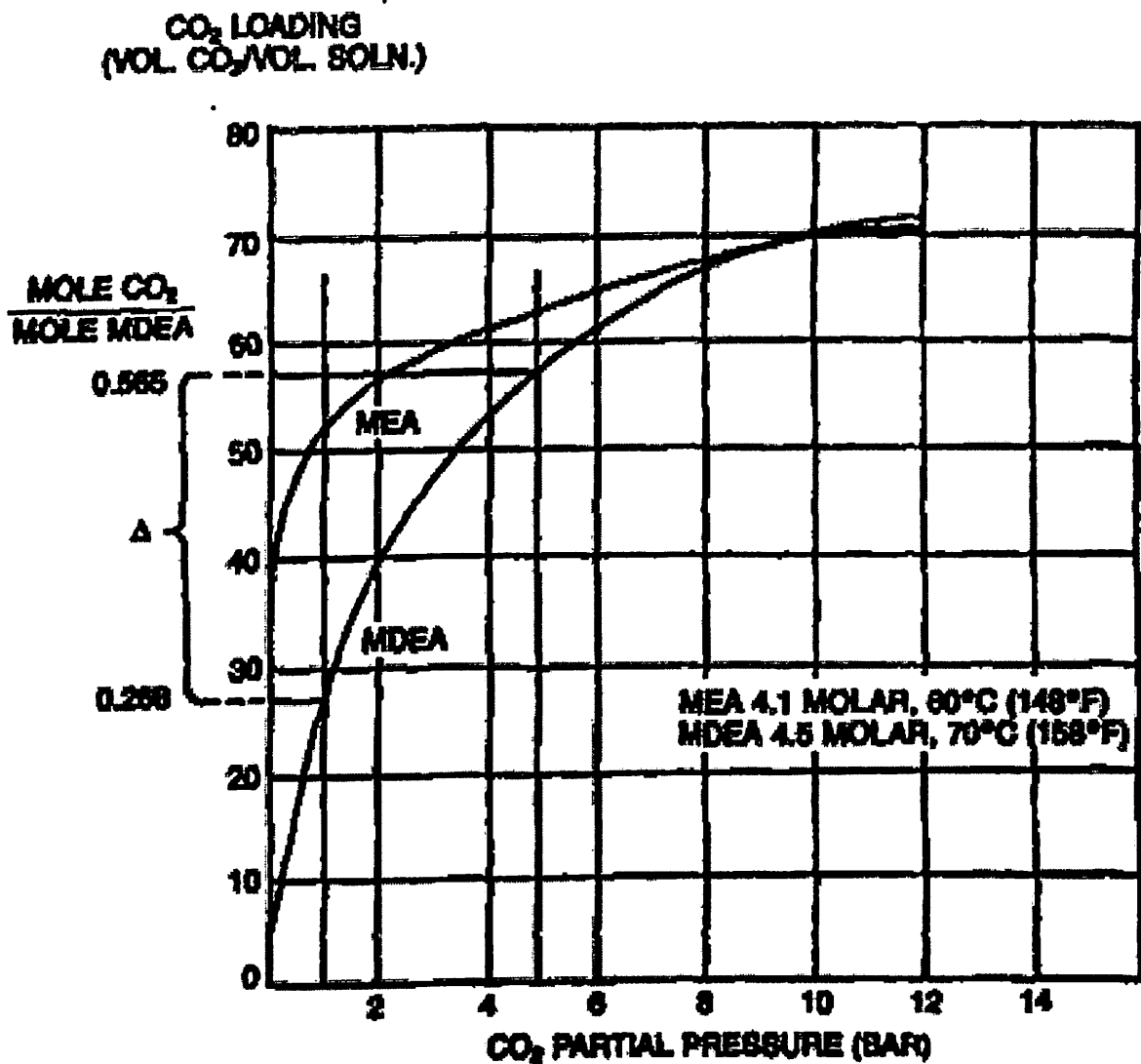


Figure 14: CO<sub>2</sub> solution isotherms in MEA and MDEA

#### DI-ISOPROPANOLAMINE:

Diisopropanolamine (DIPA) was used in the ADIP Sulfinol and processes, both under license by Shell International Petroleum (SIPM). In the process Sulfinol, di-isopropanolamine is used in conjunction with an organic solvent physics. The ADP process, which employs relatively concentrated aqueous solutions of diisopropanolamine, was described by Bally (1961) and Klein (1970). It was widely accepted mainly in Europe for the treatment of gases and liquids refinery



which beside  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , also contain COS. It is alleged that substantial amounts of COS are removed without affecting the solution. In addition, solutions have diisopropanolamine low steam requirements for regeneration and to be non-corrosive (Klein, 1970). SIPM applied the DIPA process to selective absorption of  $\text{H}_2\text{S}$  from refinery gases (Abe and Petenan, 1980) and in the SCOT process, the selective absorption of  $\text{H}_2\text{S}$  from tail gas from Claus. However, SIPM gradually replacing DIPA with MDEA in these two applications. A theoretical study of the kinetics of absorption involved in the selective absorption of  $\text{H}_2\text{S}$  in DIPA was introduced by Ouwerkerk(1978). Equations for mass transfer with chemical reaction are used in the study to develop a computer program that takes into account the competition between  $\text{H}_2\text{S}$  and  $\text{CO}_2$  when it is absorbed at the same time.

#### STERICALLY HINDERED AMINES:

In acid gas removal, steric hindrance involves modifying the reactivity of a primary or secondary amine by a change in the structure of the alkanol amine. A large hydrocarbon group attached to the nitrogen shields the nitrogen atom and hinders the carbamate reaction. The  $\text{H}_2\text{S}$  reaction is not significantly affected by amine structure, because the proton is small and can reach the nitrogen. However,  $\text{CO}_2$  removal can be significantly affected if the amine structure hinders the fast carbamate formation reaction and allows only the much slower bicarbonate formation.

#### MIXED AMINES:

The selectivity of MDEA can be reduced by the addition of MEA, DEA, or proprietary additives. Thus, it can be adapted to meet the desired amount of slippage of  $\text{CO}_2$  and still have energy requirements lower than those of primary and secondary amines.

#### Heats Of Reaction:

The magnitude of the exothermic heats of reaction, which includes the heat of solution, of the amines with the acid gases is important because the heat liberated in the reaction must be added back in the regeneration step. Thus, a low heat of reaction translates into smaller energy regeneration requirements. Table 4 summarizes the important data for the common amines. The values in Table 4 are approximate because heats of reaction vary with acid gas loading and



solution concentration. Jou et al. (1994) and Carson et al. (2000) report measured heats of reaction for CO<sub>2</sub> in MEA, DEA, and MDEA.

| AMINE | CO <sub>2</sub> , Btu/lb (kJ/kg) |
|-------|----------------------------------|
| MEA   | 825 (1920)                       |
| DEA   | 730 (1700)                       |
| DGA   | 850 (1980)                       |
| MDEA  | 610 (1420)                       |

TABLE 4: Average Heats of Reaction (include both heat of solution and heat of reaction) of the Acid Gases in Amine Solutions.

#### Process Diagram:

A typical scheme for the removal of acid gases from natural gas by the use of MEA is shown in Figure 15 representing the diagram is simplified, and all conditions of operation, not definitive. The acid gas feed enters at the bottom of the contactor at pressures of 1000 psi (70 bar) and temperatures around 90 ° F (32 ° C). The acid gas flows upwards, against the current of the lean amine solution which descends from above. The lean amine, which refers to the contactor is maintained at a temperature above the steam coming out of the contactor to prevent condensation of heavier hydrocarbon liquid. Intimate contact between the solution of gas and the amine is obtained by using two trays or packing in the contactor.

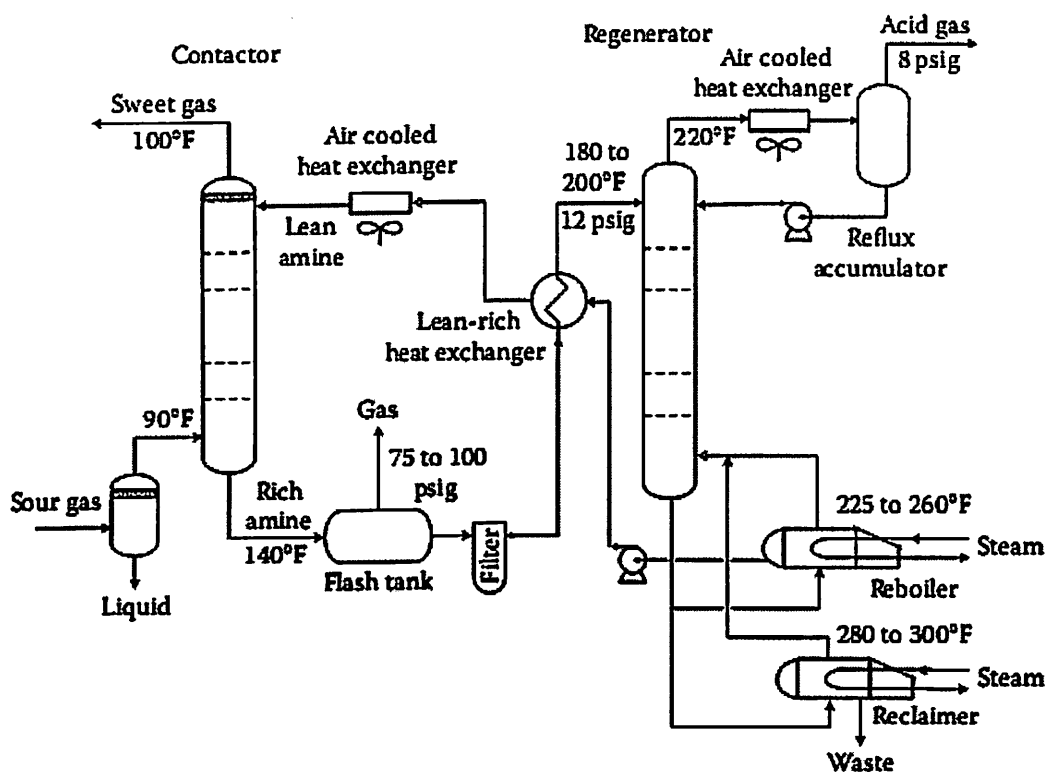


FIGURE 15: Process flow diagram for amine treating by use of MEA. Contactor commonly operates at pressures up to 1,000 psi (70 bar). Flow rates to reclaimer are 1 to 3% of amine circulation rate. (Adapted from Smith, 1996)

The contactor operates above ambient temperature because of the combined exothermic heat of absorption and reaction. The maximum temperature is in the lower portion of the tower because the majority of the absorption and reaction occurs near the bottom of the unit. The temperature “bulge” in the tower can be up to about 180°F (80°C). The treated gas leaves the top of the tower water saturated and at a temperature controlled by the temperature of the lean amine that enters, usually around 100°F (38°C).

The rich amine leaves the bottom of the device at temperatures near 140 ° F (60 ° C) and enters a flash tank, where its pressure is reduced to 75 to 100 psig (5 to 7 bar) at remove (flash), all dissolved hydrocarbons. The dissolved hydrocarbons are generally used as fuel plant. If necessary, a small stream of lean amine is contacted with the gas fuel to reduce the H<sub>2</sub>S concentration. The rich amine is then passed through a heat exchanger and enters the solvent regenerator (stripper) at temperatures of about 180 to 220 ° F (80 to 105 ° C). Reboiler on the separator generally uses low pressure steam. Steam produced at the base flows upward, either



trays or containers, where it contacts the strip and the rich amine acid gas from the liquid flowing. A stream of lean amine is removed from the stripper, cooled to about 110 ° F (45 ° C), and enters the switch at the top to cool and condense the vapor flow upward fluid. Steam, which consists mainly of acid gases and water vapor exits the top of the extractor and is usually treated sulfur recovery.

The lean amine exits the bottom of the stripper to about 260 ° F (130 ° C) and is pumped to the pressure switch, heat exchange with the rich amine stream and is further cooled before it enters the switch top . Both the treated gas leaving the contactor gas and acid gas to the Claus plant are saturated with water.

Figure 15 shows a unit of MEA. Smith (1996) sets out the main pieces of equipment and operating conditions are also representative of units of DEA and DGA, with the exception of the recovery facility. AED units have no recovery, and recovery DGA operate at temperatures slightly higher from 375 to 385 ° F (190 to 195 ° C).

Lyddon and Nguyen (1999) to evaluate several modifications to the flow regime as the basis for amine units which can increase the gas flow. When additional capacity exists in the regenerator, but not in the absorber, and the additional pressure drop is acceptable, static mixers can help. The mixture of sour gas and lean amine absorber essentially provides a stage further. Two configurations were considered. In one case, a side stream of sour gas passes through a static mixer. After separation of the amine, the gas is mixed with the sweet gas of the absorber. In either case, the entire flow passes through the static mixer upstream of the inlet separator before entering the absorber. In both cases, the rich amine from the static mixer is in the regenerator. Lyddon and Nguyen (1999) reported a case in which the use of the bypass static mixers has a 17% increase in plant capacity.

#### Amine Concentration:

The choice of amine concentration can be quite arbitrary and is usually done on the basis of operating experience. Typical monoethanolamine concentrations range from 12% to maximum 32% by weight. Based on operating experience in five plants, Feagan et al. (1954) recommended the use of a nominal concentration of 15 wt% monoethanolamine in water. The very strength solution was recommended by Connors (1958). Dupart et al. (1993a, 1993b) recommends a maximum concentration of MEA 20% by weight. However, it should be noted that higher amine



concentrations up to 32% by weight of the MEA may be used where corrosion inhibitors are added to the solution and when CO<sub>2</sub> is the component of acid gas.

Diethanolamine solutions that are used for the treatment of refinery gases are generally the concentration of 20 to 25% by weight, while concentrations of 25 to 30% by weight are commonly used for purification of natural gas. Diglycolamine solutions usually contain 40 to 60% by weight of amine in water, and concentrations of MDEA solution can vary from 35 to 55% by weight.

It should be noted that increasing the amine concentration will generally reduce the required solution circulation rate, and therefore the plant cost. However, the effect is not as great as might be expected, the principal reason being that the acid-gas vapor pressure is higher over more concentrated solutions at equivalent acid-gas/amine mole ratios. In addition, when an attempt is made to absorb the same quantity of acid gas in a smaller volume of solution, the heat of reaction results in a greater increase in temperature and a consequently increased acid-gas vapor pressure over the solution. The effect of increasing the amine concentration in a specific operating plant using DGA solution for the removal of about 15% acid gas from associated gas is shown in Figure 16. The authors of this study concluded that the optimum DGA strength for this case is about 50 wt%. The effect of the increasing amount of DGA at higher concentrations is almost nullified by the decreasing net acid gas absorption per mole of DGA (Huval and van de Venne, 1981).

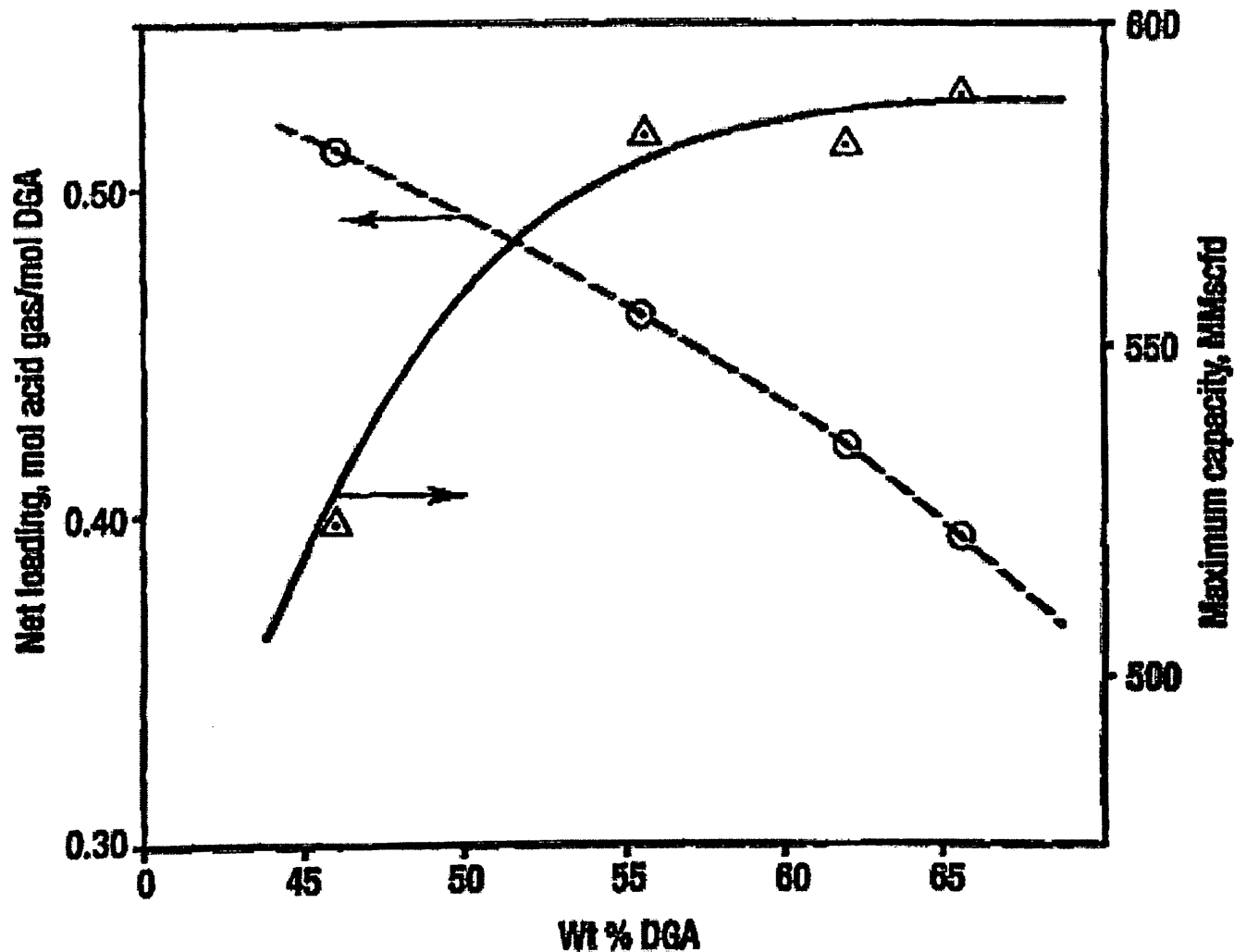


Figure 16: Effect of DGA concentration on maximum plant capacity and net solution loading in a large commercial plant (Huval and van de Venne, 1980)

#### AMINE RECOVERY:

Amines react with  $\text{CO}_2$  and contaminants, including oxygen, to form organic acids. These acids then react with the amine base to form heat stable salts (HSS). As their name suggests, these salts are stable to heat, accumulate in the amine solution, and must be removed. For MEA and DGA solutions, the salts are removed by using a reclaimer (see Figure 15), which uses a distillation process semi-continuous, as described by Smith (1996). The regenerator is filled with a lean amine, and a strong base such as sodium carbonate or sodium hydroxide, is added to the solution



to neutralize the heat stable salts. A slipstream of 1 to 3% of the circulating amine is then added continuously while the mixture is heated. The water vapor and amine are taken on top, leaving the contaminants in the bottom of the liquid. Heating is continued until the temperature is about 300 ° F (150 ° C) for MEA or from 360 to 380 ° F (180 to 195 ° C) for the DGA. The cycle is then stopped and the bottoms that contain contaminants (dissolved salts, suspended solids) are removed. DEA does not form a significant amount of non-regenerable degradation products and must be more difficult recovery by vacuum distillation or ion exchange. Further details on the collectors can be found in the book technical data (2004b), Smith (1996), Simmons (1991) and Holub and Sheilan (2000).

#### Operational Problems:

The brief discussion of their work here highlights some of the most important considerations.

Corrosion: Some of the main factors influencing corrosion are:

- Amine concentration (higher concentrations promote corrosion)
- Rich amine acid gas loading (high gas costs in favor amine corrosion)
- Oxygen concentration
- Heat stable salts (higher concentrations promote corrosion and foaming)

In addition to destroying vessels and piping, corrosion products can cause foaming.

Foam solution: Foam of liquid amine solution is a major problem because it causes contact liquid-vapor poor, poor solution distribution, and retention of solution resulting from deferral and gas spec. Among the causes of suspended solids are s foam, liquid hydrocarbons, surfactants, such as those contained in inhibitors and compressor oils, and degradation products of amines, including heat stable salts. An obvious remedy is to remove the offending material, the other is to add anti-foaming agents.

Heat stable salts: As mentioned above, these products can cause degradation of amines both corrosion and foaming. They are normally treated by using amine collectors.



## USE MDEA AND MIXTURES OF AMINO FOR CO<sub>2</sub> BULK REMOVAL:

Over the last 10 years, many plants have been built or converted methyldiethanolamine (MDEA) for its ability to take advantage of selective absorption. In the SAR, the H<sub>2</sub>S is selectively absorbed by the gas leaving large amounts of CO<sub>2</sub> in the gas. The selective absorption characteristics of MDEA were reported in a large extent. MDEA is well known for its relatively slow reaction rate of CO<sub>2</sub> emissions. Accordingly, MDEA is not generally associated with situations where the removal of large quantities of CO<sub>2</sub> is desired. However, MDEA has a number of properties that make it attractive for the removal of CO<sub>2</sub>:

- i) solution concentration high (up to 50-55% by weight).
- ii) loading high acid gas.
- iii) low corrosion even at high loads solution.
- iv) the rate of degradation.
- v) Low heat of reaction
- vi) loss of low vapor pressure and a solution.

The main drawbacks are:

- i) the slow reaction rate with CO<sub>2</sub>.
- ii) The tendency to foam at high concentrations.
- iii) Higher cost.

The disadvantage of slow reaction rate can be overcome by operating temperatures and proper design of trays in the absorber to provide sufficient residence time of the liquid. The slow reaction rate can also be overcome significantly by adding one or two more reactive primary amines or secondary amines to form a mixture in water. The primary or secondary amines are added to the amount of 5-10% of the total amine present.

If foaming occurs, it is often caused by some exotic compounds introduced into the system as a corrosion inhibitor is injected at the wellhead. If the cause can not be found and eliminated, silicon and some other types of antifoam agents have been found to work reasonably well in many cases.

In most applications, much less MDEA is consumed or lost, which helps to mitigate the higher costs. Thus, the disadvantages associated with the use of MDEA and mixtures of amine MDEA can be overcome to an acceptable level.



In this work, the use of MDEA and mixtures of amines for bulk removal of CO<sub>2</sub> are considered. The influence of process parameters the most important are studied for three cases with CO<sub>2</sub> levels ranging from moderate to high. One case also uses H<sub>2</sub>S and CO<sub>2</sub> in equal concentrations and involves a plant of Christmas and a unit tail gas cleanup.

#### Consideration Of Operating Parameters:

The operating parameters for each application should be carefully examined. For the case of bulk CO<sub>2</sub> removal using MDEA and mixtures of amines, the most sensitive operating parameters include:

##### Liquid Residence Time on Tray:

Since the CO<sub>2</sub> reaction rate with MDEA is slow, the column diameter and weir height must be adjusted to give sufficient time for the reaction to occur. The usual range of weir heights are from 2"-4" resulting in residence times from about 2-5 sec.

##### Lean Amine Temperature:

Usually the only parameter available for control of the column temperature is the lean amine temperature. Since the CO<sub>2</sub> reaction with MDEA is kinetically controlled, the hotter the column the faster the reaction rate. However, once the lean amine temperature reaches about 135-140°F, the decrease in solubility of the CO<sub>2</sub> in the amine solution will usually become the overriding factor and the net CO<sub>2</sub> pickup will begin to decrease.

##### Circulation Rate:

As is the case for primary and secondary amines, when the circulation rate is increased for any given column, the CO<sub>2</sub> pickup will increase. This usually holds true for MDEA in a column of fixed diameter even though the liquid residence time on a tray will decrease with increased circulation.

##### Steam Stripping Rate:



For any given situation, as the steam stripping rate is increased, a leaner amine will be produced which will result in a higher CO<sub>2</sub> pickup.

#### Process Calculations:

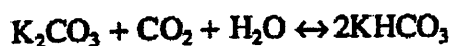
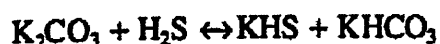
To investigate the influence of the above operating parameters on the overall unit performance, a process simulation program called TSWEET®, developed by Bryan Research & Engineering, Inc., was used. With this program, the user can draw the process flow sheet on the computer screen and enter the process operating parameters on "pop-up" forms. The program can accommodate almost any conceivable flowsheet for amine units, Claus sulfur plants and amine tailgas cleanup units, either individually or as an integrated complex. Simultaneous distillation and chemical reaction calculations are performed rigorously to model the acid gas absorption and reaction with amines. The kinetic model is used to simulate the slow reaction of CO<sub>2</sub> with amines.



### ALKALI SALTS:

The hot potassium carbonate process for removing CO<sub>2</sub> and H<sub>2</sub>S was developed by the United States Bureau of Mines and is described by Benson and co-workers in two papers (Benson et al., 1954, 1956). Although the process was developed for the removal of CO<sub>2</sub>, it can also remove H<sub>2</sub>S if H<sub>2</sub>S is present with CO<sub>2</sub>. Special designs are required for removing H<sub>2</sub>S to pipeline specifications or to reduce CO<sub>2</sub> to low levels.

The process is very similar in concept to the amine process, in that after physical absorption into the liquid, the CO<sub>2</sub> and H<sub>2</sub>S react chemically with the solution. The chemistry is relatively complex, but the overall reactions are represented by:



The process has several variations, and a simplified diagram of the single stage process is shown in Figure 17.

In a typical application, the contactor will operate at approximately 300 psig (20 barg), with the lean carbonate solution entering near 225°F (110°C) and leaving at 240°F (115°C). The rich carbonate pressure is reduced to approximately 5 psig (0.3 barg) as it enters the stripper. Approximately one third to two thirds of the absorbed CO<sub>2</sub> is released by the pressure reduction, reducing the amount of steam required for stripping (Kohl and Nielsen, 1997). The lean carbonate solution leaves the stripper at the same temperature as it enters the contactor, and eliminates the need for heat exchange between the rich and lean streams. The heat of solution for absorption of CO<sub>2</sub> in potassium carbonate is small, approximately 32 Btu/cu ft of CO<sub>2</sub> (Benson et al., 1954), and consequently the temperature rise in the contactor is small and less energy is required for regeneration. Kohl and Nielson (1997) give a thorough discussion of the process and its many modifications.

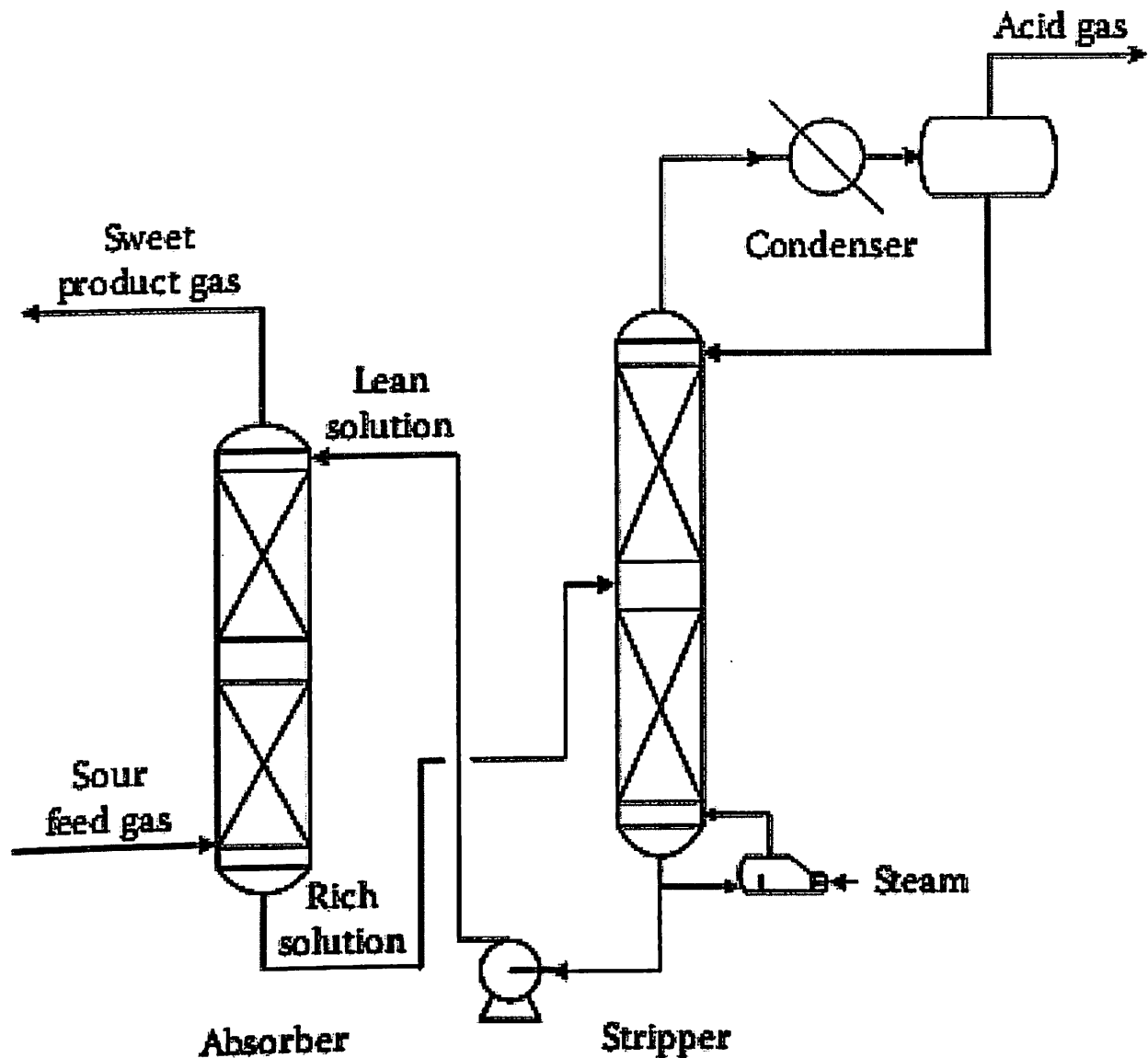


FIGURE 17: Process flow diagram for hot potassium carbonate process.

#### OPERATING ISSUES:

Since hydrogen sulfide is absorbed much more rapidly in potassium carbonate solutions than carbon dioxide, it would be expected that the process could be made at least partially selective for hydrogen sulfide. It is claimed that selective hydrogen sulfide removal can be obtained by



special design (The Benfield Corporation, 1971). Rib et al. (1982) report on the operation of a two-stage Benfield system used in a demonstration plant for selectively removing sulfur compounds from coal gas. The total acid-gas content of the gas varied from 6.4 to 17.1% CO<sub>2</sub>, 2,600 to 3,200 ppmv H<sub>2</sub>S and 106 to 216 ppmv COS. In order to obtain high selectivity the unit was operated at 85°C (185°F), and the effects of lean and semi-lean solution flow and reboiler steam rates were studied for different feed gas compositions. The results of this work showed that, under the operating conditions investigated, over 90% of the H<sub>2</sub>S and about 40% of the COS could be removed, with about 70% of the CO<sub>2</sub> retained in the product gas.

Contaminants present in gas streams in relatively small concentrations, such as carbonyl sulfide, carbon disulfide, mercaptans, thiophene, hydrogen cyanide, ammonia, and sulphur dioxide, are removed by hot potassium carbonate solution to various degrees. Parrish and Neilson (1974) report laboratory and commercial scale data obtained in purifying natural gases and gas from a pressurized Lurgi gasifier,

Carbonyl sulfide is hydrolyzed almost quantitatively to hydrogen sulfide and carbon dioxide and better than 99% removal can be achieved. Carbon disulfide is hydrolyzed in two steps- first to carbonyl sulfide and hydrogen sulfide, followed by hydrolysis of the carbonyl sulfide to hydrogen sulfide and carbon dioxide. The two-step reaction is slower than the simple hydrolysis of carbonyl sulfide with the result that only about 75 to 85% carbon disulfide removal is obtained under normal operating conditions.

Mercaptans, which are slightly acidic, react with the hot potassium carbonate solutions, forming mercaptides. Since the acidity of mercaptans decreases with their molecular weight, less complete removal of higher molecular weight mercaptans is obtained than of the lower mercaptans, i.e. methyl and ethyl mercaptan. However, the lower molecular weight mercaptans normally constitute the bulk of those present in gas streams. Removal efficiencies of upto 92% have been reported with a HiPure flow pattern. Thiophene does not react chemically with potassium carbonate, and any removal of this compound could only be attributed to physical solubility in the carbonate solution.

Ammonia is readily absorbed by potassium carbonate solutions. Sulfur dioxide and hydrogen cyanide, both acidic compounds, are also readily absorbed by hot carbonate solutions. After



absorption, these compounds react further forming a variety of compounds, such as sulfates, thiosulfates, thiocyanates, polysulfides, and elemental sulfur, which accumulate in the solution.

Typical operating data from a commercial absorber are presented in Table 5. Contact in this absorber is by means of perforated trays. Unfortunately, the number of trays is not specified so that tray efficiencies cannot be calculated from the data. However, since this has been shown to be a liquid-film controlled system, tray efficiencies would be expected to be quite low. Data reported from other installations have indicated tray efficiencies (Murphree vapor) to be on the order of 5% for absorption of CO<sub>2</sub> in hot potassium carbonate solutions.

| <b>Absorber Data</b>                                                                        | <b>1</b> | <b>2</b> | <b>3</b> | <b>4</b> | <b>5</b> |
|---------------------------------------------------------------------------------------------|----------|----------|----------|----------|----------|
| <b>Feed-gas rate, MMSCF/day</b>                                                             | 1.13     | 2.60     | 4.32     | 5.80     | 8.56     |
| <b>Lean-solution rate, gpm</b>                                                              | 95.0     | 95.9     | 95.9     | 84.2     | 117.5    |
| <b>Gas composition, percent CO<sub>2</sub>:</b>                                             |          |          |          |          |          |
| Inlet                                                                                       | 7.2      | 7.8      | 7.7      | 7.6      | 7.7      |
| Outlet                                                                                      | 0.4      | 2.0      | 3.0      | 2.7      | 4.0      |
| <b>Lean-solution characteristics:</b>                                                       |          |          |          |          |          |
| Specific gravity                                                                            | 1.23     | 1.27     | 1.26     | 1.205    | 1.275    |
| Equivalent K <sub>2</sub> CO <sub>3</sub> concentration, wt%                                |          | 28.9     | 28.0     | 30.0     | 27.7     |
| Free K <sub>2</sub> CO <sub>3</sub> concentration, wt%                                      |          | 18.5     | 16.8     |          | 16.7     |
| KHCO <sub>3</sub> concentration<br>(as equivalents of K <sub>2</sub> CO <sub>3</sub> ), wt% |          | 10.4     | 11.2     |          | 11.0     |
| CO <sub>2</sub> concentration in solution, cu ft/gal                                        |          | 3.0      | 3.3      |          | 3.2      |
| <b>Rich-solution characteristics:</b>                                                       |          |          |          |          |          |
| KHCO <sub>3</sub> concentration<br>(as equivalent K <sub>2</sub> CO <sub>3</sub> ), wt%     |          | 13.8     | 16.7     |          | 17.5     |
| CO <sub>2</sub> concentration in solution, cu ft/gal                                        |          | 4.0      | 4.8      |          | 5.1      |
| Percent of K <sub>2</sub> CO <sub>3</sub> reacted                                           |          | 47.6     | 59.5     |          | 63.1     |
| <b>Percent of inlet CO<sub>2</sub> absorbed</b>                                             | 95.0     | 68.3     | 62.7     | 68.6     | 48.5     |
| <i>Source: Buck and Leitch, 1958</i>                                                        |          |          |          |          |          |

TABLE 5: Operating data for commercial perforated-tray absorber



## REGENERATION:

As shown in Figure 18, the CO<sub>2</sub> concentration in the solution decreases rapidly with decreased partial pressure of CO<sub>2</sub> over it. Because of this, solution regeneration can be carried out most effectively at a very low pressure. Benson et al. (1956) employed 2 to 10 psig and found the 2 psig regeneration pressure more favorable. Because of the strong dependence of CO<sub>2</sub> concentration in the solution on partial pressure, an appreciable portion of the regeneration is affected when the pressure is reduced over the rich solution leaving the absorber. From one-third to two-third of the absorbed carbon dioxide is released during this flashing operation.

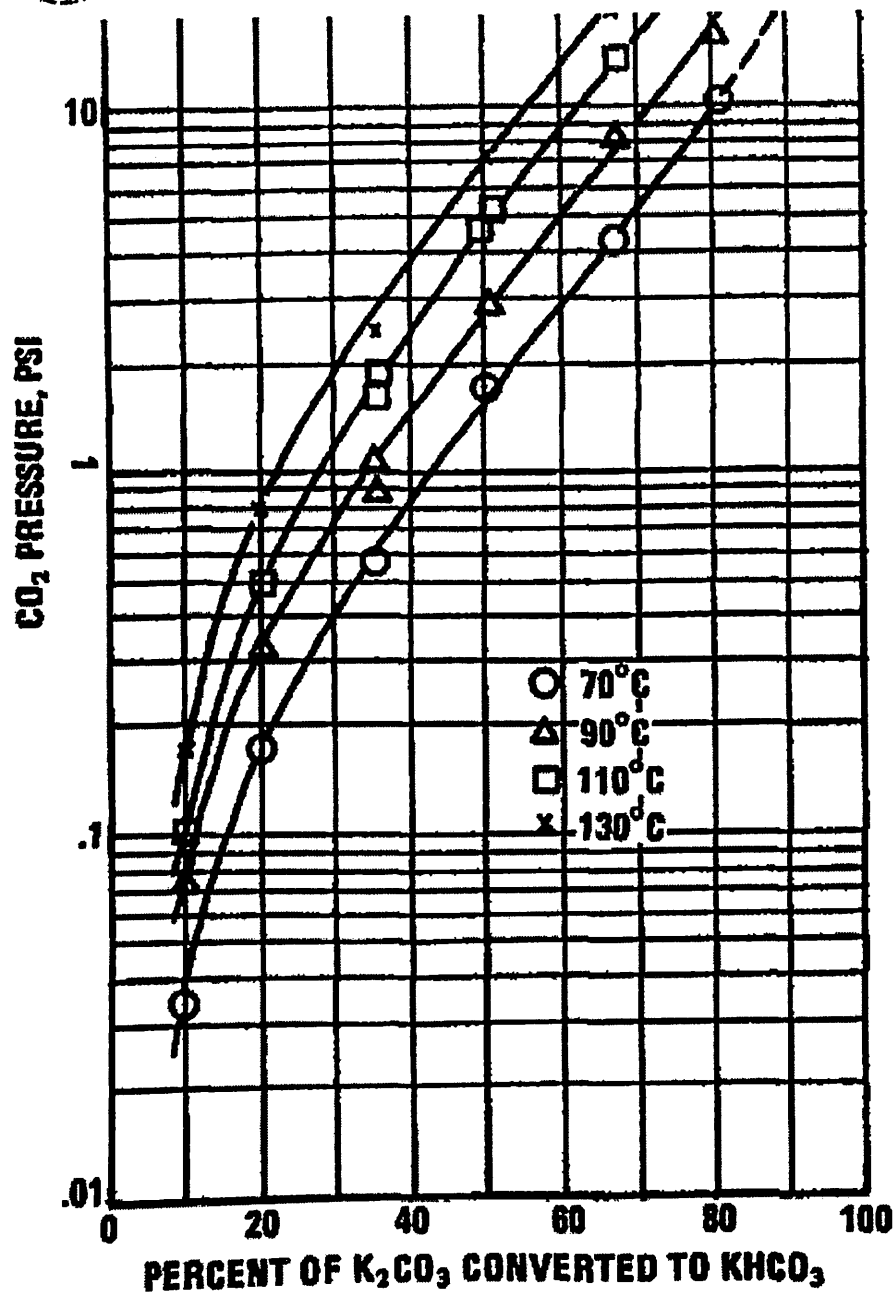


Figure 18: Equilibrium vapor pressure of  $CO_2$  over 20 percent equivalent potassium carbonate solution. (Tosh et al, 1959)

The heat of reaction of carbon dioxide with the hot potassium carbonate solution is relatively small (about 32 Btu/cu ft of  $CO_2$ ) (Benson et al., 1954), and theoretically, this heat would not need to be supplied in the regeneration step if only a simple flash were used and cooling of the



solution were allowed to occur. Since a simple flash does not give adequate regeneration, it is necessary to provide stripping vapor in the regeneration column, and this is done by evaporating water in the reboiler. Essentially all of the heat added goes to the vaporization of water, and this heat must be removed from the system in the overhead condenser of the regenerator. A small amount of additional heat must, of course, be added to make up for heat losses from vessels and lines and to provide latent heat of vaporization for any water evaporated into the gas stream in the absorber.

The effect on regeneration efficiency of altering the operation to give increased solution-carrying capacity is illustrated (Figure 19) for two product-gas purity conditions. This figure is based on operations of the U.S. Bureau of Mines pilot plant, in which the solution-capacity changes were effected by varying the degree of stripping of the lean solution. As can be seen, attempting to increase the solution-carrying capacity to more than about 4 ft<sup>3</sup> CO<sub>2</sub>/gal resulted in a decreased efficiency for both product purity conditions. Comparison of the two curves shows that operating to produce a 0.6% CO<sub>2</sub> product gas instead of a 2% CO<sub>2</sub> product results in a steam-consumption increase of about 30%. The tests illustrated were made with split-stream flow at an absorption pressure of 300 psig and with a feed gas containing 20% CO<sub>2</sub> and 80% nitrogen.

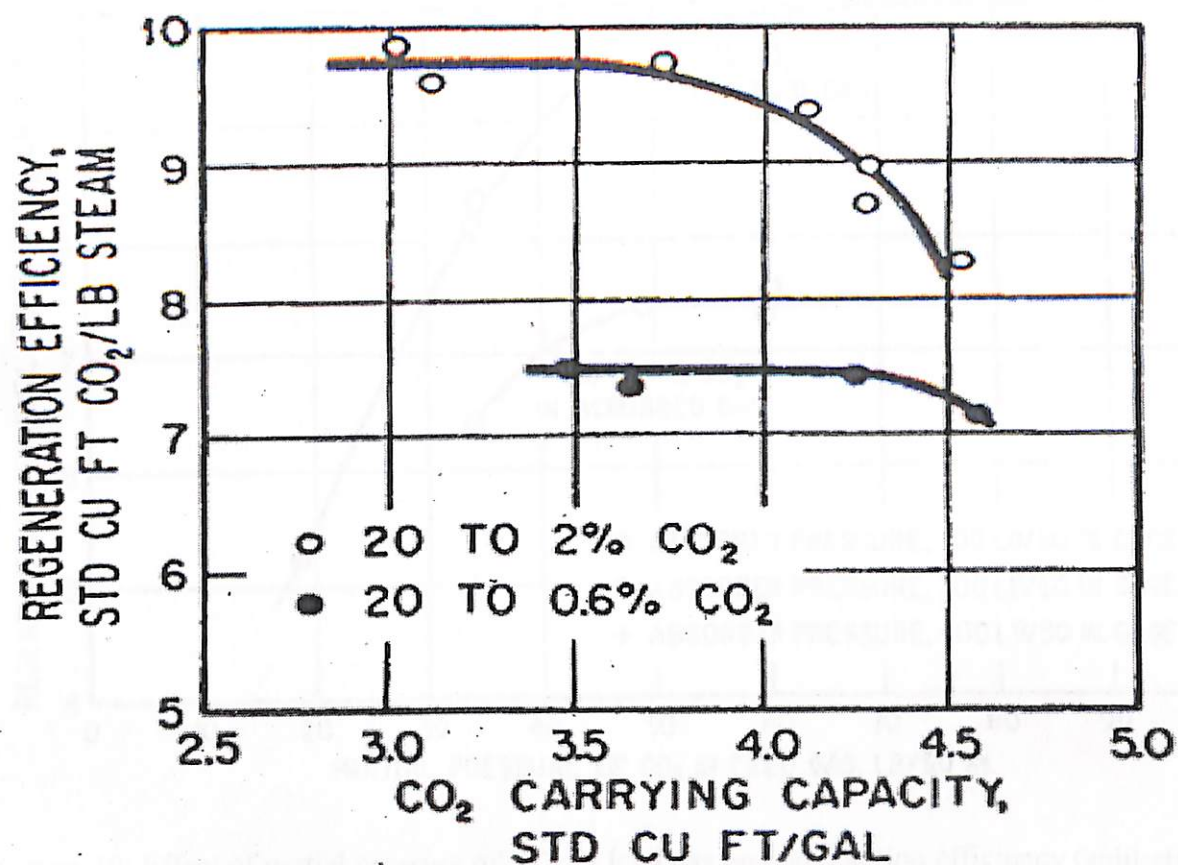


Figure 19: Effect of product gas purity and CO<sub>2</sub>-carrying capacity of solution on regeneration efficiency (split stream at 300 psig and 12,000 SCF/hr). Data of Benson et al, (1956)

Since operation of the hot potassium carbonate process is based primarily on the difference in the solubility of CO<sub>2</sub> at high partial pressure (absorber conditions) and that at low partial pressure (stripper conditions), it would be expected to be more efficient with increased CO<sub>2</sub> partial pressure in the feed gas. The magnitude of this effect for the pilot-plant operations is shown in Figure 20, which includes curves for two outlet-gas compositions.

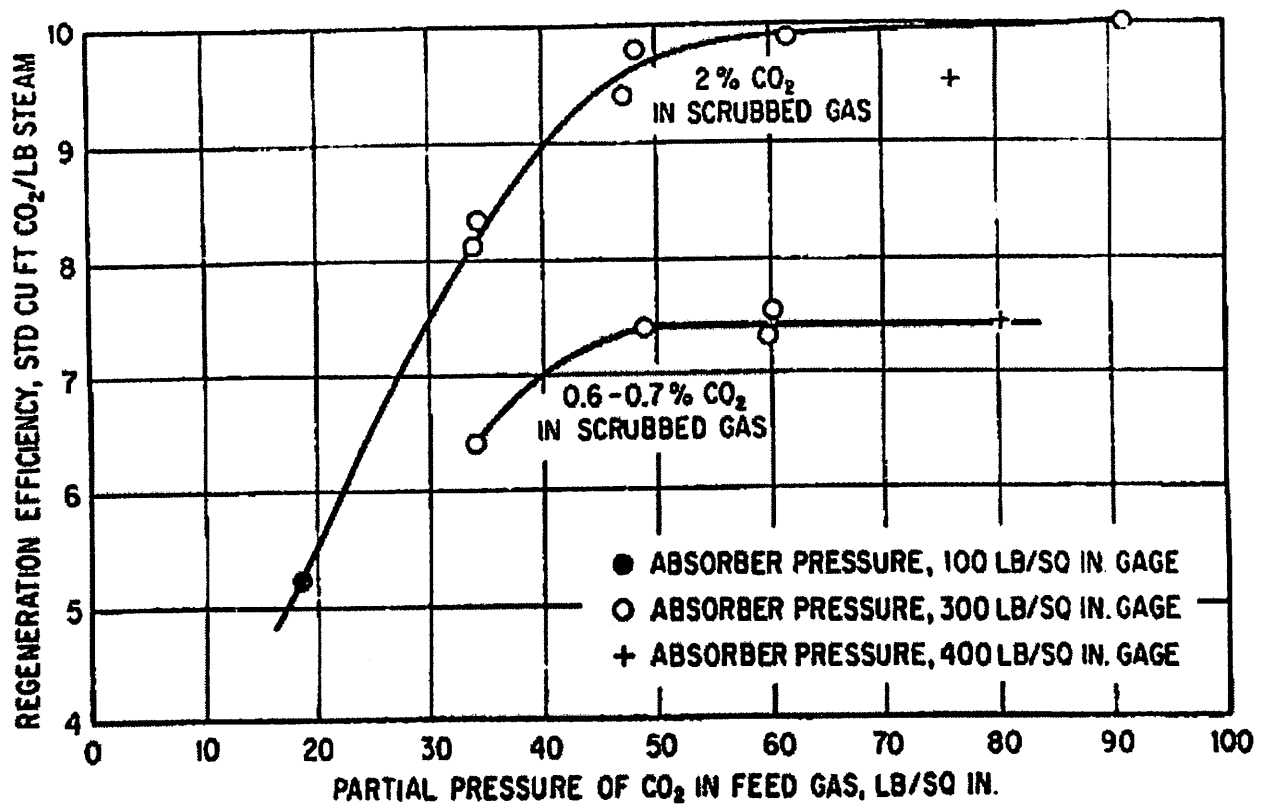


Figure 20: Effect of partial pressure of CO<sub>2</sub> in feed gas on regeneration efficiency (split-stream operation). Data of Benson et al (1956)



### PHYSICAL ABSORPTION:

In the amines salt and alkali process, acid gases are removed in two stages: physical absorption followed by a chemical reaction. In such processes as Selexol Rectisol, no chemical reaction occurs and the acid gas removal depends entirely on the physical absorption. Some of the advantages and disadvantages of physical absorption processes are summarized below:

- absorption processes are generally more effective when the partial pressures of acid gases are relatively high, because the partial pressure is the driving force for absorption.
- heavy hydrocarbons are strongly absorbed by the solvents used, and therefore the acid gas removal is more efficient than natural gas with low concentrations of heavier hydrocarbons.
- Solvents can be chosen for the selective removal of sulfur compounds, allowing  $\text{CO}_2$  to be slid into the gas streams and reduce costs of separation.
- The energy requirements for solvent regeneration are lower than in systems that involve chemical reactions.
- Separation can be performed at near room temperature.
- partial dehydration occurs with acid gas removal, while the amine process to produce a saturated water flow of product to be dried in most applications.

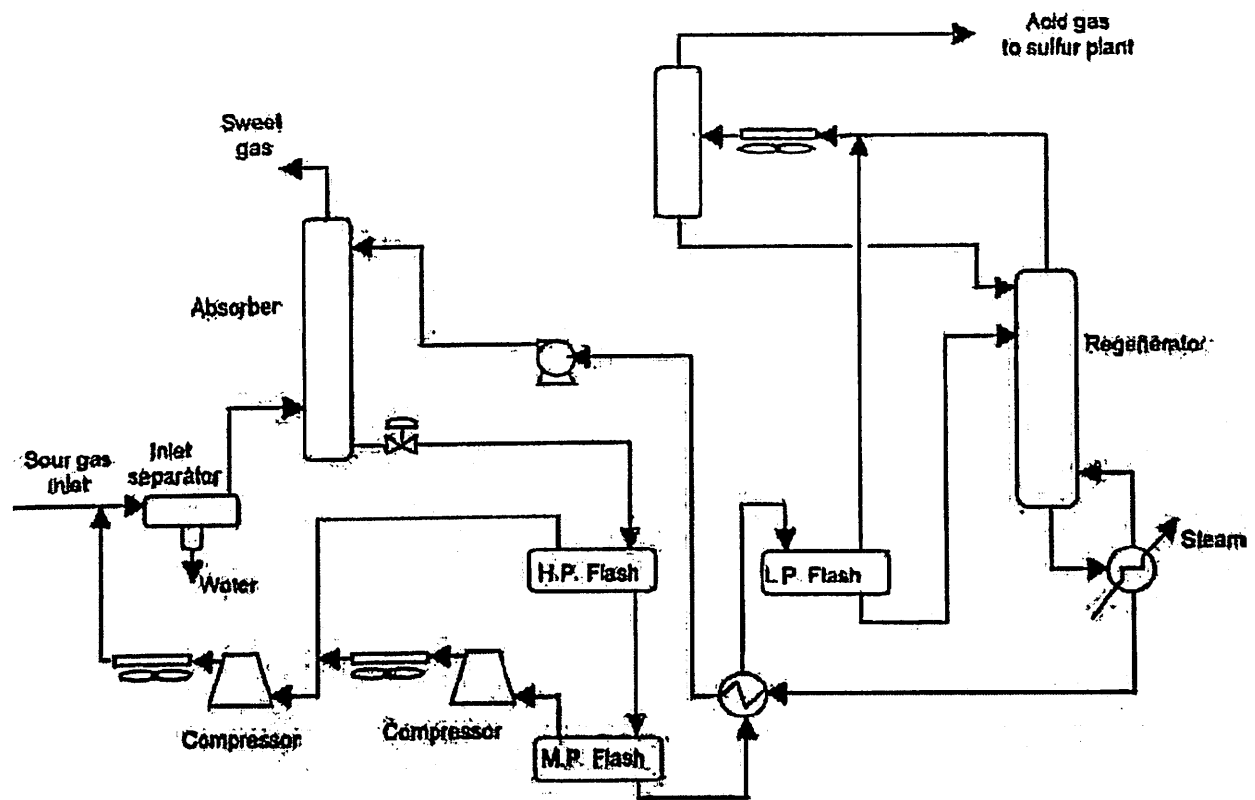


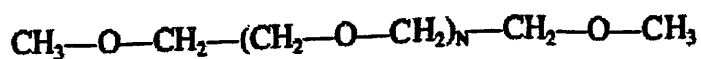
**Figure 21:** Schematic drawing of physical solvent process equipment.

### SELEXOL PROCESS:

SELEXOL is a typical application of physical absorption and a number of open literature articles describe the process. Consequently, it was selected as an example to describe the absorption process.

#### Solvent Properties:

SELEXOL is a polyethylene glycol and has the general formula:





| Component              | $R_K$ | Component                      | $R_K$ |
|------------------------|-------|--------------------------------|-------|
| $\text{CH}_4$          | 1     | $\text{H}_2\text{S}$           | 134   |
| $\text{C}_2\text{H}_6$ | 6.4   | $\text{C}_6\text{H}_{14}$      | 165   |
| $\text{CO}_2$          | 15    | $\text{CH}_3\text{SH}$         | 340   |
| $\text{C}_3\text{H}_8$ | 15.3  | $\text{C}_7\text{H}_{16}$      | 360   |
| Isobutane              | 28    | $\text{CS}_2$                  | 360   |
| n-Butane               | 35    | $\text{SO}_2$                  | 1400  |
| COS                    | 35    | $\text{C}_8\text{H}_6$         | 3800  |
| Isopentane             | 67    | $\text{C}_4\text{H}_4\text{S}$ | 8100  |
| n-Pentane              | 83    | $\text{H}_2\text{O}$           | 11000 |

$R_K = (K_{\text{CH}_4}/K_{\text{Component}})$  in Selexol<sup>®</sup> solvent for various solutes, where  $K_{\text{CH}_4} = 1$ .

Source: Sweny (1980).

TABLE 6: Typical relative ratio of K-values

Because Selexol is a mixture of homologues (the value of N in the general formula for Selexol varies), the physical properties discussed below are approximate. Table 6 (Sweny, 1980) presents  $R_K$ , the ratio of the K-value\* for methane,  $K_{\text{CH}_4}$  (arbitrarily assigned a value of 1), to the K-values of the other component,  $R_K = K_{\text{CH}_4}/K_{\text{component}}$ . Table 7 lists some physical properties of Selexol. An  $R_K$  value greater than unity indicates that the solubility of the component in Selexol is greater than that of methane, whereas a value less than unity indicates the opposite. The values should be regarded as only representative because pressure and temperature are not specified and, as previously noted, the composition of Selexol is variable.

[\* The K-value is the ratio of the mole fraction of the component in the vapor phase (y) to its mole fraction in the liquid phase (x),  $K = y/x$ . High K-values indicate the material is predominately in the vapor phase, whereas low K-values indicate a higher concentration in the liquid phase (x).]



Molar mass (approximate) = 280  
Flash point (Cleveland open cup) = 304°F (151°C)  
Freezing point\* = -8 to -20°F (-22 to -28°C)  
Vapor pressure at 25°C = <0.01 mm Hg  
Specific heat at 77°F (25°C) = 0.49 Btu/lbm °F  
= 2.0 kJ/kg K  
Density at 77°F (25°C) = 1030 kg/m<sup>3</sup> (8.60 lb/gal)  
Viscosity at 77°F (25°C) = 5.8 cp ( $5.8 \times 10^{-3}$  Ns/m<sup>2</sup>)  
Thermal conductivity at 77°F (25°C) = 0.11 Btu/(h)(ft)(°F)  
= 0.19 W/m K  
Surface tension at 77°F (25°C) = 34.3 dynes/cm  
Heat of solution at 77°F, Btu/lb of solute (kJ/kg)  
CO<sub>2</sub> = 160 (372)  
H<sub>2</sub>S = 190 (442)  
CH<sub>4</sub> = 75 (174)  
Odor = very mild  
Toxicity = nil

\* Slush appears at -8°F complete solidification at -20°F

Sources: Sweny and Valentine (1970) and Clare and Valentine (1975).

TABLE 7: Representative data properties of SELEXOL®

Because RK for CO<sub>2</sub> and H<sub>2</sub>S are 15 and 134, respectively, these gases are preferentially absorbed (compared to CH<sub>4</sub>), and therefore, physical absorption is an effective technique for removal of acid gases. The process can reduce to 4 ppmv H<sub>2</sub>S, reduce CO<sub>2</sub> emissions to levels below 50 ppmv, and essentially remove all mercaptans, CS<sub>2</sub>, COS and two other features of Table 6 are noteworthy. Because the values of RK heavier hydrocarbons as CH<sub>4</sub> are quite high (6.4 for C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> 15.3, and 35 for n-C<sub>4</sub>H<sub>10</sub>), Selexol will remove significant amounts of these hydrocarbons, a feature that may be either positive or negative, depending on the composition of the gas being processed and the desired products. Finally, the value of Rk H<sub>2</sub>O is extremely high and, therefore, provides some Selexol dehydration.

Bucklin and Schendel (1985) reported data of solubility of gas in the form of absorption coefficients (volume of gas absorbed per volume of liquid). We converted the values of certain compounds in gases absorbed scf / gal Selexol and plotted in Figure 22. The figure assumes Henry's law, which provides approximate solubility at higher pressures. The lines also ignore the



likely interaction between solutes. Epps (1994) discusses the limited solubility of hydrocarbons in the liquid (when the liquid is saturated, a second liquid hydrocarbon phase forms above the phase Selexol) and the effect of absorption of water on the solubility of hydrocarbons.

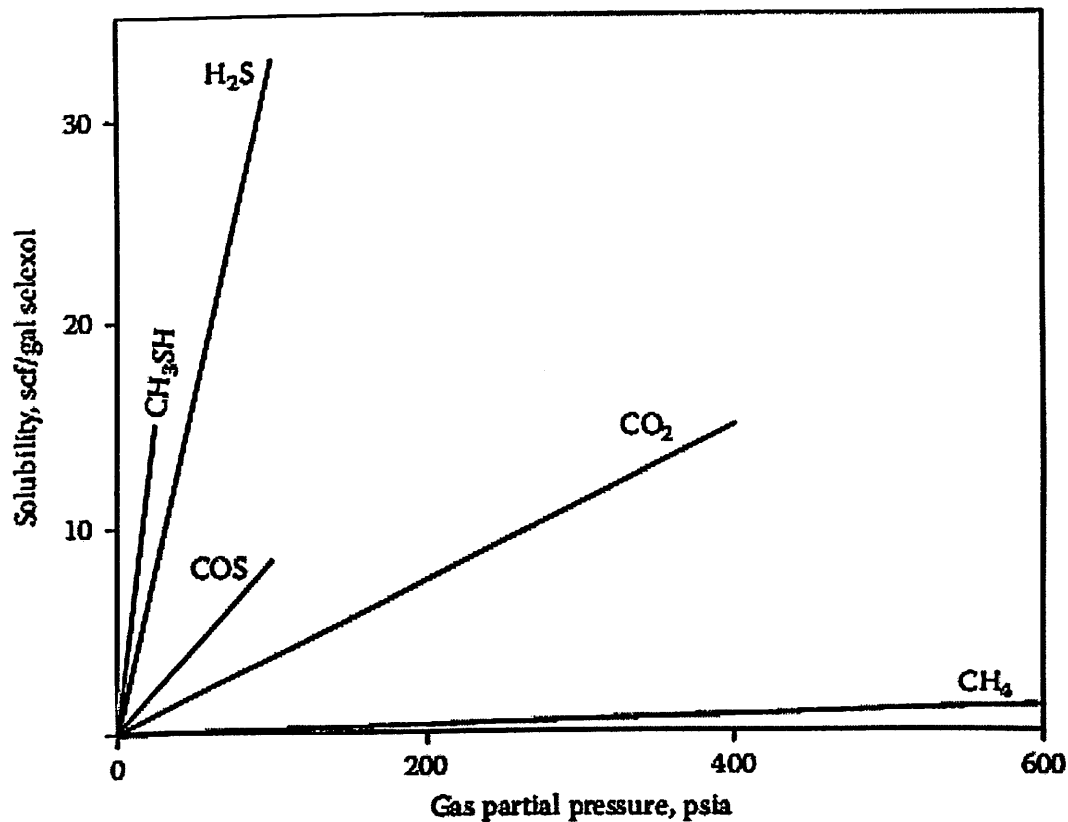


FIGURE 22: Solubility of various gases in Selexol solvent at 70°F (21°C) as a function of partial pressure. (Based on data by Sweny and Valentine, 1970)

#### Conditions Representation Process:

Selexol applications are varied and, consequently, no common process flow diagrams are available. Sweny (1980) present flow charts for nine different applications, and Epps (1994) deals with plants for natural gas dehydration and control of hydrocarbon dew point.

A plant considered by Epps (1994), identified only as a European distribution center, is shown in Figure 23. This plant has been selected for discussion because it is a modern application, and the two compositions of entry and exit of gas were reported (Table 8). The factory pre-treated to reduce the gases ethane and CO<sub>2</sub> levels of heavier hydrocarbons before the final purification of



molecular sieve and subsequent liquefaction. The plant is designed to treat 26 MMSCFD (0.74 MMSCMPD) entering the unit at 603 psia Selexol (41.6 bar) and 32 ° F (0 ° C). The poor solvent, cooled to 25 ° F (-3.9 ° C) with a propane refrigerant between the absorber where it absorbs CO<sub>2</sub> and part of the ethane and heavier hydrocarbons. The rich solvent from the absorber is regenerated by reducing pressure in three balls for relaxation, from 603 to 106 psia (from 41.6 to 7.3 bar) in the high pressure drum, from 106 to 16 psia (7.3 to 1.1 bar) in the medium-pressure drums, and from 16 to 3 psia (1.1 to 0.21 bar) in the vacuum drum. Lean Selexol the vacuum drum is recompressed and sent to the propane refrigerator. The treated gas leaving the absorber passes through a knockout drum and the filter separator to remove oil and condensed Selexol resulted. Table 8 shows that the treated gas meets the specifications of a maximum of 0.50% CO<sub>2</sub> and a maximum of 6.5% ethane and heavier hydrocarbons. In addition, the water content of the gas is reduced from 75 to 12 ppmv ppmv H<sub>2</sub>S is reduced to 2 ppmv to virtually nothing, and methyl mercaptan is reduced from 5 to 1 ppmv ppmv. Unlike amine systems, no products are generated in the irreversible process, which eliminates the need for recovery.

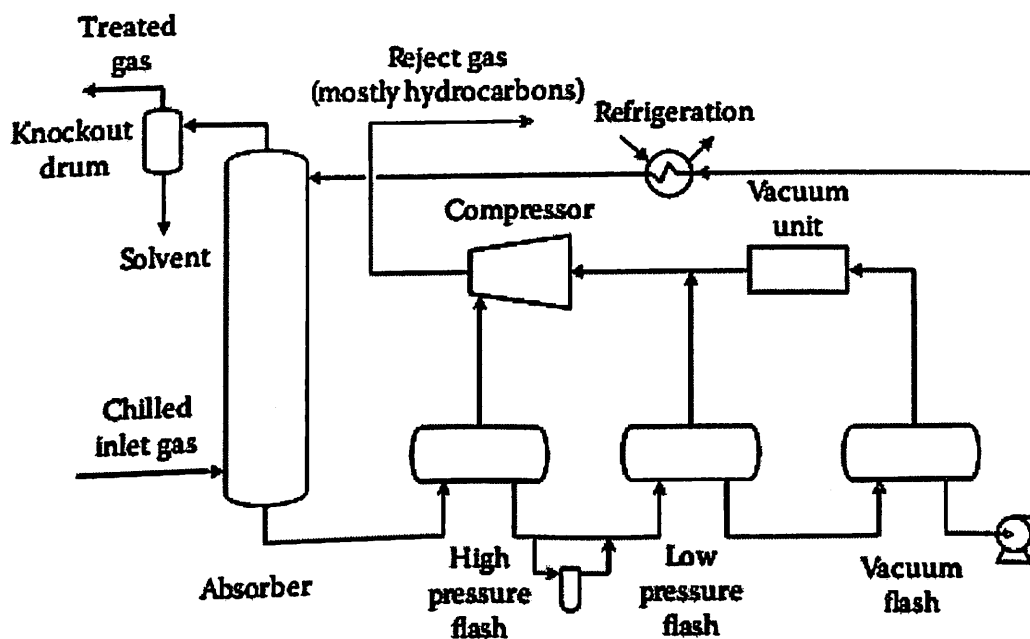


FIGURE 23: Process schematic for a Selexol gas treating facility. (Adapted from Epps, 1994)



| Component            | Gas Composition (Mol%) |         |
|----------------------|------------------------|---------|
|                      | Inlet                  | Outlet  |
| Hydrogen sulfide     | 0.0002                 | —       |
| Methyl mercaptan     | 0.00050                | 0.00012 |
| Carbon dioxide       | 2.44                   | 0.29    |
| Nitrogen             | 0.785                  | 0.88    |
| Methane              | 86.317                 | 93.02   |
| Ethane               | 7.539                  | 5.33    |
| Propane              | 2.403                  | 0.35    |
| Heavier hydrocarbons | 0.515                  | 0.130   |

Source: Epps (1994).

TABLE 8: Composition of inlet and outlet gas in a SELEXOL® unit

#### FLUOR SOLVENT TREATMENT:

The Fluor solvent process, which is authorized by Fluor Daniel, Inc., was introduced in 1960 (Kohl and Buckingham, 1960). Although several solvents were covered by patents in the United States, propylene carbonate has been used commercially only. The method was applied in 13 commercial plants processing gas natural-nine, two of ammonia synthesis gas and two hydrogen.

#### Background:

Some physical properties of propylene carbonate are tabulated in Tables 9 and 10. Data on the solubility of various gases in propylene carbonate have been reported by several researchers (Dow Chemical Company, 1962; Schmack and Bittrich, 1966; Makranczy et al, 1965; Bucklin and Schendel, 1985). The equilibrium solubility of hydrogen sulfide and carbon dioxide as a function of pressure are shown in Figure 24. Although there is some dispersion of points, it is evident that the solubility of acid gases both follow Henry's law up to a pressure of about 20



hours. The effect of temperature is shown for carbon dioxide and hydrogen in Figure 25. It is interesting to note that the solubility of hydrogen increases with temperature.

| Process Solvent                                                        | Selexol<br>(DMPEG)    | Purisol<br>(NMP)    | Fluor<br>Solvent<br>(PC) | Rectisol<br>(Methanol) |
|------------------------------------------------------------------------|-----------------------|---------------------|--------------------------|------------------------|
| Vapor Pressure, mm Hg @ 25°C                                           | $.073 \times 10^{-2}$ | $40 \times 10^{-2}$ | $8.5 \times 10^{-2}$     | —                      |
| Viscosity, cp @ 25°C                                                   | 5.8                   | 1.65                | 3.0                      | 0.6                    |
| Maximum feasible operating<br>temperature, °C                          | 175                   | —                   | 65                       | —                      |
| Density, kg/m <sup>3</sup> @ 25°C                                      | 1,030                 | 1,027               | 1,195                    | 785                    |
| Boiling point, °C                                                      | 240                   | 202                 | 240                      | 65                     |
| Freezing point, °C                                                     | -28                   | -24                 | -48                      | -92                    |
| Molecular weight                                                       | 280                   | 99                  | 102                      | 32                     |
| Specific heat @ 25°C,<br>Btu/(lb)(°F)                                  | 0.49                  | 0.40                | 0.339                    | 0.556                  |
| Thermal conductivity,<br>Btu/(hr)(ft <sup>2</sup> )(°F/ft)             | 0.11                  | 0.095               | 0.12                     | 0.122                  |
| <i>Data from Bucklin and Schendel (1985) and Ranke and Mohr (1985)</i> |                       |                     |                          |                        |

Table 9: Solvents Comparative Data

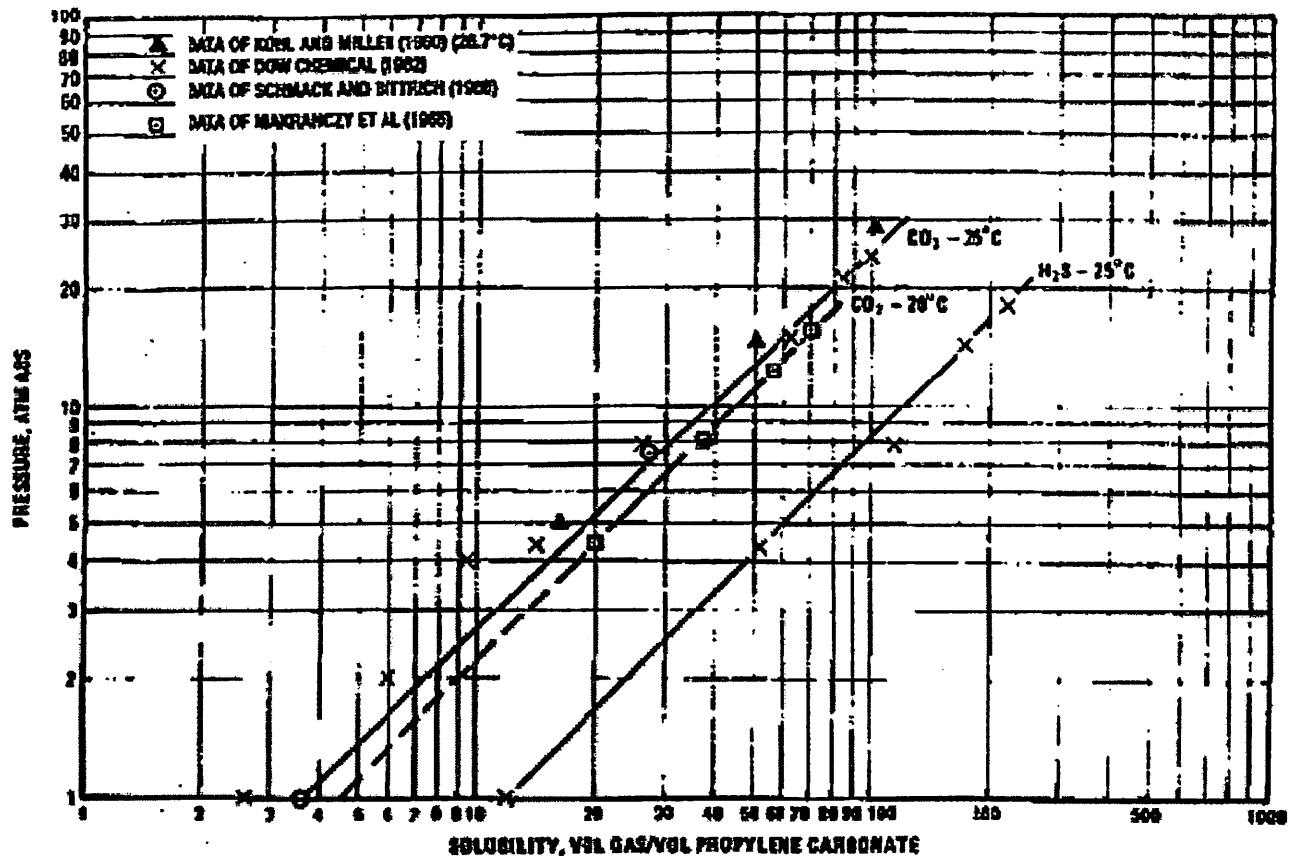


Figure 24: Effect of pressure on the solubility of carbon dioxide and hydrogen sulfide in propylene carbonate (gas volumes at 0°C and 760 mm Hg)

**Empirical formula**

$C_4H_6O_3$

**Molecular weight**

102.09

**Vapor Pressure at 60°F**

0.046 mm Hg

**Viscosity at 60°F  
at 0°F**

2.6 centistokes

6.4 centistokes

**Water Solubility in Solvent @ 25°C**

94 g/l

**Solvent solubility in  
water @ 25°C**

236 g/l

**CO<sub>2</sub> solubility in  
solvent @ 25°C, 1 atm**

0.455 R<sup>3</sup>/US gal

**Sources:** Dow Chemical Canada, Ltd. (1962); Fluor Daniel (1993); Bucklin and Schendel (1985)

Table 10: Physical Properties of Propylene Carbonate

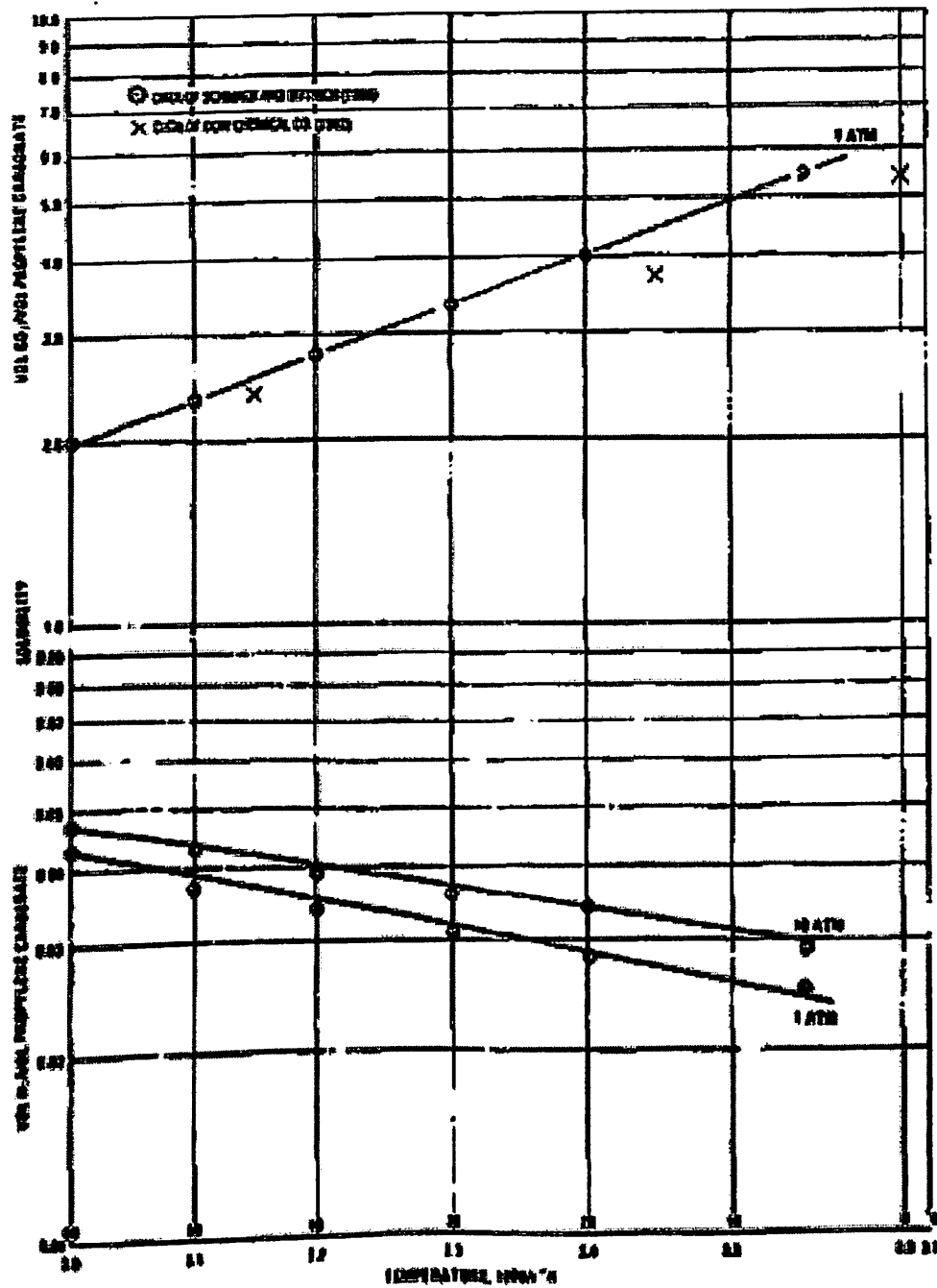


Figure 25: Effect of temperature on the solubility of hydrogen and carbon dioxide in propylene carbonate (gas volumes at 0°C and 760 mm Hg).



No data seem to be available in the literature on the specific effects of dissolved carbon dioxide, hydrogen sulfide and other gases on the solubility of individual components. However, fragmentary information on gas mixtures containing carbon dioxide and methane indicates that at high partial pressures of methane on the solubility of carbon dioxide is slightly reduced, whereas the solubility of methane is significantly enhanced by the presence of dissolved carbon dioxide (Dow, 1962; Makranczy et al, 1965) .. Given the low solubility of hydrogen in propylene carbonate, it is reasonable to assume that its presence does not significantly affect the solubility of carbon dioxide or hydrogen sulfide. Additional solubility data are included in Table 11.

| <b>Gas</b>         | <b>Selexol<br/>(DMPEG)</b> | <b>Purisol<br/>(NMP)</b> | <b>Fluor Solvent<br/>(Propylene Carbonate)</b> |
|--------------------|----------------------------|--------------------------|------------------------------------------------|
| H <sub>2</sub>     | 0.047                      | 0.020                    | 0.027                                          |
| N <sub>2</sub>     | —                          | —                        | 0.029                                          |
| CO                 | 0.10                       | 0.075                    | 0.072                                          |
| C <sub>1</sub>     | 0.24                       | 0.26                     | 0.13                                           |
| C <sub>2</sub>     | 1.52                       | 1.36                     | 0.58                                           |
| CO <sub>2</sub>    | 3.63                       | 3.57                     | 3.41                                           |
| C <sub>3</sub>     | 3.70                       | 3.82                     | 1.74                                           |
| iC <sub>4</sub>    | 6.79                       | 7.89                     | 3.85                                           |
| nC <sub>4</sub>    | 8.46                       | 12.4                     | 5.97                                           |
| COS                | 8.46                       | 9.73                     | 6.41                                           |
| iC <sub>5</sub>    | 16.2                       | —                        | 11.9                                           |
| NH <sub>3</sub>    | 17.7                       | —                        | —                                              |
| nC <sub>5</sub>    | 20.1                       | —                        | 17.0                                           |
| H <sub>2</sub> S   | 32.4                       | 36.4                     | 11.2                                           |
| nC <sub>6</sub>    | 39.9                       | —                        | 46.0                                           |
| CH <sub>3</sub> SH | 82.4                       | 121                      | 92.7                                           |

*Data from Bucklin and Schendel (1985)*

Table 11: Gas Solubility Data for Selexol, Purisol, and Fluor Solvent Process Absorbents.  
Volume Gas/Volume Liquid at 25°C and 1 atm

Process Design And Operation:



The process uses the solvent regeneration Fluor flash. Commercial plants using several flashes of rich solvent to lower pressure levels with recycling of gases from the flash at high pressure. Lean solvent temperature as low as 0 ° F were used in this process. A modification of the process resulting in a significant reduction in the loss of hydrocarbon gases has been described by Freireich and Tennyson (1977). In this scheme, the gas from the intermediate pressure second flash is washed with solvent in a small canister. The overhead of this absorber is recompressed and recycled to the entry of plants. It is claimed that the value of recovered gas offsets the cost of additional equipment, and a payment as low as three months is made with a fuel cost of \$ 2 per MMBTU.

The process works Fluor solvent in the commercial plant was originally described by Buckingham (1961). This author has also provided performance data for four processing plants Natural Gas (Buckingham, 1964). Data from these plants are given in Table 12.

| Plant | Design feed gas rate<br>MMscfd | Feed gas composition |                  | Absorption pressure, psig | Acid gas partial pressure in feed, psia     | Sales gas specification |                  |
|-------|--------------------------------|----------------------|------------------|---------------------------|---------------------------------------------|-------------------------|------------------|
|       |                                | CO <sub>2</sub>      | H <sub>2</sub> S |                           |                                             | CO <sub>2</sub>         | H <sub>2</sub> S |
| A     | 220                            | 53%                  | 3 gr/100 scf     | 850                       | CO <sub>2</sub> : 458                       | 2%                      | 0.25 gr/100 scf  |
| B     | 10                             | 17%                  | —                | 450                       | CO <sub>2</sub> : 79                        | 5%                      | —                |
| C     | 20                             | 22.8%                | —                | 800                       | CO <sub>2</sub> : 186                       | 1%                      | —                |
| D     | 28                             | 10-30%               | 5-15%            | 1,000                     | CO <sub>2</sub> + H <sub>2</sub> S: 250-300 | 0.1%                    | 0.8 gr/100 scf   |

Source: Buckingham (1964)

TABLE 12: Operating Data of Fluor Solvent Process Plant.

An economic study comparing the Fluor solvent process in hot potassium carbonate process enabled the elimination of carbon dioxide from synthesis gas to produce ammonia and urea has been reported by Cook and Tennyson (1969). The authors concluded that the process is cheaper than potassium carbonate heat activated in all cases studied, which included production of ammonia and urea by steam reforming of natural gas and naphtha and partial oxidation. A comparison of Fluor solvent other physical solvent (Bucklin and Schendel, 1985) shows that for cases where the requirements for disposal of CO<sub>2</sub> dictate the design of the plant, ie, where



little or no  $H_2S$  is present, the Fluor solvent process has a significant advantage over the other processes due to the low solubility of purified gas, light hydrocarbons in the case of natural gas and  $H_2$  gas in the case of synthesis. This advantage translates into either a hydrocarbon percent or more hydrogen recovery or demands for lower compression of the gas flashed rich solvent at intermediate pressures.



## CHAPTER 5

### WATER AS AN ABSORBENT FOR CO<sub>2</sub> REMOVAL

The main advantage of water as an absorbent for the impurities of the gas is, of course, its availability at low cost. This factor alone is enough to make use of water to consider the elimination of impurities from gases that are reasonably soluble. Water is particularly applicable to processing large volumes of low-pressure exhaust gas to the prevention of air pollution because solvent losses are difficult to avoid in such facilities. Organic solvents, in general, a vapor pressure sufficient to cause the occurrence of losses by vaporization in the purified gas stream. Virtually all chemicals other than water absorbent requires a sealed system and unless a reaction product formed is salable, a regeneration cycle. Water, on the other hand, can be used in units of simple washing with less fear of a flow and often on a single pass with the rich solution being discarded.

Water may also be applicable to the gas cleaning at high pressure where the solubility of an impurity (such as CO<sub>2</sub>), which is poorly soluble at low pressure, is increased to a high economic level by the high partial pressure CO<sub>2</sub>.

The absorption of carbon dioxide in water at high pressure was once an important industrial processes, particularly for the purification of synthesis gas for ammonia production. The process has generally been replaced by more efficient systems that use chemical solvents or physical capacity with much higher carbon dioxide than water. A description of the process of water washing for removal of carbon dioxide is included in this chapter because of its historical significance, its value as a standard operation technique of liquid film controlled, and the hope that the important work the process will be useful in developing new processes or applications. A diagram of a simple process water washing for removal of carbon dioxide is shown in Figure 26. In its simplest form, the installation consists of nothing more than an absorption tower operating at high pressure, an expansion chamber where the CO<sub>2</sub> is released from the water after pressure reduction, and a pump to return water to the top of the absorber. In the diagram shown, a power recovery turbine was added to recover some of the available power from the pressure reduction and subsequent expansion of the liquid gas absorbed, and a degassing tower allows for more complete elimination of Emissions of CO<sub>2</sub> from the water that could be obtained with a single flash. In one such arrangement, it is possible to operate the decompression chamber at an



intermediate pressure and get her a gas rich enough in fuel elements for use as fuel gas with low Btu. Alternatively, the gas tank pressure relief means may be recompressed and returned to the entrance of the absorber.

In general, the process is limited to gas streams containing carbon dioxide at a partial pressure greater than about 50 psia to provide a capacity of carbon dioxide economically valuable water solvent. For ammonia plants, this in effect limits the absorption process pressures of about 200 psig, as the ammonia synthesis gas streams typically contain about 25% CO<sub>2</sub>.

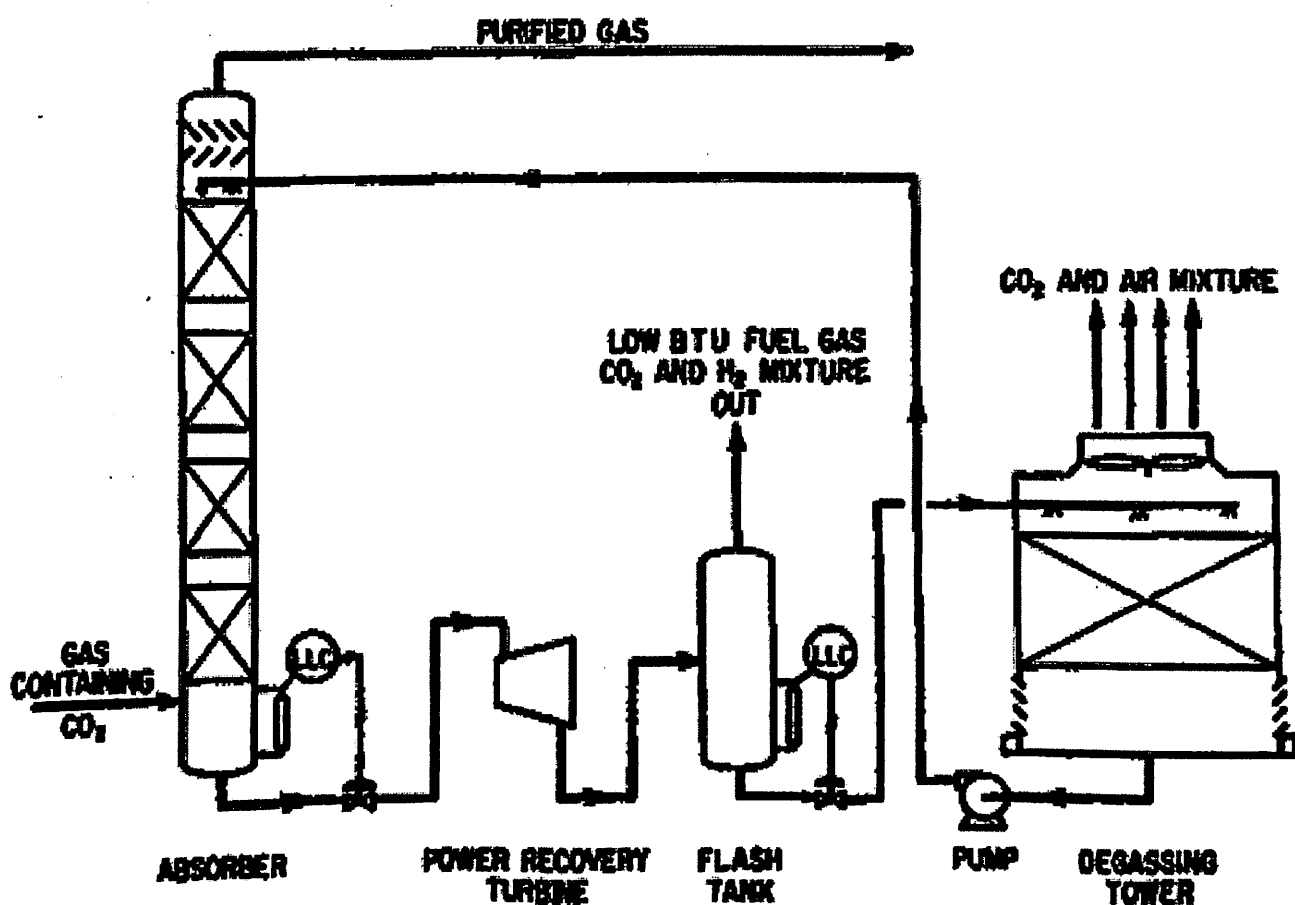


Figure 26: Simplified flow diagram of process for absorption of carbon dioxide from gas streams with water.

The use of water as an absorbent offers the following advantages as compared, for example, to monoethanolamine solutions:



- i) Simple plant design (no heat exchangers or reboilers)
- ii) No heat load
- iii) Inexpensive solvent
- iv) Solvent not reactive with COS, O<sub>2</sub>, and other possible trace constituents.
- v) No nitrogenous solvent vapors introduced into the gas stream.

The principal disadvantages of the water-wash process are:

- i) Substantial loss of hydrogen or other valuable constituents of the gas stream.
- ii) Very high pumping load
- iii) Poor CO<sub>2</sub>-removal efficiency
- iv) Impure by-product CO<sub>2</sub>.

#### BASIC DATA:

The solubility of carbon dioxide in water, considered as a function of pressure and temperature, is presented in Figures 27 and 28, which are based upon the compilation of Dodds et al.(1956). Figure 27, which covers pressures from 1 to 700 atm, represents smooth curves of the data from numerous investigators. Figure 28, which covers primarily the region of sub-atmospheric pressures, is based entirely on the data of Morgan and Maass (1931) and the experimental points are therefore shown.

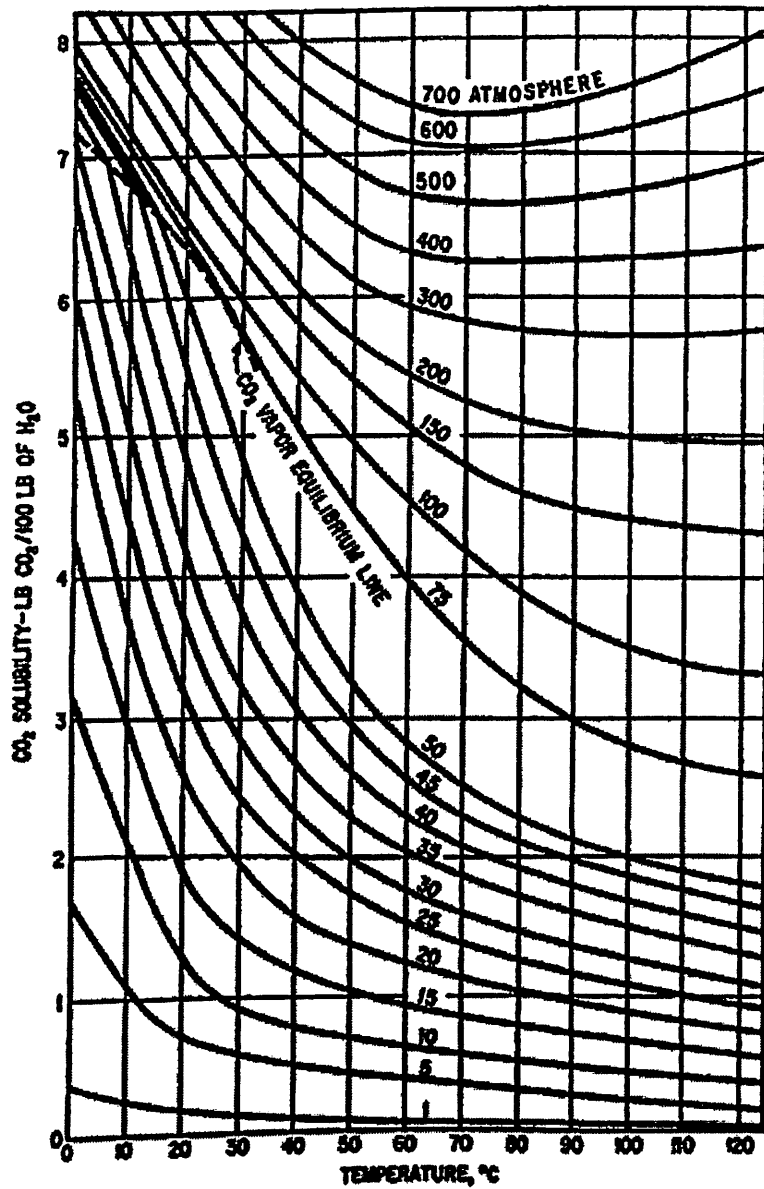


FIGURE 27: Solubility of CO<sub>2</sub> in Water at pressure of 1 atm and greater.( From Dodds et al, 1956).

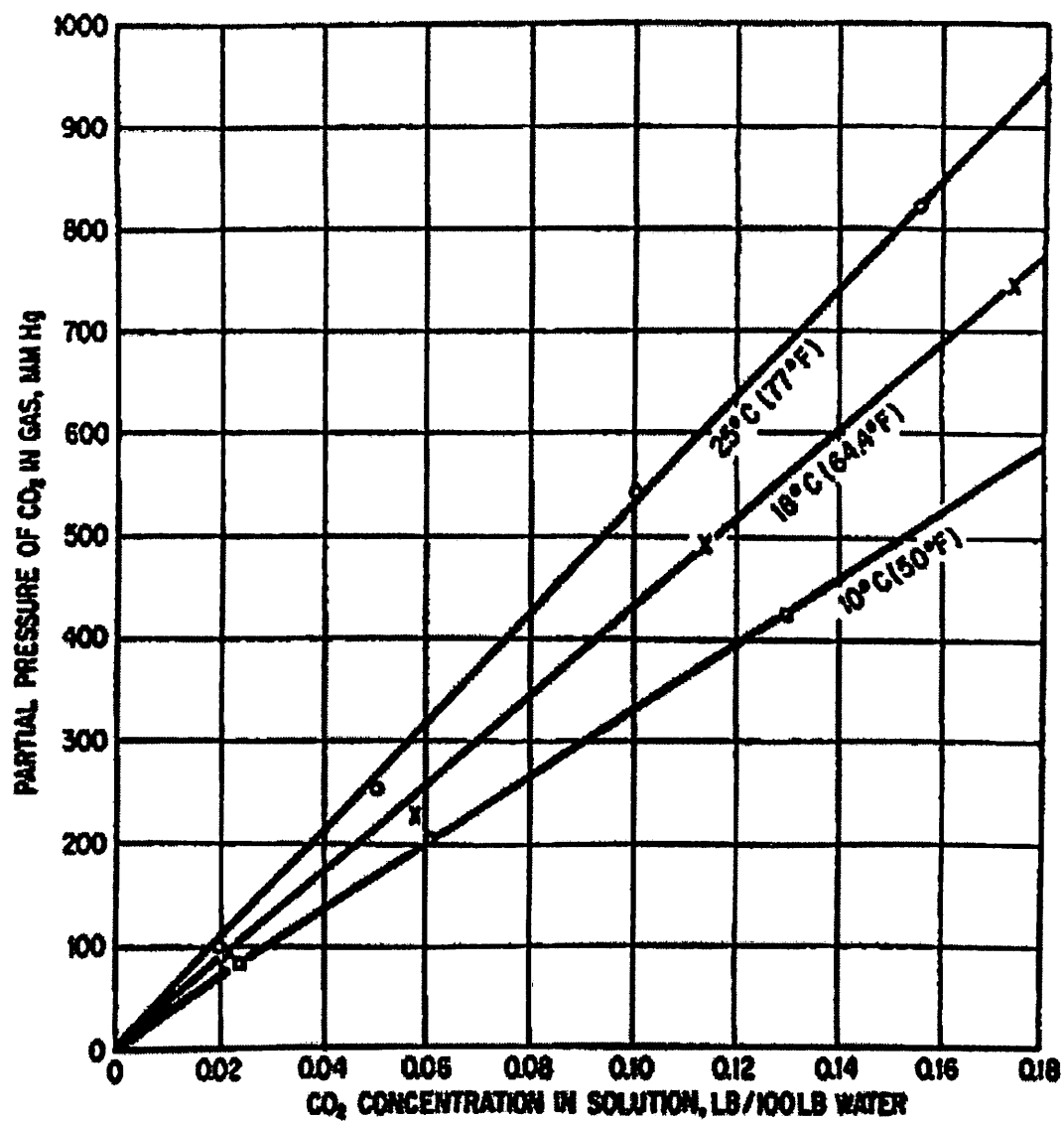


Figure 28: Solubility of carbon dioxide in water at low pressure. Data of Morgan and Maass (1933)



## CRYOGENIC FRACTIONATION:

Distillation is the most widely used process to separate liquid mixtures, and at first glance it seems a good prospect for removing  $\text{CO}_2$  and  $\text{H}_2\text{S}$  from natural gas, because the vapor pressures of the principal components are considerably different (Figure 29). However, problems are associated with the separation of  $\text{CO}_2$  from methane,  $\text{CO}_2$  from ethane, and  $\text{CO}_2$  from  $\text{H}_2\text{S}$ . These difficulties are summarized below (Engineering Data Book, 2004 b).

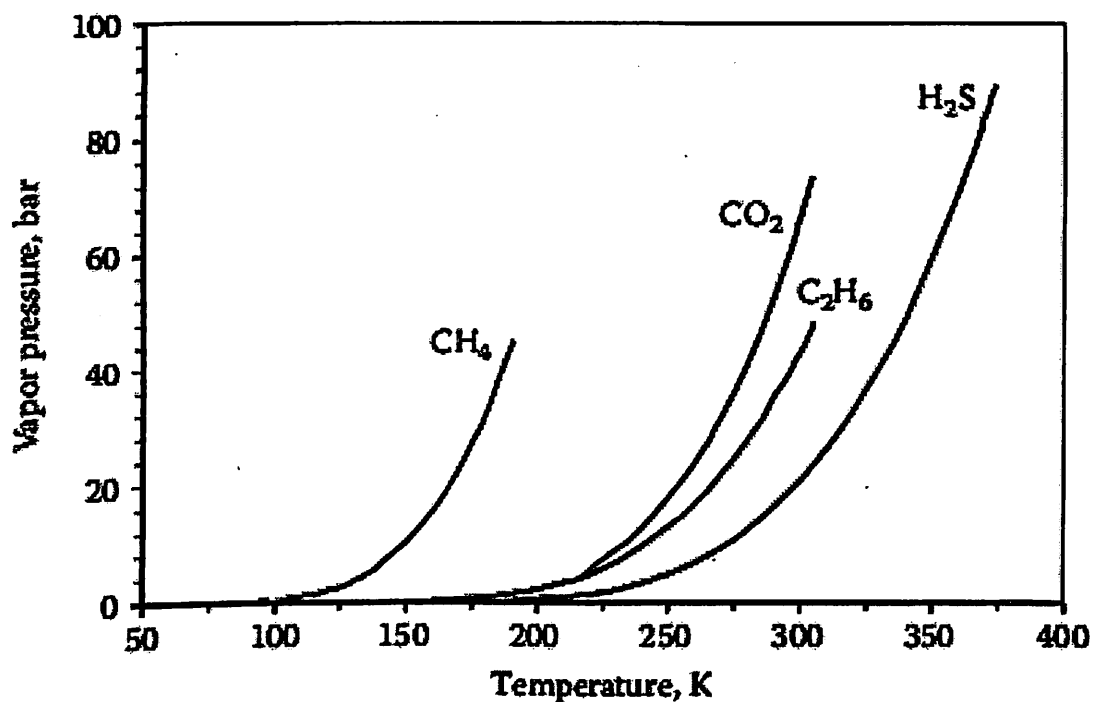


FIGURE 29: Vapor pressure of light natural gas components (NIST, 2005)

$\text{CO}_2$  from methane: Relative volatilities ( $K_{\text{C1}}/K_{\text{CO}_2}$ ) at typical distillation conditions are about 5 to 1. Therefore one would expect simple fractionation to work. However, because the liquid  $\text{CO}_2$  phase freezes when it becomes concentrated, the practical maximum-vapor concentration of methane is only 85 to 90 mol%.



CO<sub>2</sub> from ethane: In addition to solidification problems, CO<sub>2</sub> and ethane form an azeotrope (liquid and vapor compositions are equal) and consequently, a complete separation of these two by simple distillation is impossible. Fig. 30 shows an isotherm at -64°F (-53°C) for the system, and the azeotrope appears at approximately 0.6 mole fraction of CO<sub>2</sub>.

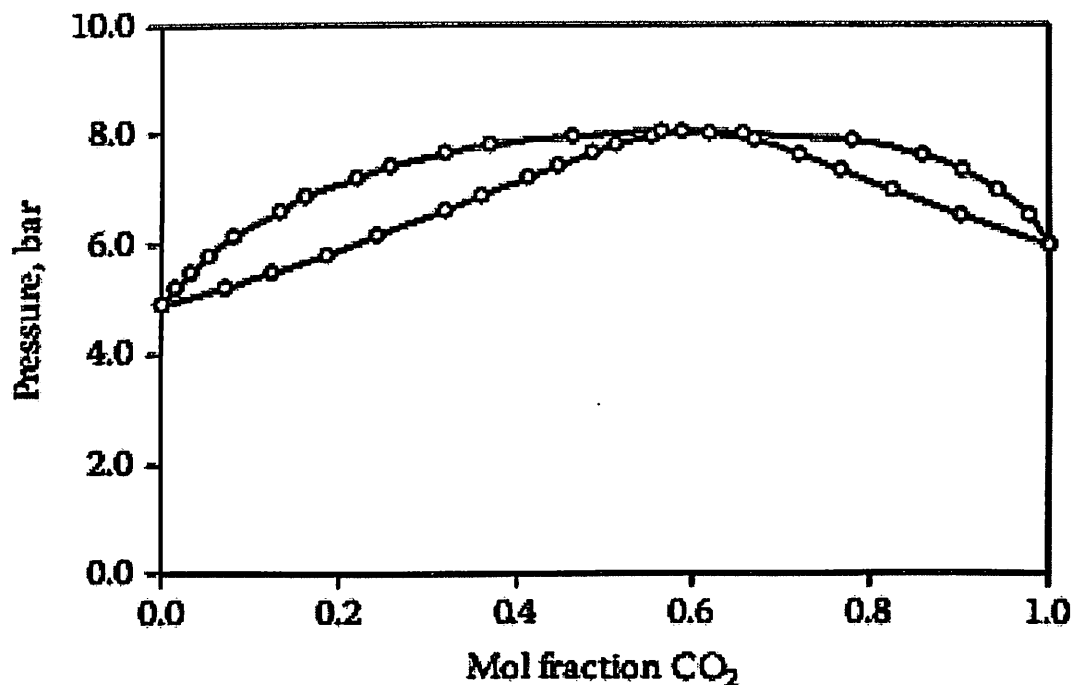


FIGURE 30: Vapor-liquid equilibrium curve for CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> at -64°F (-53°C). Azeotropic composition is 0.60 mol fraction CO<sub>2</sub>. (Data from Brown et al., 1988.)

CO<sub>2</sub> from H<sub>2</sub>S: This distillation is difficult because, as Fig. 31 shows the mixture forms a pinch at high CO<sub>2</sub> concentrations. This separation by conventional distillation is complicated by the need to have an overhead product that has roughly 100 ppmv H<sub>2</sub>S if the stream is vented. The bottoms product should contain less than two-thirds CO<sub>2</sub>, assuming the stream is feed to a Claus unit.

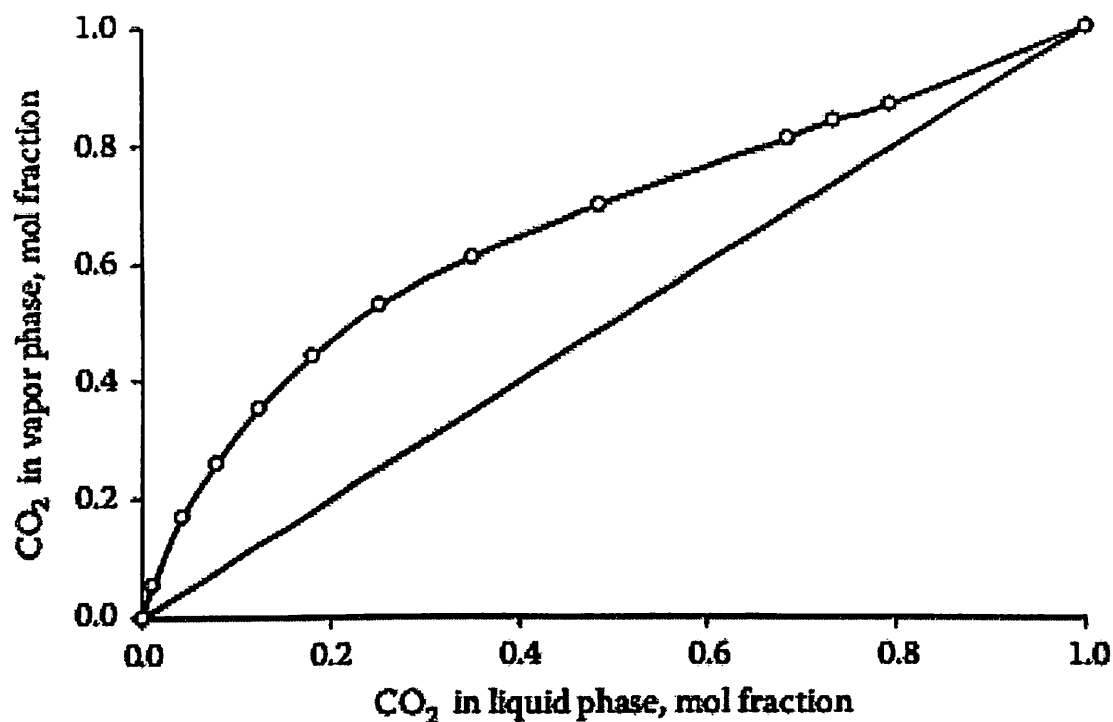


FIGURE 31: Vapor-liquid equilibrium curve for CO<sub>2</sub> and H<sub>2</sub>S at 20 atm. (Data from Bierlein and Kay, 1953.)

A number of techniques are available for solving these problems, but the Ryan/Holmes process (Holmes et al., 1982) is probably the most widely used.

This process is an extractive distillation process that uses hydrocarbons to significantly alter the behavior of the system and thus, effectively eliminate the distillation problems. The hydrocarbons are normally mixtures of propane and heavier hydrocarbons obtained from the feed mixture. As a result, no additional separations are required.



## MEMBRANES

The membranes are used in the processing of natural gas for dehydration, fuel gas conditioning, and bulk removal of CO<sub>2</sub>, but at present the removal of CO<sub>2</sub> is by far the most important application. We first present the basic principles of membrane separation and then discuss their application to the removal of CO<sub>2</sub>.

## FUNDAMENTAL OF MEMBRANE:

Of thermodynamics, the driving force for movement across the membrane is the chemical potential difference,  $\mu$ , for a given component on both sides of the membrane. If the index  $i$  is the diffusing component, then:

$$\mu_{i,feed} > \mu_{i,permeate}$$

where the material is moving from feed side to the permeate side. To make the equation physically comprehensible in gas systems, fugacity,  $f$ , which is proportional to the chemical potential is used and gives:

$$f_{i,feed} > f_{i,permeate}$$

If ideal behavior is assumed for the diffusing gas, then the fugacities can be replaced by the partial pressures and

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

where  $y$  is the mole fraction and  $P$  is the total pressure. This equation shows what terms affect the driving force across the membrane. The equation can be rearranged to obtain

$$\left( \frac{y_{i,permeate}}{y_{i,feed}} \right) \leq \left( \frac{P_{feed}}{P_{permeate}} \right)$$

This relation tells us that the separation achieved  $(y_{i,permeate}/y_{i,feed})$  can never exceed the pressure ratio  $(P_{feed}/P_{permeate})$ .

Because the discussion above was based on classical thermodynamics, it tells us nothing about the rate at which the diffusion processes take place. A discussion of diffusion rate requires use of



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

$$J_i = (S_i D_i p_i)/L$$

where  $J$  is the flux of component  $i$ , that is, the molar flow of component  $i$  through the membrane per unit area of membrane,  $S_i$  is the solubility term,  $D_i$  is the diffusion coefficient,  $\Delta p_i$  is the partial pressure difference across the membrane, and  $L$  is the thickness of the membrane. Customarily,  $S_i$  and  $D_i$  are combined into a single term, the permeability,  $P_i$ , and thus divides Fick's law into two parts,  $P_i/L$ , which is membrane dependent and  $\Delta p_i$ , which is process dependent. Note that  $P_i/L$  is not only dependent on the membrane but also dependent on operating conditions, because  $S_i$  and  $D_i$  depend on both temperature and pressure.  $P_i$  also depends weakly upon the composition of the gases present.

All the mixture components have a finite permeability, and the separation is based upon differences in them. Customarily, selectivity  $\alpha$ , is used, which is the ratio of two permeabilities,  $P_1/P_2$ , a term important in process design and evaluation. An  $\alpha$  of 20 for  $\text{CO}_2/\text{CH}_4$  means that  $\text{CO}_2$  moves through the membrane 20 times faster than does methane.

#### Carbon Dioxide Removal:

Many different types of membranes have been developed or are under development for industrial separation (Echt et al, 2002; Baker, 2002), but for the removal of  $\text{CO}_2$ , the industry standard is currently in acetate cellulose. These membranes are the type of solution-diffusion, in which a thin (0.1 to 0.5  $\mu\text{m}$ ) cellulose acetate is above a thick layer of a porous support material. Permeable compounds dissolve in the membrane, diffuse through it, then travel through the material support inactive. The membranes are thin to maximize the mass transfer and thus to minimize the area and cost, so that the support layer is necessary to provide the necessary mechanical strength.

Configurations of commercial membranes are either hollow fiber members or flat sheets wrapped in spiral wound elements. Currently, approximately 80% of gas separation membranes are formed in hollow fiber modules (Baker, 2002), like those in Figure 32. The low pressure bore starting configuration is a configuration against the tide like a heat exchanger shell-tube with the



inlet gas on the side of the tube. It has the advantage of being more resistant to fouling because the inlet gas flows through the inside of the hollow fibers. However, the strength of the membrane limits the pressure drop across the membrane. The configuration is only used in low pressure applications such as air separation and dehydration of air (Baker, 2002).

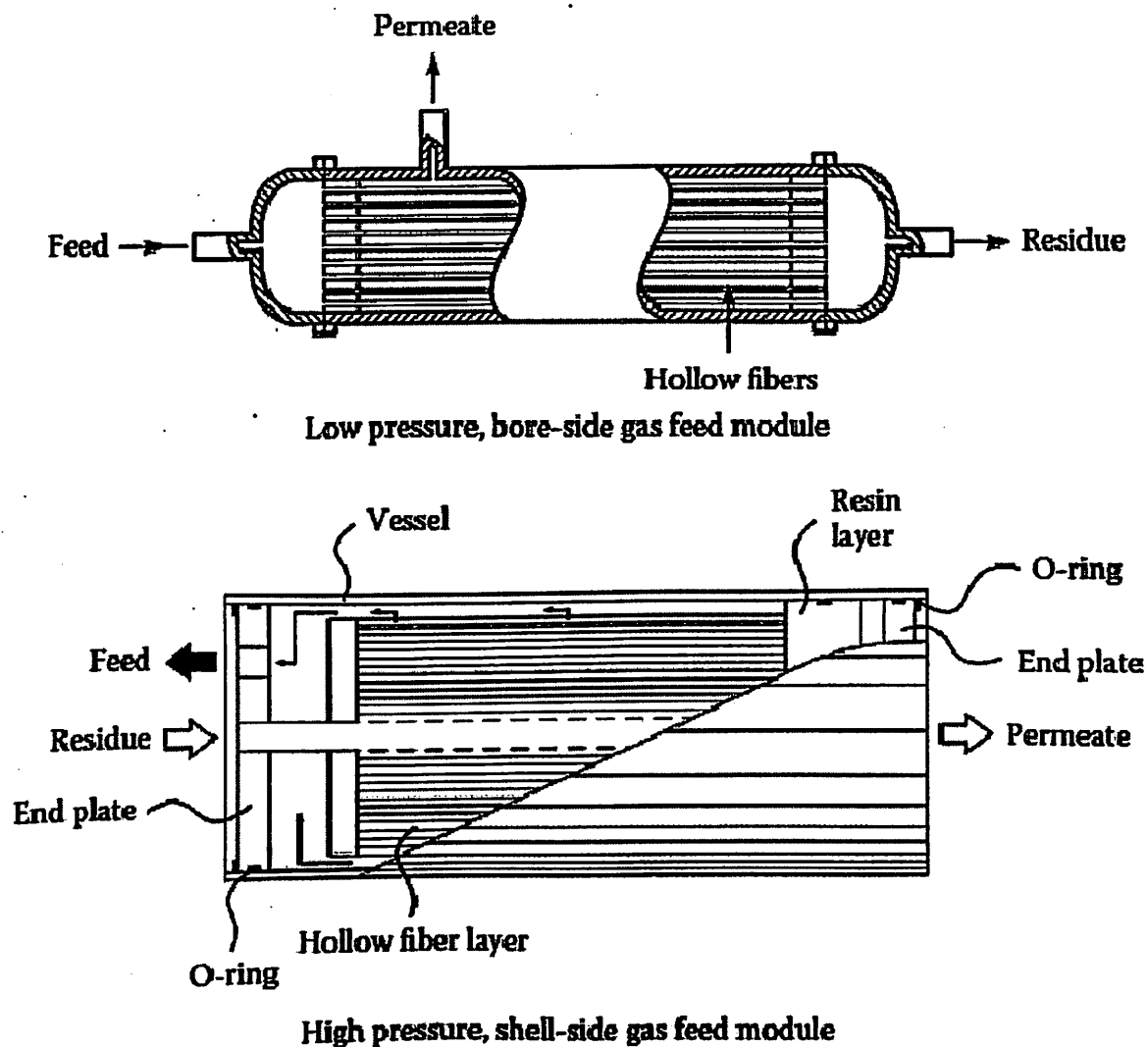


**FIGURE 32:** Cutaway view of the two module configurations used with hollow fiber membranes.

To cope with high pressures, the permeate flux in hollow fiber side of the grille. This feature makes the membrane more susceptible to plugging, and pretreatment of gas is usually required (Baker, 2002). The gas flow is cross current and ensures the distribution of food vouchers in the



module. This configuration is widely used to remove CO<sub>2</sub> from natural gas.

In the spiral wound element in Figure 33, two sheets of membrane are separated by a spacer and permeate stuck close to three ends to form an envelope or a sheet. Many of these sheets, separated by struts supply, are wound around the permeate tube, with the open end of the leaves in front of the tube. Feed gas travels along the spacers, permeating species diffuses through the membranes and spacers into the permeate tube, and residual gas outlets at the end. The gas flow is cross flow in this configuration.

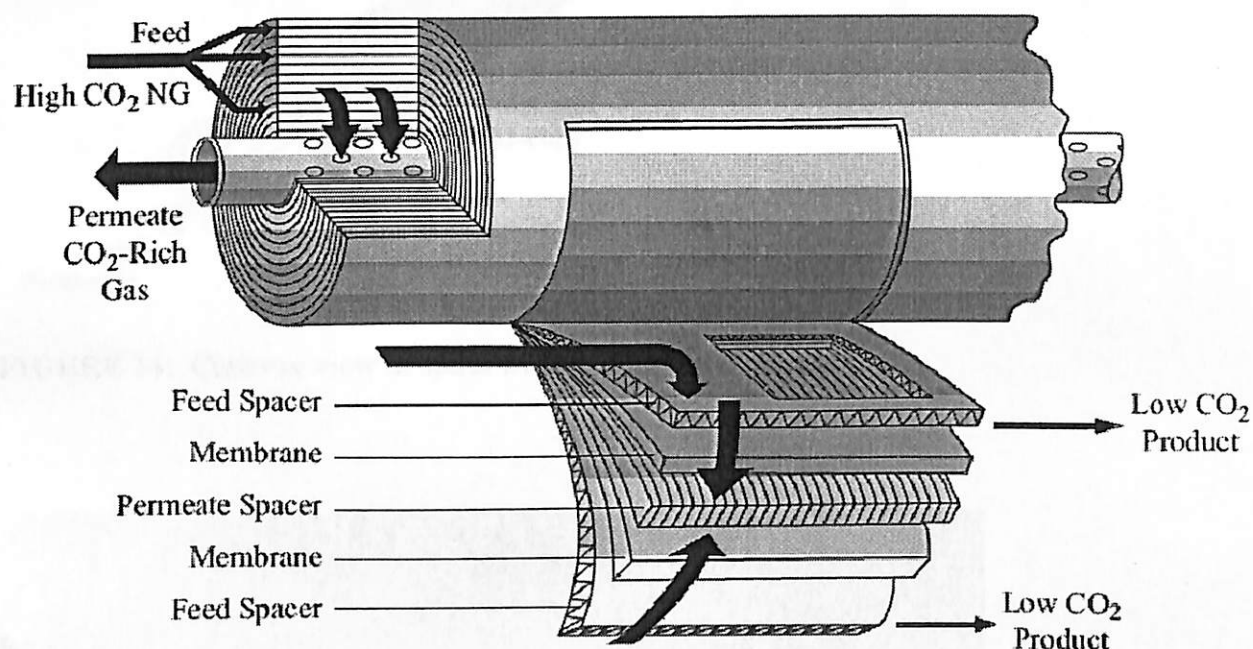


**FIGURE 33:** Cutaway view of spiral wound membrane element.

The spiral configuration is inherently more resistant than hollow fiber membranes for trace components which may affect the permeability of polymer. Also allows a wider range of membrane materials to use. However, the hollow fiber membranes are cheaper to manufacture, and therefore dominate the field (Baker, 2002).

Once the items were manufactured, they are grouped into modules, as shown in Figure 34. These modules are then mounted on a chassis to a complete unit, as shown in Figure 35. The unity of the left of the image composed of long cylindrical tubes containing membranes, and the entity on the right of the image is the power unit pretreatment.

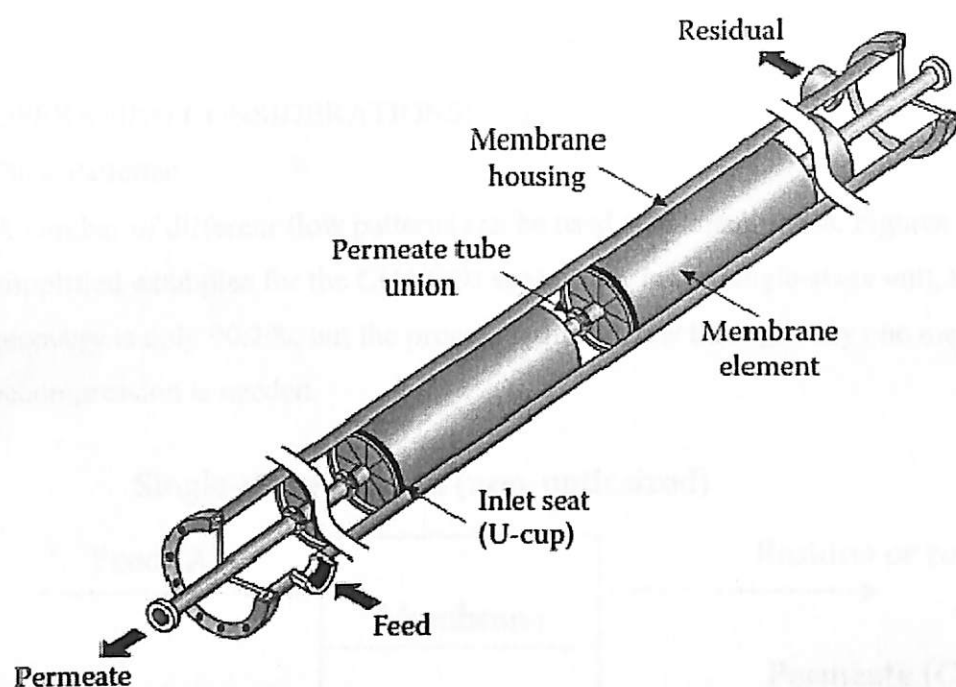


**FIGURE 34:** Cutaway view of spiral wound membrane module.

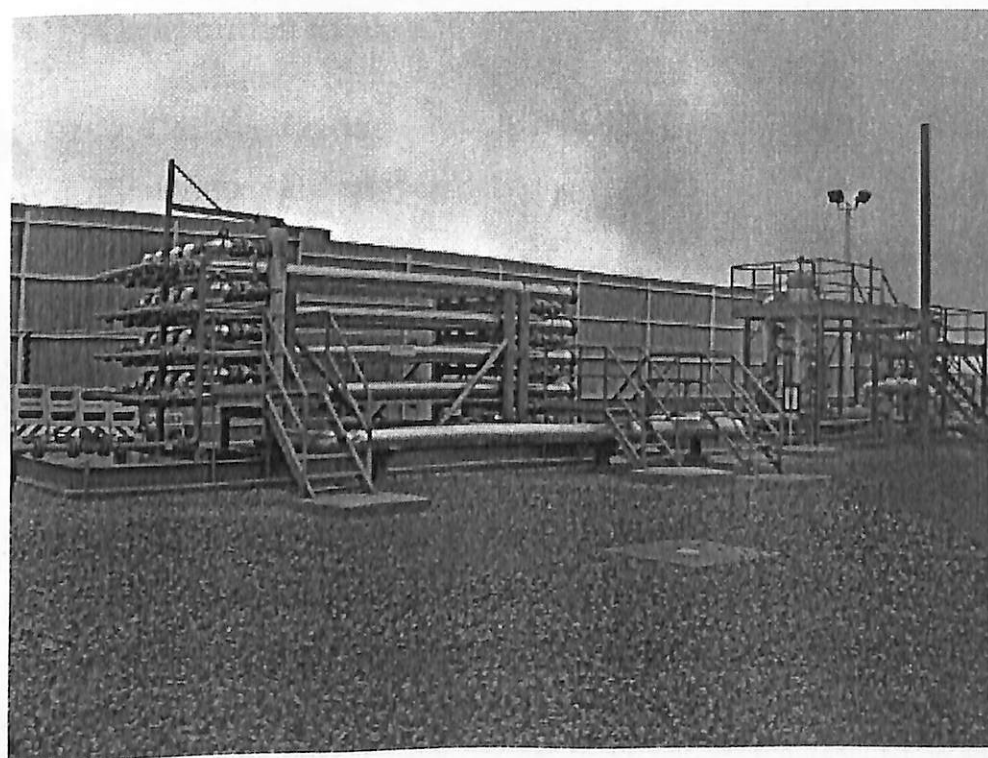


**FIGURE 35:** Carbon dioxide membrane skid installed in gas plant.

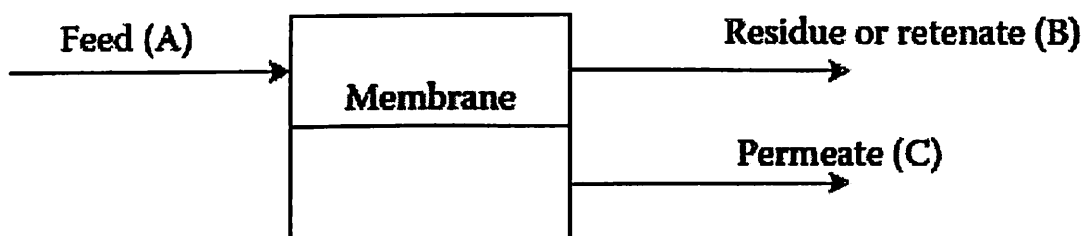


## OPERATING CONSIDERATIONS:

### Flow Patterns:

A number of different flow patterns can be used with membranes. Figures 36 and 37 show simplified examples for the CH<sub>4</sub>/CO<sub>2</sub> separation. In the single-stage unit, the overall methane recovery is only 90.2%, but the process requires flow through only one membrane, and no recompression is needed.

### Single-stage process (non-optimized)

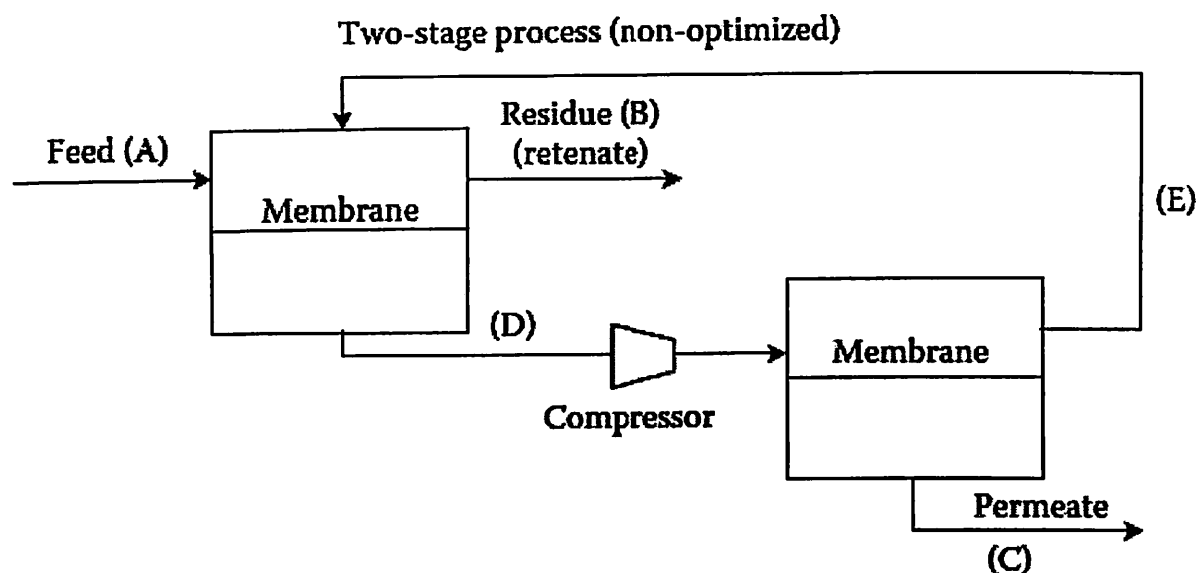


|                             | A     | B     | C    |
|-----------------------------|-------|-------|------|
| <b>Composition (mole %)</b> |       |       |      |
| Methane                     | 93.0  | 98.0  | 63.4 |
| Carbon dioxide              | 7.0   | 2.0   | 36.6 |
| <b>Flow rate (MMscfd)</b>   | 20.00 | 17.11 | 2.89 |
| <b>Pressure (psig)</b>      | 850   | 835   | 10   |

**Methane recovery = 90.2%**

FIGURE 36: A non-optimized single-stage CO<sub>2</sub>/CH<sub>4</sub> membrane separation process (Spillman and Cooley, 1989).

To increase methane recovery to 98.7%, a two-stage unit requires recompression of the first-stage permeate. Greater levels of methane recovery are obviously possible by application of three or more stages, but additional elements can quickly become uneconomical because of both membrane cost and recompression energy required.



|                             | A     | B     | C    | D    | E    |
|-----------------------------|-------|-------|------|------|------|
| <b>Composition (mole %)</b> |       |       |      |      |      |
| Methane                     | 93.0  | 98.0  | 18.9 | 63.4 | 93.0 |
| Carbon dioxide              | 7.0   | 2.0   | 81.1 | 36.6 | 7.0  |
| <b>Flow rate (MMscfd)</b>   | 20.00 | 18.74 | 1.26 | 3.16 | 1.90 |
| <b>Pressure (psig)</b>      | 850   | 835   | 10   | 10   | 850  |

**Methane recovery = 98.7%**

**FIGURE 37:**A non-optimized two stage CO<sub>2</sub>/CH<sub>4</sub> membrane separation process (Spillman and Cooley, 1989).

The second law of thermodynamics states that energy is needed for separation. For membrane processes, this means the law in pressure loss. However, in many processes, the cost of recompression, if any, is still a method of separating membranes attractive.

#### Flow:

A maximum acceptable level of feed gas per unit area applied to the membrane, and demanded the membrane surface is directly proportional to flow. Membrane units perform well in entry rates reduced, but their performance decreases when flow rates are exceeded. Additional modules are added in parallel to accept higher rates.



#### Operating Temperature:

An increase in temperature increases the membrane permeability decreases and food selectivity. The requirement of membrane surface is decreased, but the losses of oil and the compressor power recycling systems are increased in several stages, as shown in Figure 38.

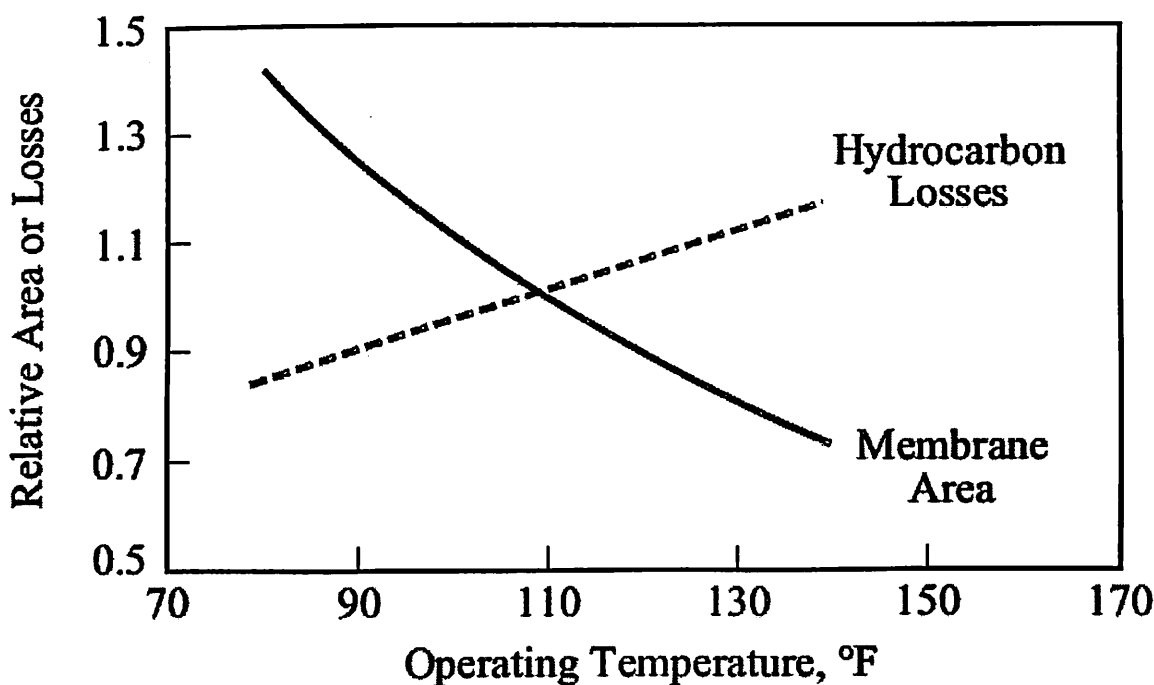


FIGURE 38: Effect of Operating Temperature

#### Supply Pressure:

An increase in the supply pressure reduces the membrane permeability at a time and selectivity. However, increased pressure creates a force of more than drive through the membrane. A net increase of permeation through the membrane and results in the requirement of membrane surface therefore drops. Compressor power increases slightly, and hydrocarbon losses decrease slightly (Figure 39).

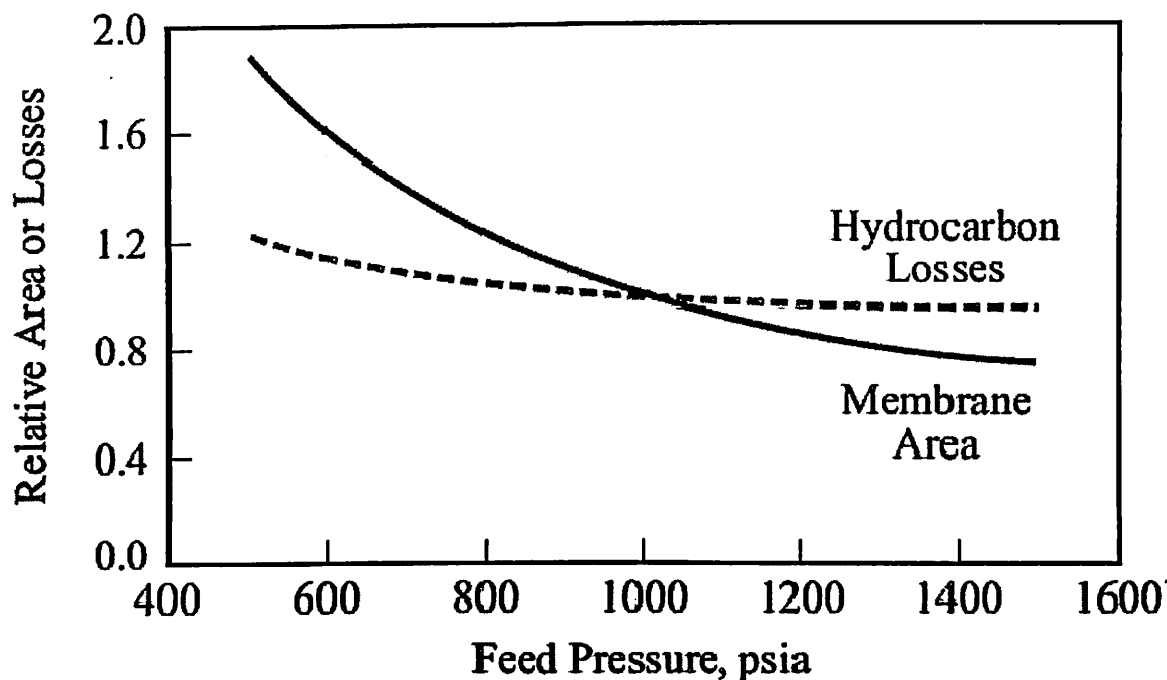


Figure 39: Effect of Feed Pressure

Because the requirement of membrane surface is so affected by pressure, while other variables are not, designers are trying to use the maximum pressure possible to achieve a cheaper and smaller system. A limiting factor is the maximum pressure limit for the elements of the membrane and the cost and weight of equipment to a high pressure rating.

#### Permeate pressure:

The effect of permeate pressure is the opposite of the effect of supply pressure. The higher the permeate pressure, the higher the engine and therefore longer required membrane surface. Contrary to the supply pressure, however, the permeate pressure has a significant effect on hydrocarbon losses (Figure 40).

The pressure difference across the membrane is not the only consideration. A detailed analysis shows that an equally important factor in system design is the pressure ratio across the membrane. This ratio is strongly influenced by the pressure of the permeate. For example, a feed



pressure of 90 bar and permeate pressure of 3 bars produce a pressure ratio of 30. The decrease in permeate pressure at 1 bar pressure increases the rate to 90 and has a dramatic effect on system performance. For this reason, design engineers try to achieve membrane pressure lowest permeate. This need is an important consideration in deciding how to continue processing the permeate flux. For example, if it should be burned, design, and rounding must be optimized for low pressure drop. If the permeate gas is compressed, for example, feed to a second membrane stage or inject it back into a well, the compressor power and increased size at low permeate pressures must be balanced by the reduced requirements for membrane surface.

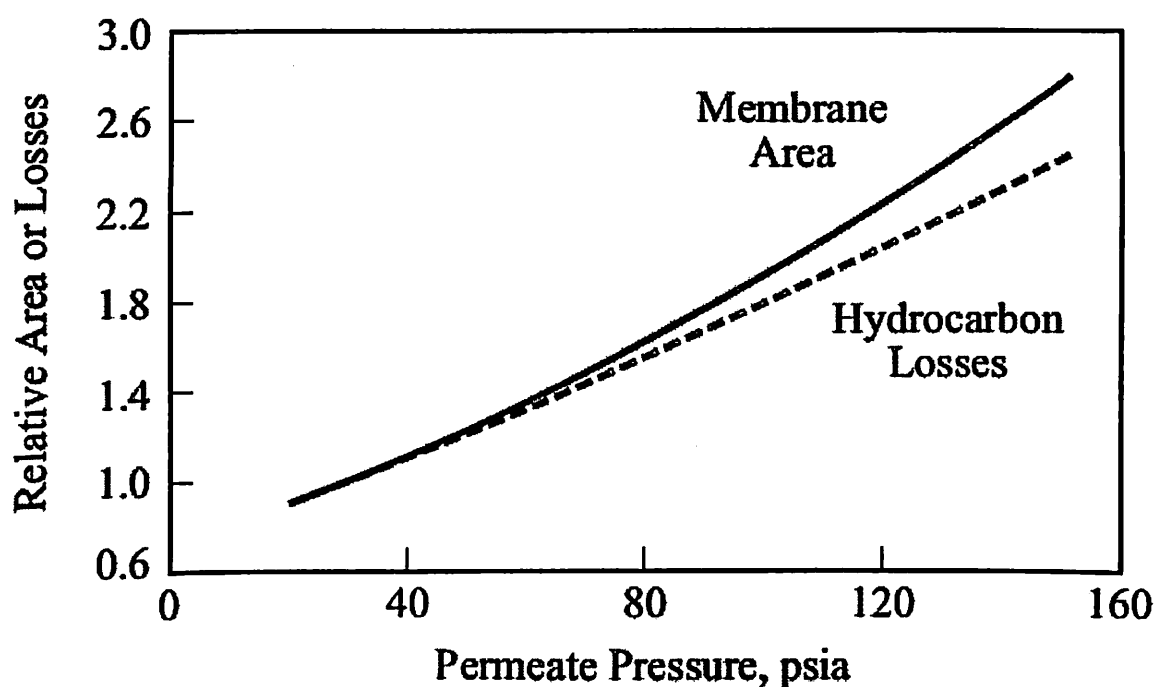


Figure 40: Effect of Permeate Pressure

#### FEED GAS PRETREATMENT:

The membranes are susceptible to degradation impurities, pretreatment is usually required. Any impurities present in the natural gas that can cause membrane damage (. Echt et al, 2002) include:

- i) Liquids: Liquids can be carried into the power unit or condensation in the unit. Liquids can cause the membrane to swell, resulting in decreased flow rates and membrane damage as possible. Liquids can form inside by two mechanisms: (1) due to the condensation of higher



molecular weight compounds caused by the cooling that occurs (Joule-Thomson) that the gas expands at a lower pressure through the membrane, and (2) because CO<sub>2</sub> and light hydrocarbons diffuse faster than heavier hydrocarbon dewpoint gas diffusion can not increase to the point where condensation occurs.

ii) high molecular weight hydrocarbons (C<sub>15</sub> +) such oils lubricating the compressor: These compounds coat the surface of the membrane and lead to a loss of performance. Concentrations are low, but the effect is cumulative.

iii) Particles: These materials block small flow passages in the membrane element. The erosion of the membrane could also be a problem.

corrosion inhibitors

iv) and many additives: Some of these compounds are destructive of the membrane material.

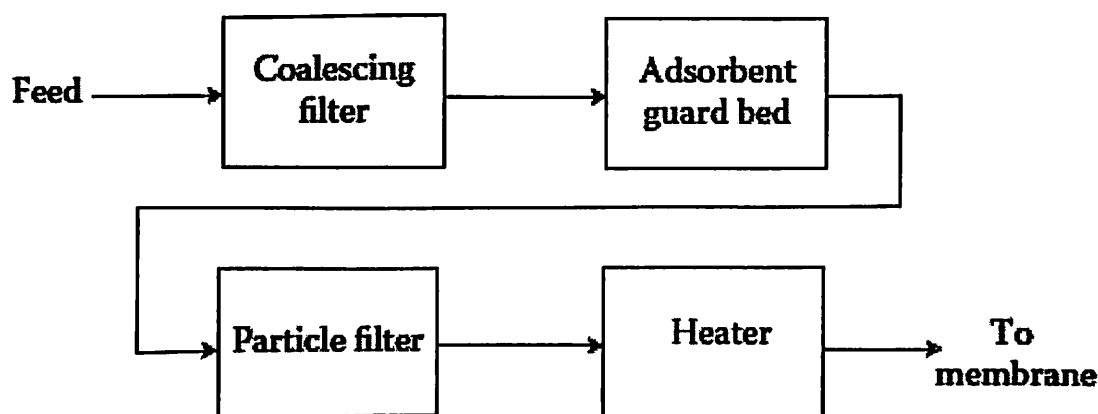


FIGURE 41: Schematic of membrane-pre treating equipment. (Adapted from Echt et al, 2002)

A common method for treating the feed gas for a membrane system is shown in Figure 41. The coalescing filter removes any entrained liquid and the adsorbent bed fate of trace contaminants such as volatile organic compounds

(VOCs), particulate filter removes all traces of dust from the adsorbent bed and the radiator overheated gas to prevent the formation of fluid in the membrane unit. The system shown has the following disadvantages (Echt et al, 2002).

- The adsorbent bed is the only unit that removes the heavy hydrocarbons. Therefore, if the gas contains hydrocarbons heavier than expected, or in the case of an outbreak of these materials, the



adsorbent bed can be saturated in a relatively short time, thus permitting the heavy hydrocarbons in contact the membrane.

- Only heating provides heating and, therefore, if this unit fails, the entire membrane system must be stopped. Echt et al (2002) discuss methods of pretreatment others who meet the drawbacks mentioned above.

#### ADVANTAGES AND DISADVANTAGES OF MEMBRANE SYSTEMS:

##### Benefits

- Low capital investment compared with the solvent systems
- Ease of use: The process can run unattended
- Easy installation: The units are normally mounted on skids
- Simplicity: No moving parts for the units in a single step
- High Dynamic Range: The system's modular nature means turndown ratios can be achieved very high
- Reliability and life cycle
- No chemicals required
- Good weight and space efficiency

##### Disadvantages

- Economy of scale: Because of their modular nature, they offer little economy of scale
- Clean feed: pretreatment of the feed to the membrane to remove particulates and liquids is usually required
- Gas compression: Because the pressure difference is the driving force for membrane separation, considerable recompression may be required for any residue and permeate flux.

For natural gas systems, the following disadvantages also apply:

- In general, the loss of hydrocarbons higher than that of solvent systems
- withdrawal H<sub>2</sub>S: H<sub>2</sub>S and CO<sub>2</sub> permeation rate are almost the same, so the specifications H<sub>2</sub>S can be difficult to answer
- The bulk removal: Ideal for bulk removal of acid gases; membranes alone can not be used to meet the specifications ppmv.



For offshore applications, the membranes are attractive because of unattended operation without chemical products or required, and good weight and space efficiency.



### METHANATION:

Catalytic hydrogenation of carbon monoxide and carbon dioxide to methane is normally used to eliminate small quantities of these compounds remaining in gas streams after bulk removal by other techniques. A typical application of the process is in the removal of small amounts of residual CO and CO<sub>2</sub> from hydrogen, following shift conversion and bulk removal of CO<sub>2</sub> by absorption. The methanation process is suitable for the purification of gas streams containing the oxides of carbon at a maximum concentration of about 2.5 mole%, and is particularly advantageous if the presence of methane in the treated gas is not objectionable in processes following the methanation step. Under proper operating conditions, the reaction goes almost to completion, and exit gases containing only a few ppm of the oxides of carbon are obtained.

Removal of carbon monoxide and carbon dioxide by methanation is required for the protection of certain hydrogenation and ammonia synthesis catalysts against rapid deactivation. It is also necessary when the hydrogen is used in hydroprocessing operations because CO<sub>2</sub> and CO can lead to temperature excursions and catalyst damage in the reactors. Furthermore, methanation is an essential step in the reaction systems associated with the Fischer-Tropsch synthesis and with the production of synthetic natural gas from liquid hydrocarbons and coal. Grayson (1956) presented a detailed discussion of methanation in connection with the Fischer-Tropsch process.

The methanation process used in the production of synthetic natural gas is substantially different from the purification application described in this section. It involves the methanation of high concentrations of carbon oxides and is conducted at high temperatures. The heat evolved during the reaction is usually recovered by the generation of high-pressure steam.

One version, the RM process, in which methanation is carried out in several stages, is described by White et al. (1974).

A description of methanator design and operation is given by Allen and Yen (1973). These authors point out the danger of forming nickel carbonyl (a highly toxic gas) by the reaction of elemental nickel in the catalyst with CO in the gas. The reaction is favored by high pressure and low temperature. To avoid the formation of nickel carbonyl, it is recommended that the operating temperature be maintained above 400°F whenever the pressure is above 300 psig.



An alternative technique for removing CO and CO<sub>2</sub> from synthesis gas is a two-step process involving methanolation (the conversion of the carbon oxides to methanol) to remove most of the impurities, followed by methanation to remove the last traces. The production of methanol has the potential advantage over methane of using less hydrogen and producing a potentially useful byproduct. The methanol is removed from the gas stream by water scrubbing. The resulting solution may then be distilled for recovery of a commercially pure methanol byproduct or recycled to the reformer to recover the hydrogen content (Sogaard-Andersen and Hansen, 1991).

#### PROCESS DESCRIPTION:

Although many types of catalysts have been investigated for the hydrogenation of carbon monoxide and carbon dioxide to methane, catalysts of high nickel content are most commonly used for gas purification. Typical commercial preparations contain 20 to 35% nickel and are available in the form of tablets, extruded pellets, rings, and small spheres of various sizes. The catalyst does not require regeneration, and has a typical service life on the order of ten years when operated with a poison-free feed gas. The properties of a typical methanation catalyst are given in Table 13.

|                                           |                         |
|-------------------------------------------|-------------------------|
| Catalyst designation                      | PK-5                    |
| Composition                               |                         |
| Carrier                                   | Alumina                 |
| Catalyst, wt % Ni in reduced catalyst     | 27                      |
| Surface area, m <sup>2</sup> /g           | 250                     |
| Configuration                             | ¼-in. OD extruded rings |
| Normal inlet temperature, °F              | about 570               |
| Maximum contin. operating temperature, °F | 840                     |
| Temperature increase across methanator,   |                         |
| °F per 1% CO                              | 135                     |
| °F per 1% CO <sub>2</sub>                 | 108                     |
| °F per 1% O <sub>2</sub>                  | 315                     |

*Data of Haldor Topsøe, Inc. (1988)*

TABLE 13: Properties of Methanation Catalyst



Methanation catalysts are easily poisoned by sulfur, and, therefore, sulfur compounds must be removed from the gas stream before it enters the methanator. The flow scheme of the process is quite simple. A flow diagram typical of the final purification step in a hydrogen plant using either a physical or reactive solvent is depicted in Figure 42. A heat exchanger using high-temperature shift-converter effluent is used to start the methanator by heating the feed gas to about 600°F. When the methanator is operating, the temperature rise across the reactor is approximately 50°F, resulting in an outlet temperature of about 650°F. With this temperature rise, the methanator feed effluent heat exchanger can be designed to supply all the heat required for feed preheat during normal operation, and the heat exchanger using the high-temperature shift effluent for heating the methanator feed is often not required after steady-state operation has commenced. Commercial methanation reactors normally contain a single bed of catalyst with a minimum depth to diameter ratio of 1: 1.

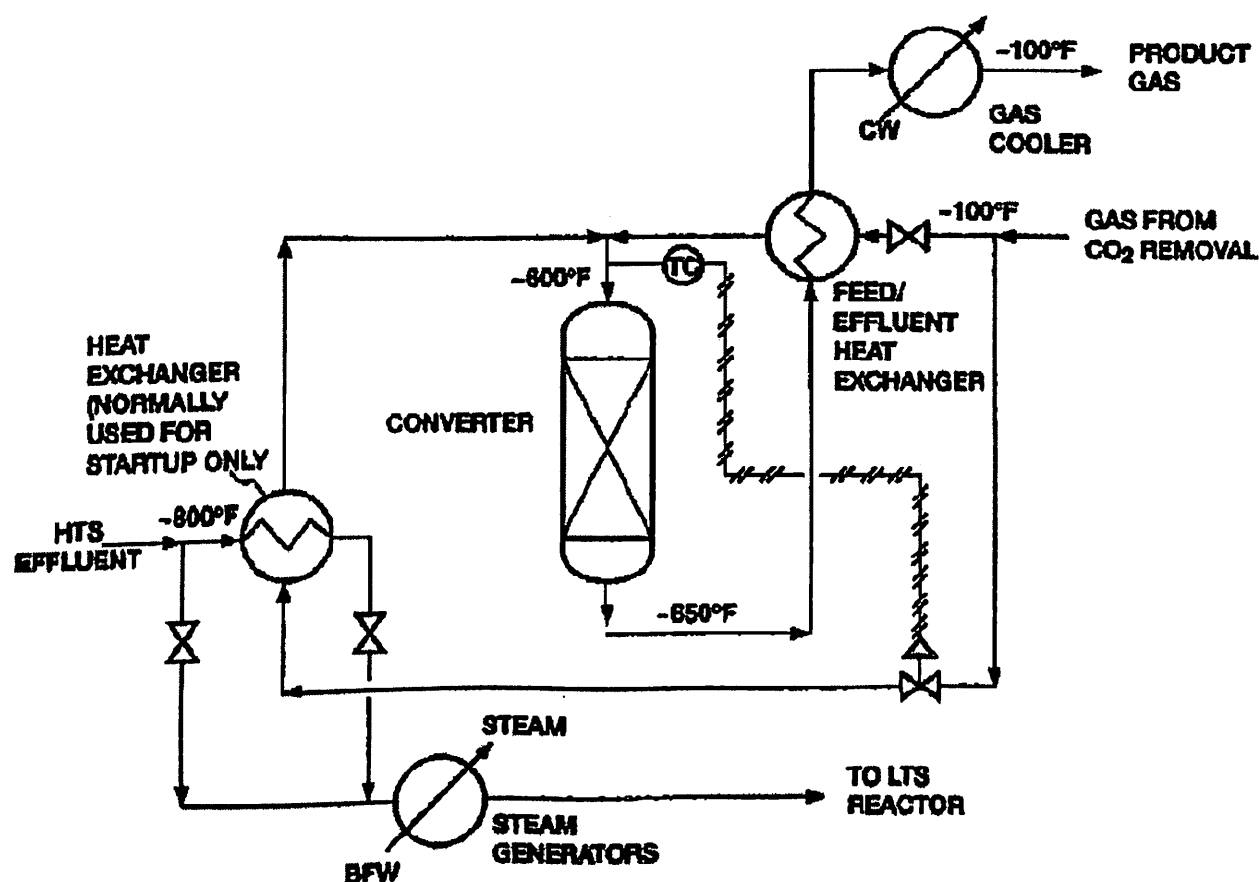
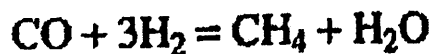
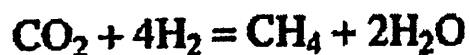


FIGURE 42: Schematic flow diagram of a methanation unit.



## BASIC CHEMISTRY:

The reactions involved in methanation of carbon monoxide and carbon dioxide can be represented by equations below:



The heats of reaction and equilibrium constants within the range of 400 to 1,000°K (261 to 1,341°F) are shown in Table 14.

| Temperature,<br>°K      °C |     | Heat of Reaction<br>ΔH cal/g mole |            | $K = \frac{(\text{CH}_4)(\text{H}_2\text{O})}{(\text{CO})(\text{H}_2)^3}$ |
|----------------------------|-----|-----------------------------------|------------|---------------------------------------------------------------------------|
|                            |     | First equation                    | Second one |                                                                           |
| 400                        | 127 | -50.353                           | -40.643    | $4.009 \times 10^{15}$                                                    |
| 500                        | 227 | -51.283                           | -41.763    | $1.148 \times 10^{10}$                                                    |
| 600                        | 327 | -52.061                           | -42.768    | $1.980 \times 10^6$                                                       |
| 700                        | 427 | -52.703                           | -43.652    | $3.726 \times 10^3$                                                       |
| 800                        | 527 | -53.214                           | -44.412    | 27.97                                                                     |

Table 14: Heats of Reaction and Equilibrium Constants for Methanation of Carbon Monoxide and Carbon Dioxide

## DESIGN AND OPERATION:

The method can be used in a large range of temperatures and pressures. Inlet gas temperatures can vary from 350 to 750 ° F, but because of the unfavorable balance at an elevated temperature, the temperature of exhaust gas must not exceed 825 ° F. The highly exothermic reaction resulting in a rise in temperature during the conversion of 135 ° F for every 1% CO, 108 ° F for every 1% CO<sub>2</sub> and 315 ° F for every 1% O<sub>2</sub>. These values can be used to estimate the inlet temperature required which will result in the desired final temperature. The large amount of heat produced by the reaction is the main reason that the process is considered unsuitable for the treatment of gases



containing more than 2.5 mol% of oxides of carbon.

The pressure range over which the process can be operated ranges from essentially atmospheric pressure at 12,000 psig. Space velocities of 1,000 to 2,000 volumes per volume per hour are typical for operation at atmospheric pressure. Much higher speeds and space up to 20,000 volumes per volume per hour can be used at high pressures. Operation at very high pressure usually leads to concentrations of carbon monoxide below detectable limits. Typical operating conditions for a commercial facility are presented in Table 15. The data indicate no significant change in catalyst activity or pressure drop occurred over a period of over four years.

| Catalyst age, months | 33   | 86   |
|----------------------|------|------|
| Temperature, °F      |      |      |
| Inlet                | 601  | 597  |
| Midpoint             | 621  | 642  |
| Bottom of bed        | 621  | 643  |
| Pressure, psig       |      |      |
| Inlet                | 402  | 401  |
| Outlet               | 397  | 396  |
| CO Concentration     |      |      |
| Inlet, %             | 0.22 | 0.38 |
| Outlet, ppmv         | <1   | —    |

*Data of Haldor Topsøe, Inc. (1988)*

Table 15: Methanator Operating Data for 1150 t/d NH<sub>3</sub> Plant.



## CHAPTER 9

### CHOOSING BEST GAS TREATING TECHNOLOGY

For solution of this question, we first need to define what is required and what constraints are in place. This will comprise knowing what contaminants are present and requirement to be removed, the inlet and discharge operating parameters and specifications (such as pressure, temperature, flow rate, gas composition and allowable contaminant concentration in the sales gas) and site location and situations (for instance, power availability, ambient conditions and regulatory restrictions).

Once you have this information, the review process can begin and a preliminary assessment can be made. Always start at the beginning of the process and work in the system, taking care to understand the effect of each contaminant on the process at hand immediately, and subsequent procedures downstream. The evaluation process should also include a comparison of capital costs not only, but also operating costs and maintenance, equipment and disposal costs of purchase, costs of fuel and losses products to vent or flare.

It is imperative to understand the capabilities and limitations of various technologies to the study and how different processes can complement or conflict with another. For example,  $O_2$  in the gas stream have an adverse effect on amine, but has no impact at all on the membranes.

Thus, if amine is the technology of choice, an  $O_2$  removal system, such as X- $O_2$  catalytic removal system, should be considered for installation upstream of the plant, although this stage may be required if the membranes are used, depending on  $O_2$  inlet concentration and specifications of the pipeline. Unlike amine, the membranes are unable to reach the exit  $H_2S$  levels required by most pipeline specifications. In cases where  $H_2S$  is present and the membranes must be used, an  $H_2S$  scavenger can be installed on the current input or output, or you could follow up with an amine unit, depending on the concentration of  $H_2S$ . This could also be a viable configuration when trying to minimize overall energy consumption and product losses in high concentrations of polluting gas streams.

Now, when becoming generally more economical to use a membrane system instead of an amine unit? This can first be evaluated by examining the consumption of fuel oil input MSCF v /



s hydrocarbon losses for each system. For example, an inflow of gas containing 5% CO<sub>2</sub> must be reduced to less than 2% CO<sub>2</sub> current gas sales can be treated with six gallons of amino MSCF gas entry :

$$(1000 \text{ scf/Mscf}) \times (0.03 \text{ scf CO}_2/\text{scf inlet}) \times (1 \text{ gal amine}/5 \text{ scf CO}_2)$$

The fuel gas required to operate the amine plant in this case will be approximately 0.75% of the inlet hydrocarbon content:

$$(6 \text{ gal amine/Mscf In} \times 0.12 \text{ MSCF FG}/100 \text{ gal amine} \times \text{Mscf In}/0.95 \text{ Mscf HC})$$

On the other hand, if you have gas input currents with 15% and 30% CO<sub>2</sub> and still need to meet the output specifications of 2% CO<sub>2</sub>, the amine and fuel gas requirement increases to 30 gallons of amine / MSCF inlet gas and fuel gas shrinkage of 4.25% for entry 15% of cases of CO<sub>2</sub> and 60 gallons and 10.3% fuel gas shrinkage in the 30% inlet CO<sub>2</sub> case.

It is doubtful that the single stage membrane can ever match hydrocarbon losses from a plant amine, even if CO<sub>2</sub> input of 30%. However, installing a second membrane stage can almost always maintain total losses of hydrocarbons, including recycling, fuel compression, less than 5%. So the first rule to follow is to consider using a membrane system to a system of amine when the CO<sub>2</sub> content of entry is greater than 15% and we are only trying to meet pipeline specifications.

In addition, the use of a membrane system in conjunction with central amine can be a viable option. For example, a flow of gas 50 mmscfd be brought to a cryogenic gas plant, but containing 30% CO<sub>2</sub>, CO<sub>2</sub> must be treated less than 0.10% in the treated gas stream. If the treatment was carried out strictly amine, a velocity of over 2,000 gpm would be required:

$$(50 \text{ MMscfd}) \times (0.3 \text{ scf CO}_2/\text{scf inlet}) \times (1 \text{ gal amine}/5 \text{ scf CO}_2) \times (1 \text{ day}/1440 \text{ min})$$

This is not just a big plant, but a energy hog. If, on the other hand, a membrane in two steps is used to reduce the CO<sub>2</sub> content of 2%, the amine circulation rate would be reduced to about 100 gpm, resulting in significant capital and operating costs.



### CASE STUDIES

#### FOR MEMBRANE PROCESS:

##### Assumption Considered In These Cases:

The following assumptions were made for this article and can vary to some extent in practice. However, they must be representative of what we see on the field:

- i) Amine will be regenerated with steam 1.0 lb per gallon of distributed amine (950 btu / lb). Thus, a 100 gpm amine plant will utilize approximately 5.7 million Btu / hr heat output. Assuming an efficiency of 80% of heating fuel gas for this system will be about 171 Mscfd (0.12 gal Mscf/100).
- ii) 30 wt% DEA remove 4 scf acid gas per gallon, while a 50% solution by weight amine acid gas will drop 5 scf / gal without exceeding a load of rich amine 0.45 mol / mol.
- iii) Depending on the operating pressure, an amine plant will consume more electricity from 2.0 to 2.5 HP per liter of amine circulated (i.e. 100 GPM plant will take operating electrical load of 200-250 HP)
- iv) The membranes will be considered for disposal of CO<sub>2</sub>, although progress is being made to also use this technology for nitrogen removal too.
- v) The membrane must have a minimum inlet operating pressure of at least 400 psig to operate efficiently and profitably, even if the systems were operated as low as 125 psig.
- vi) When using membrane units in two stages, the permeate flux of the first stage is recompressed to the pressure of the first floor entrance, plus 15 pounds per square inch, before entering the second stage membranes.
- vii) A plant using membrane power does not exceed 5 kW / mmscf, compression, not including the power recompression.
- viii) H<sub>2</sub>S scavenger vessels are generally undertaken to maintain a superficial gas velocity of less than 9 ft per minute.
- ix) Unless otherwise noted, all cases that follow assume a composition of base gas methane 84%, 9% ethane, propane and butane from 3% to 4% and heavier hydrocarbons, each



adjusted prorated to account for CO<sub>2</sub>, H<sub>2</sub>S and N<sub>2</sub> in the gas stream to be treated.

x) The specifications of the pipeline are 2% CO<sub>2</sub> (max) 3% inert total (max), 4 ppmv H<sub>2</sub>S (max), 20 ppmv O<sub>2</sub> (max) and 7 lb (max H<sub>2</sub>O/MMscf)

xi) Reciprocating compressors, operating at 80% efficiency and requires a heat input of 7200 Btu / hp-hr, are supposed to be used for all compression operations.

#### CASE STUDY 1:

10 MMscfd gas stream at 1000 psig and 160F, containing 2.7% CO<sub>2</sub>, needs to be treated to less than 2.0% CO<sub>2</sub> in the outlet stream.

There is no H<sub>2</sub>S in the inlet gas stream.

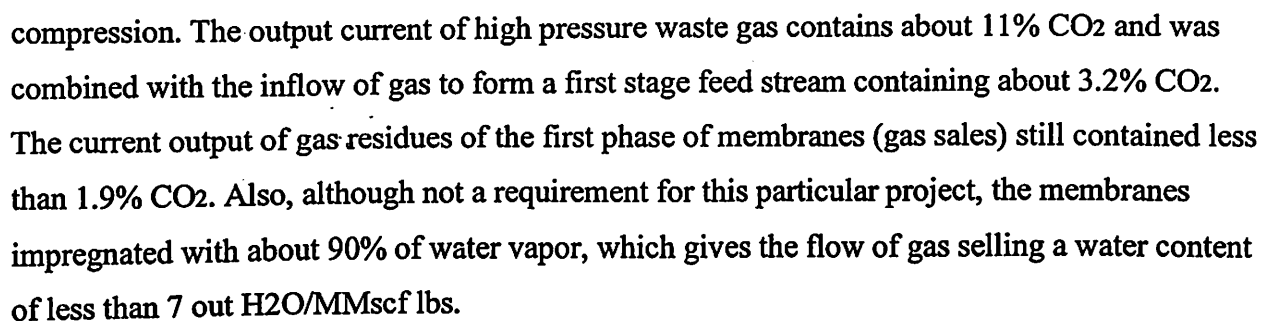
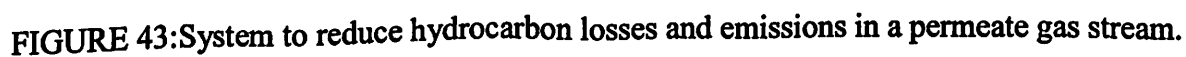
The gas stream is located on a small platform in the Gulf of Mexico and there is no electrical power supply.

#### SOLUTION:

This is an excellent choice for a 10 gpm amine unit, except that there is no source of energy available to power the pump and cooler motors. Although the inlet pressure is high enough, a membrane system would not normally be the technology of choice because of the fine-tuning aspect, rather than eliminating bulk necessary for this process. However, in this case, the lack of power makes the membrane system is the only viable alternative.

Initially, a membrane unit in a single step has been proposed to perform this service. The process of reducing the CO<sub>2</sub> content in gas sales to about 1.8%, although it suffered a loss of oil by 3.2% in the permeate flux. However, the lower capital and operating costs of the unit membrane, compared to the amine unit, makes this acceptable alternative. Although this was considered acceptable to the client, the Minerals Management Service said the plant would not be authorized unless the total hydrocarbon emissions could be limited to less than 50 MSCFD (0.5% of the entry). It was initially believed that this limitation would kill the project and the property would not produce, so the closure of 10 MMSCFD of gas production.

Refusing to give up this opportunity, company suggested that the client consider installing a second stage of membranes for the treatment of permeate gas flow and reduce hydrocarbon losses / emissions to acceptable levels (Figure 43). The new design required the flow of the first stage permeate gas to be compressed to the pressure gas inlet, and then processed by a second stage membrane treatment. It took the client to install approximately 160 hp recycle





More importantly, during the second stage permeate membrane contained significantly less than 50 MSCFD hydrocarbons. This current of the second stage permeate gas is then released into the atmosphere.

Thus, an increase of approximately 25% of capital cost and the monthly lease cost of compression, the client was able to produce gas and increase the sales volume of gas flow (by reducing losses ventilation) of about 200 Mscfd for a turnover increased by \$ 1300/day (\$ 475 000/year) on this single volume. The overall capital cost of the membrane system in two stages, recycling less compression, is comparable to a 10 gpm amine plant and resulted in approximately the same amount of the loss of hydrocarbons.

#### CASE 2:

landfill gas flow to 6 mmscfd contains 36% CO<sub>2</sub>, N<sub>2</sub> 3.2%, 0.8% O<sub>2</sub> and H<sub>2</sub>S 2500 ppmv (balance is methane).

Enter the plant mainly atmospheric conditions.

#### SOLUTION:

The flow of low-Btu gas is currently routed through a sponge iron for the removal of H<sub>2</sub>S, compressed to 600 psig, then routed through a small unit Selexol to remove trace contaminants and partial dehydration before being sold. But new regulations require the customer to convert to high Btu (> 900 Btu / scf) sales flow, although the new buyer will always 1% O<sub>2</sub> in the feed gas sales. The factory is located in an urban area, industrial area of a large city.

The gas is already being treated for the removal of H<sub>2</sub>S, is dehydrated to levels of pipeline specifications and the final gas flow can have up to 8% inert and still meet the minimum specifications Btu. The oxygen in the gas stream will have detrimental effects on any system of amine, so that a membrane system appears to be the best solution, even if the CO<sub>2</sub> reduction to less than 3% in the current gas sales will result in higher than acceptable hydrocarbon losses. In fact, simulations of the system indicate that over 20% methane input is lost to the permeate flux of the first floor.

To make a project profitable, the customer believes they need to maintain the overall hydrocarbon losses to less than 5%. Again, using compression to increase the pressure of the permeate flux of the first floor to the inlet pressure of the first floor (900 hp), then processing



through a second membrane stage, leads to a permeate flux the second floor containing less than 3% of the total content of hydrocarbon input (Figure 44).

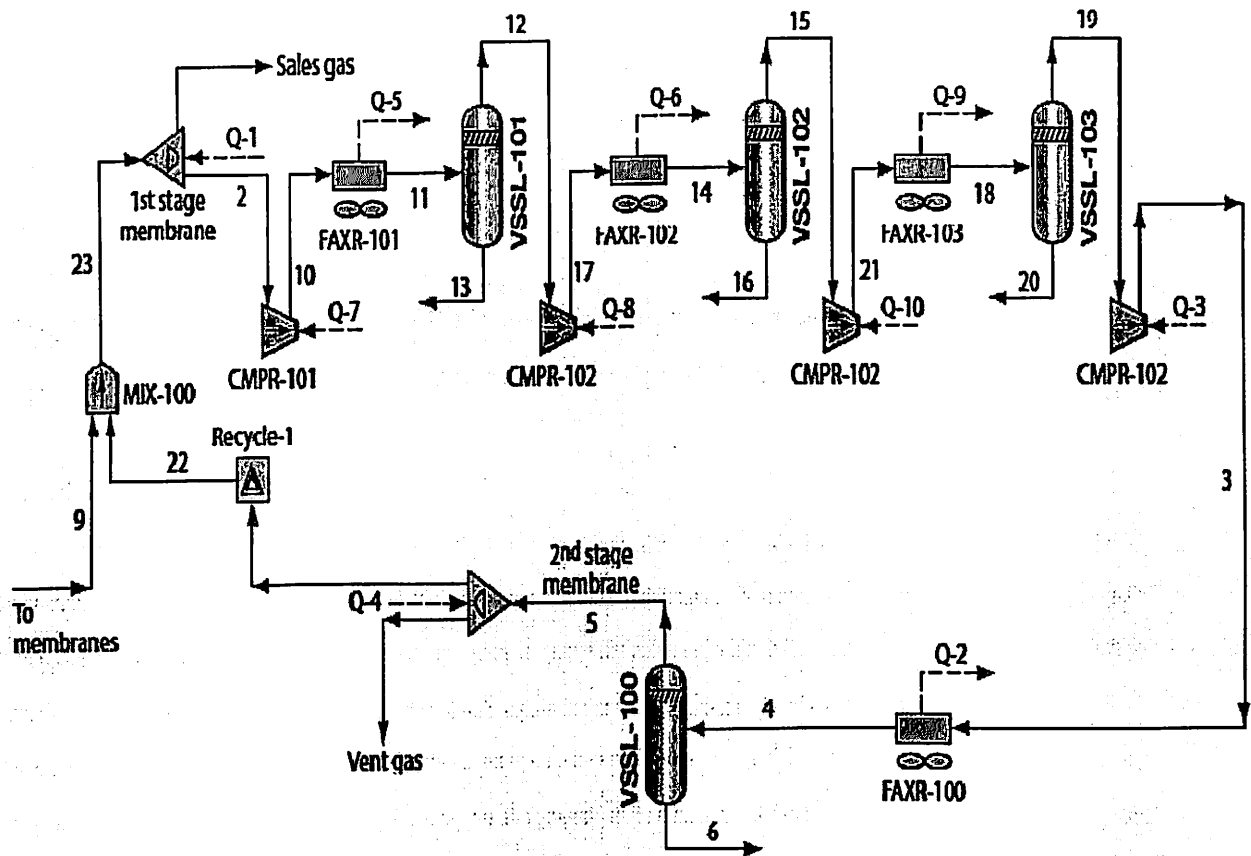


Figure 44: A second membrane stage results in a permeate stream containing less than 3% of total inlet hydrocarbons

The installation of the second membrane stage has saved nearly 1 mmscfd hydrocarbon gases that would otherwise have been lost in the atmosphere. It was not only good for the environment, but increased the supply of gas and client income and more than enough to pay the second stage of membranes and the rental cost of compression.

It should be noted that the membrane was the option more attractive because of the permissible oxygen content in the current sale of gas and the presence of the sponge iron units and existing Selexol to the factory for the removal of H<sub>2</sub>S and contaminants such as siloxanes which are detrimental to membranes. If this had been a grassroots operation, with more stringent product



specifications, a different approach might have been the most logical choice and profitable.

### CASE 3:

A flow of gas 100 mmscfd

At 700 psig and 100F, contains CO<sub>2</sub> by 9.5% and 4% and 2000 ppm N<sub>2</sub> O<sub>2</sub> is sent to a processing plant for gas cryogenic deep ethane recovery (> 95%) and release of N<sub>2</sub>.

### SOLUTION:

Due to the composition of inlet gas and pressure, a PSA unit will not be considered for removal N<sub>2</sub> in this case, because of high hydrocarbon losses and demands excessive compression. This may be a good application for withdrawal of the membrane of the N<sub>2</sub>, but this technology is not considered in this article. Because of the willingness of the plant to obtain the maximum recovery of ethane, as specified liquid, then reject using cryogenic N<sub>2</sub>, CO<sub>2</sub> removal to less than 300 ppmv should be considered. We know that a unit membrane does not allow gas to be treated to these levels, we chose an amine plant for this application. Or do we? The O<sub>2</sub> will have a negative effect on the system and amine, with or without O<sub>2</sub> concerns will require an amine plant energy intensive.

However, following the rule to always start at the beginning of the process and eliminate the contaminant (s) to be detrimental to any further processing, the question of O<sub>2</sub> is the first element that must be addressed. Using X-O<sub>2</sub> catalytic process of oxygen removal (Figure 45), the inlet gas is first heated by heat exchange with a cross and then heating the gas to reach the required reaction temperatures. At this stage, the gas enters the catalytic reactor and oxidizes a portion of the hydrocarbon stream inlet to form CO<sub>2</sub> and water vapor, which are contaminants that can easily be removed in downstream processes. As the oxidation process is exothermic, the gas flow increases the temperature in the reactor. The amount of temperature rise depends on the amount of oxygen contained in the flow of incoming gas. It should be noted that the outflow gas were generally less than 10 ppmv O<sub>2</sub> and the reactor can be designed to provide a feed gas containing



less than 5 ppmv O<sub>2</sub>. The flow of hot gases exiting is then cooled by heat exchange and bottom cooling air before going to the next processing step:

$$(100 \text{ MMscfd}) \times (0.095 \text{ ft}^3 \text{ CO}_2/\text{ft}^3 \text{ Inlet}) \times (1 \text{ day}/1440 \text{ minutes}) \times (1 \text{ gpm amine}/5 \text{ ft}^3 \text{ CO}_2) = \text{approximately } 1300 \text{ gpm of amine circulation.}$$

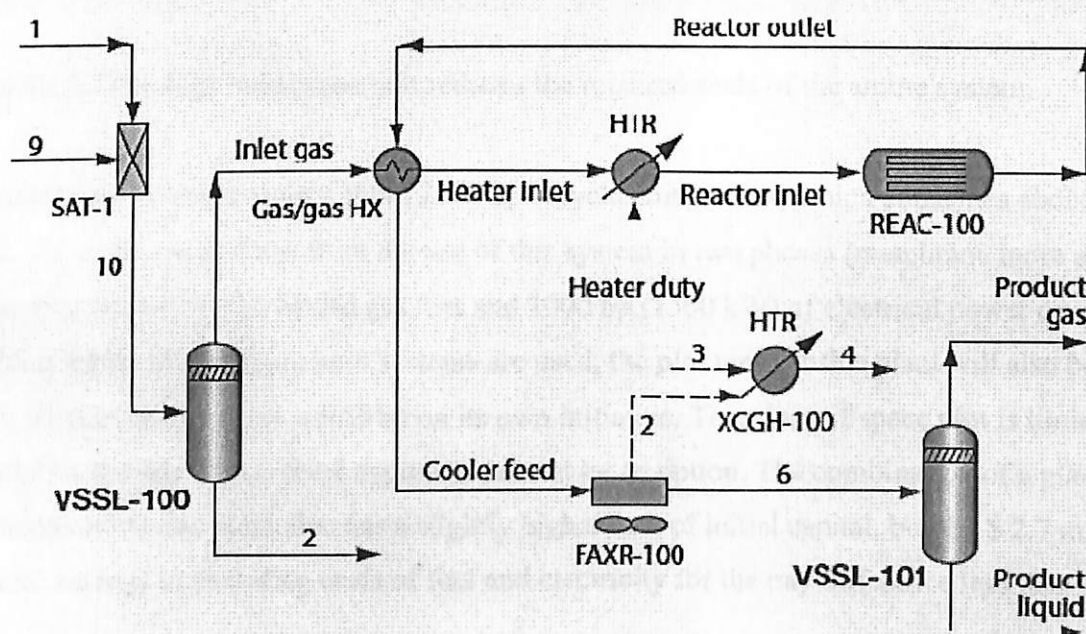


Figure 45: X-O<sub>2</sub> plant

This equates to a right of reboiler of about 74 million Btu / h, a rate of about 2.22 mmscfd fuel, or nearly 2.5% of the oil content of entry. In addition, the electrical charge of the plant would be around 2200 hp.

On the other hand, if the flow of gas is first processed using a membrane unit into two stages to reduce the CO<sub>2</sub> content of 5%, while keeping the loss of hydrocarbons to less than 1%, the system amine could then be further reduced in size to 650 gpm (Figure 46), reducing fuel and electricity consumption by 50% while meeting the desired specifications of 300 ppm CO<sub>2</sub> in the treated gas. The treated gas can now be dried and sent to the cryogenic portion of the recovery plant liquid products and release of N<sub>2</sub>.

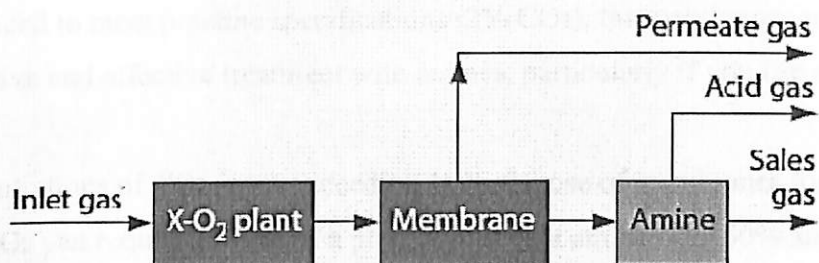


Figure 46: A two-stage membrane unit reduces the required scale of the amine system.

The membrane system requires about 2100 hp recycle compressor, which consumes about 360 Mscfd. Thus, the net savings from the use of this system in two phases (membrane more amine) will be approximately 730 Mscfd gas fuel and 2000 hp (1500 kW) of electrical power over the use of the amine alone. Since both systems are used, the plot area for this plant will also be about double what an amine plant would be on its own initiative. Therefore, if space plot is limited or unavailable, the use of two-level approach can not be an option. The combination of a plant membrane and amine plant also has a slightly higher cost of initial capital, but the \$ 2.7 million in annual savings in operating costs of fuel and electricity for the pay difference less than a year.

## CONCLUSION:

Gas treatment technologies have made great progress in the last ten years to 20 years and have received much attention in the last five to ten years due to the increased demand for energy worldwide and search result of operating on alternative sources that were previously considered unprofitable. It is now up to system designers and operators to determine the most efficient and effective use of these technologies and / or develop new ways to apply them. To assist in this process of development and evaluation, the following rules of thumb can be used as a guide:

- i). Understand all the contaminants in the stream to be treated and develop a process flow that will first remove the contaminants that are harmful to the subsequent downstream process.
- ii) Review the proposed site for the plot area available, utilities and so on, these constraints may



determine the type of design are viable.

iii) Where only need to meet pipeline specifications (2% CO<sub>2</sub>), the membranes may be a cost effective alternative and effective treatment with amines, particularly if you use a two-tier system.

iv) Where concentrations of CO<sub>2</sub> input exceeding 10%, the use of membranes for bulk materials for disposal of CO<sub>2</sub> can reduce the size of a plant subsequent amine over 50% and save proportion of fuel and energy.

v) Amine is still the only reasonable way to remove CO<sub>2</sub> at levels required for the cryogenic gas processing or for removing large amounts of sulfur. However, amine is also energy intensive, thought must be given to using amine in conjunction with other technologies (especially if waste heat is not available).

vi) the use of a sensor of H<sub>2</sub>S may be the best option for low pressure and low volume flows that do not require the removal of CO<sub>2</sub>, but the costs of replacement chemicals (material plus labor) may make this option very costly as gas prices and increased concentration of H<sub>2</sub>S.

#### CASE STUDIES FOR MDEA:

The use of MDEA and mixtures of amines for CO<sub>2</sub> removal in bulk is explored through three case with CO<sub>2</sub> levels ranging from about 3-15%. MDEA is compared to the MEA, DEA, and DGA for a set of basic conditions for the elimination of bulk CO<sub>2</sub>. The effect of operating parameters on the most important performance of a device using solvent of MDEA is also explored.

#### CASE 1 - CO<sub>2</sub> Moderate:

The basic conditions for Case 1 are based on data from North Carolina Plant, Alberta, Canada. The inlet gas was 800 psia and contained 3.5% CO<sub>2</sub> and 60 ppm H<sub>2</sub>S. The base operating conditions for this case was 33% by weight of MDEA, 116 gpm flow, the temperature of 115°F lean amine and 2.6 sec. residence time of liquid on each tray. The circulation system was a standard unit without sweeteners expansion tank on the rich amine.

The influence of type of amine on the overhead of CO<sub>2</sub> and various functions within the plant is shown in Table 16. Solution concentrations default and maximum loads were chosen for rich



DEA, DGA and MEA as shown in Table 16. Because of the limit load solution for the maximum allowable DEA, DGA and MEA, significantly higher rates of movement and rights of heat were required for these amines

| Amine    | GPM | CO <sub>2</sub> Overhead | Loading | Condenser Duty | Reboiler Duty | Trim Duty |
|----------|-----|--------------------------|---------|----------------|---------------|-----------|
| 33% MDEA | 116 | 1.09%                    | 0.49    | 1.2            | 5.0           | 2.4       |
| 35% DEA  | 220 | 48 ppm                   | 0.35    | 2.7            | 9.2           | 5.5       |
| 50% DGA  | 230 | 400 ppm                  | 0.35    | 1.5            | 9.5           | 7.1       |
| 18% MEA  | 350 | 60 ppm                   | 0.40    | 5.6            | 14.4          | 7.9       |

Table 16: Effect on amine solution on CO<sub>2</sub> overhead, case 1(3.5% CO<sub>2</sub>)

The effect of MDEA circulation rate, the residence time of liquid on the tray, and temperature on amine based CO<sub>2</sub> and H<sub>2</sub>S overhead of the absorber were investigated as shown in Figures 47, 48 and 49.

Each of these parameters have been disrupted by the basic conditions given above. As expected, CO<sub>2</sub> and H<sub>2</sub>S expenses continued to decline with increased flow rate. Below 80 gpm, overhead CO<sub>2</sub> increases very rapidly, leading to good conditions for the rejection of CO<sub>2</sub> in the sweet gas. As shown in Figure 48 above for the given operating conditions, overhead CO<sub>2</sub> is very sensitive to the residence time of liquid while H<sub>2</sub>S is not.

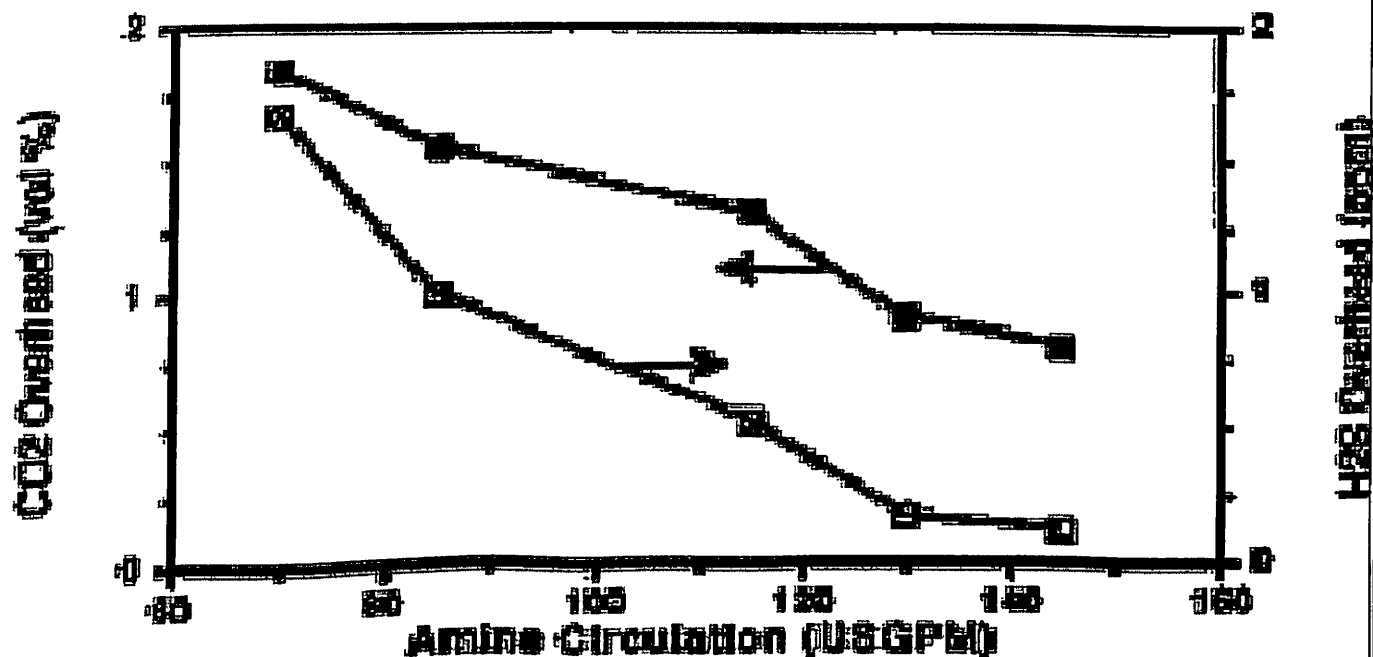


Figure 47: Effect of amine circulation on acid gas overhead: Case 1 (3.5% CO<sub>2</sub>)

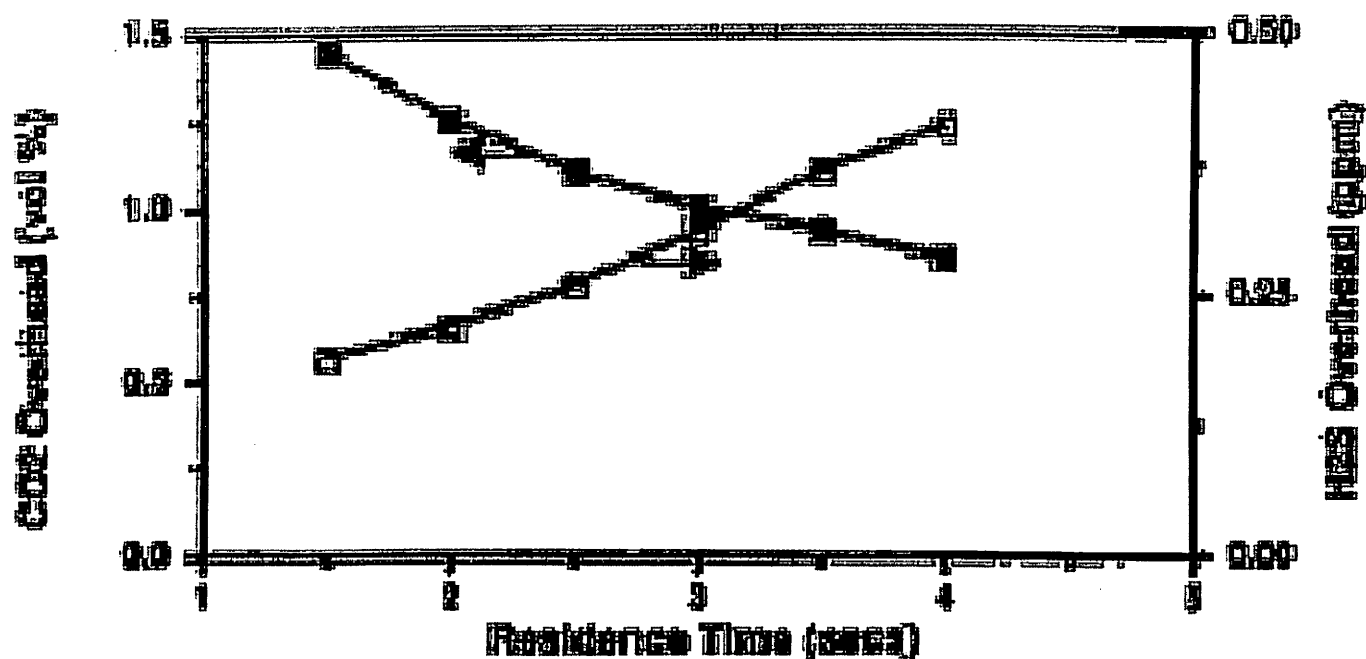


Figure 48: Effect of residence time on acid gas overhead: Case 1 (3.5% CO<sub>2</sub>)

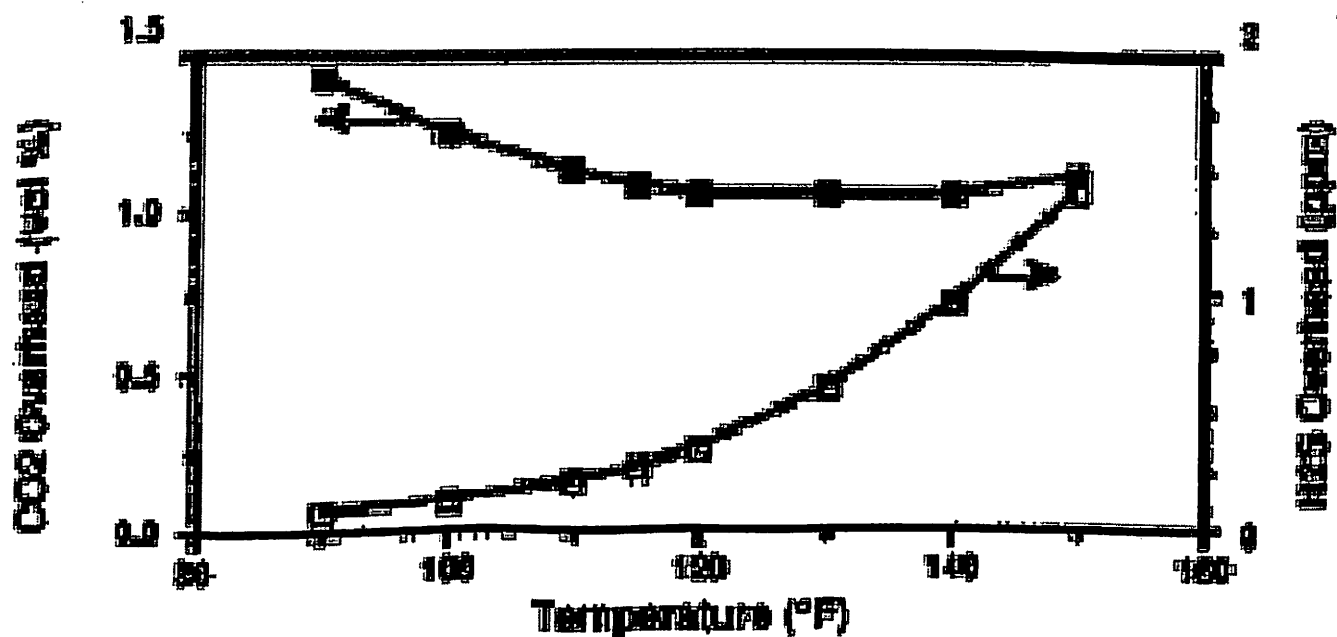


Figure 49: Effect of lean amine temperature on acid gas overhead: Case 1 (3.5% CO<sub>2</sub>)

The competitive effects of solubility and kinetic reaction rates are shown in Figure 49 where the overhead of CO<sub>2</sub> goes through a minimum around the 120-130°F temperature lean amine. Below



110°F, the kinetic effects tend to dominate in this case while high on the solubility limits 140°F start controlling.

The addition of DEA to MDEA solution will increase the collection of CO<sub>2</sub> for the entire residence time of the liquid is not given the trends discussed above should hold for MDEA.

## CASE 2 - HIGH CO<sub>2</sub>

The gas at the entrance of this case was selected at 800 psia with 15% CO<sub>2</sub>. The base operating conditions were selected to be 50% by weight of MDEA, 350 gpm flow, the temperature of 115°F lean amine and 2.5 sec residence time of liquid on each tray. The flow arrangement was a standard sweetening unit with a flash tank operating at 60 psia on the rich amine.

An analysis similar to Case 1 was performed. As shown in Table 17, the performance of various amines is radically different due largely to the concentration of the solution maximum, and loading. Due to degradation problems of corrosion and solution, these maximum can not be ignored, except for loading on MDEA. If the specification overhead CO<sub>2</sub> is less than 0.89%, the rate of movement of MDEA should be increased somewhat as shown in Figure 50. Once the circulation rate reaches about 380 gpm MDEA CO<sub>2</sub> is down to 0.2%.

| Amine    | GPM  | CO <sub>2</sub> Overhead | Loading | Condenser Duty | Reboiler Duty | Trim Duty |
|----------|------|--------------------------|---------|----------------|---------------|-----------|
| 50% MDEA | 350  | 0.89%                    | 0.62    | 11.86          | 23.8          | 10.1      |
| 35% DEA  | 922  | 31 ppm                   | 0.35    | 16.00          | 44.7          | 27.8      |
| 50% DGA  | 712  | 17 ppm                   | 0.35    | 25.70          | 57.6          | 30.5      |
| 18% MEA  | 1460 | 53 ppm                   | 0.40    | 20.70          | 60.7          | 38.7      |

TABLE 17: Effect of amine selection on CO<sub>2</sub> overhead, case 2 (15% CO<sub>2</sub>)

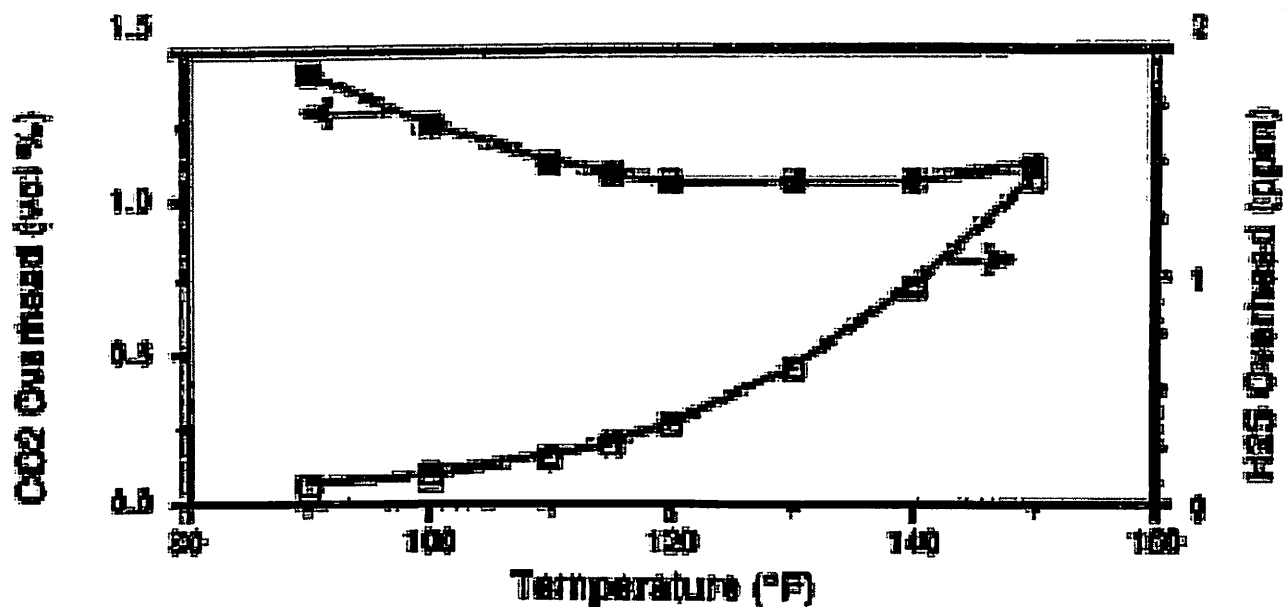


Figure 50: Effect of amine circulation rate on CO<sub>2</sub> overhead: Case 2 (15% CO<sub>2</sub>)

At a flow rate of 350 gpm, overhead CO<sub>2</sub> is only moderately sensitive liquid residence time as shown in Figure 51. Due to the entry of CO<sub>2</sub> resulting from high loading and a high solution, the effects of solubility as shown in Figure 52 becomes dominant at temperatures much lower than for Case 1.

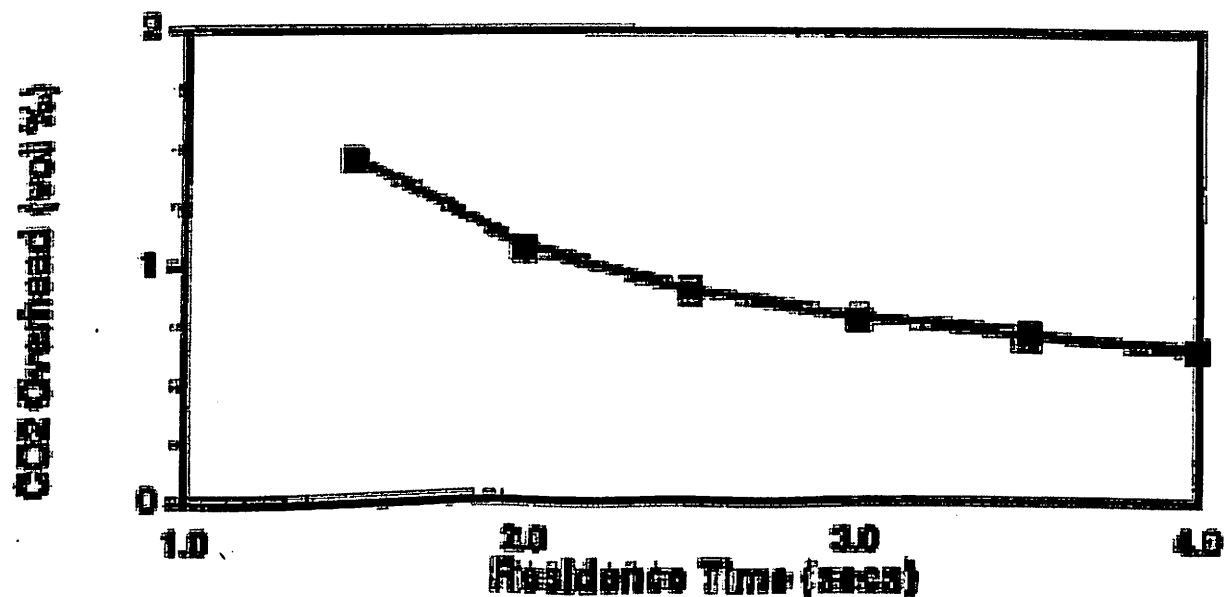


Figure 51: Effect of residence time on CO<sub>2</sub> overhead: Case 2 (15% CO<sub>2</sub>)

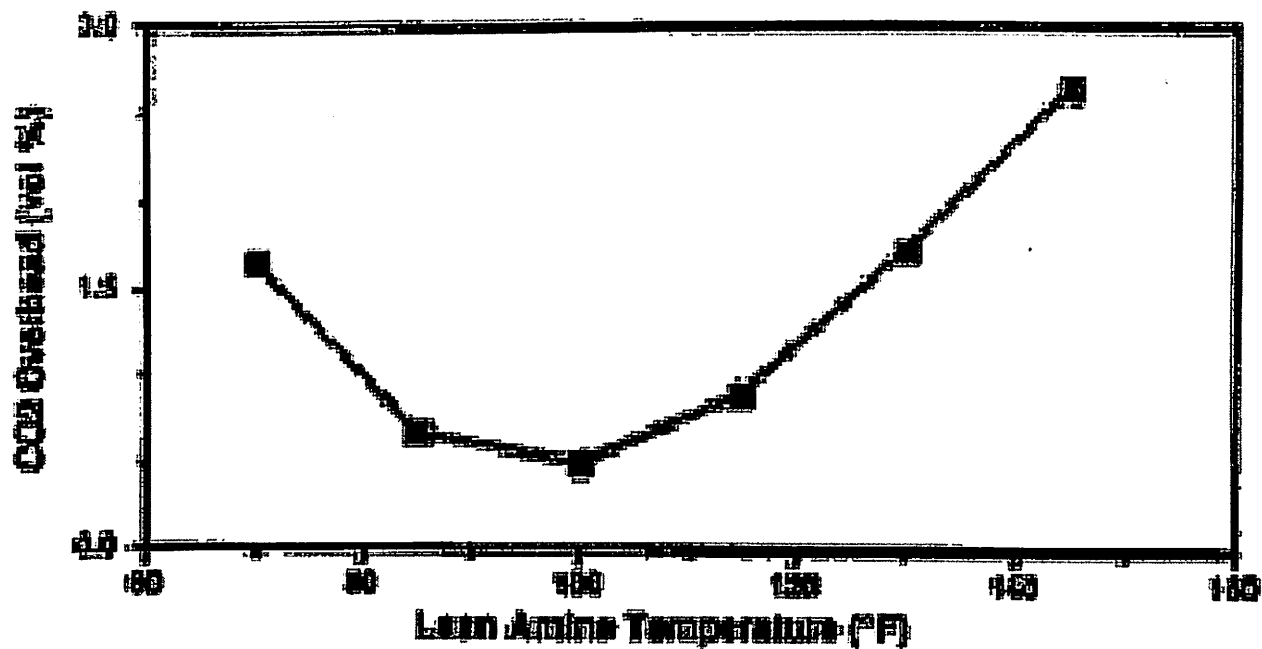


Figure 52: Effect of lean amine temperature on CO<sub>2</sub> overhead: Case 2 (15% CO<sub>2</sub>)

In the basic conditions for this case, little benefit would be realized from the addition of an amine to form a more reactive amine mixture.

### CASE 3 - EQUAL CO<sub>2</sub> and H<sub>2</sub>S:

To provide an interesting contrast in pick-up of CO<sub>2</sub> and CO<sub>2</sub> rejection, an integrated complex consisting of a sweetening unit, Claus sulfur plant and amine tailgas cleaning unit (TGCU) as shown in Figure 53 was chosen for this case. The sour gas was 5% CO<sub>2</sub> and H<sub>2</sub>S 5% to 210 psia. The basic operating conditions for the almost complete elimination of CO<sub>2</sub> in the main absorber was 50% by weight of MDEA, 200 gpm, 120 ° F lean amine temperature and liquid residence time of 1.75 sec.

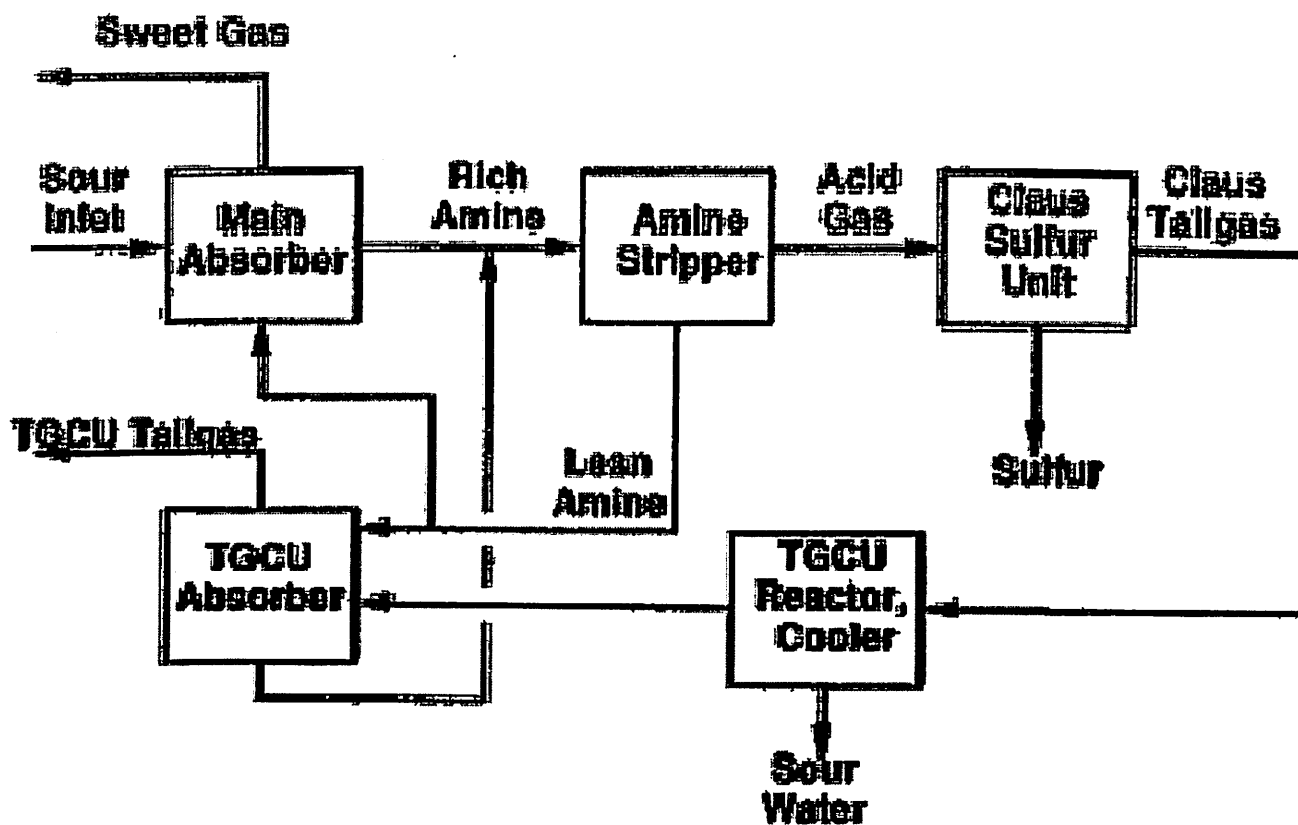


Figure 53: Schematic diagram of amine/Claus unit with tailgas cleanup unit.

An analysis of the influence of operating parameters on absorption performance was conducted and the results are shown in Figures 54, 55 and 56. Parametric studies for this case were carried out on the dampers of the unit while holding all other parameters constant. In the integrated complex shown in Figure 53, the performance of the absorbers and the Claus unit and a simulation program such as tsweet process that can handle the complete unit and integrated approach is needed. As can be seen in Figure 54, CO<sub>2</sub> and H<sub>2</sub>S Expenses increased very rapidly as the velocity decreases to about 190 gpm. For basic operating conditions given above, this



absorber could respond to a grain 1 / 4 (3.5 ppm) H<sub>2</sub>S specification with a flow rate of 200 gpm.

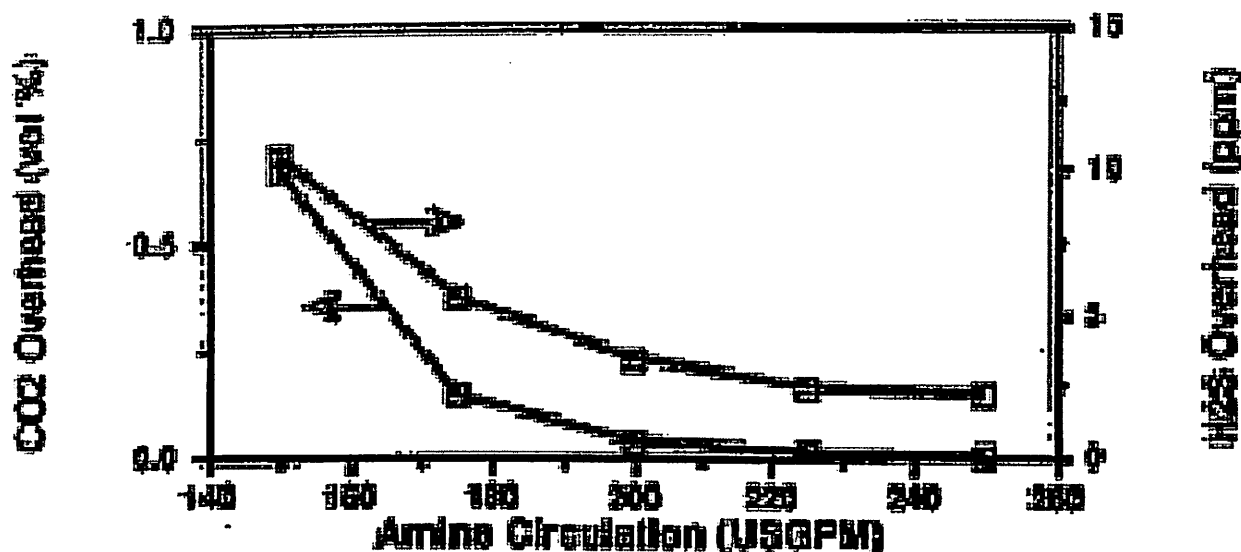


Figure 54: Effect of amine circulation on acid gas overhead: Case 3 (5% CO<sub>2</sub>, 5% H<sub>2</sub>S) Main Absorber.

As shown in Figure 55, CO<sub>2</sub> and H<sub>2</sub>S are very sensitive to changes in residence time of the liquid to about 2 sec. for the base operating conditions. Once the temperature reaches 100 ° F lean amine, the removal of CO<sub>2</sub> is not affected until it reaches 180 degrees F or so. However, as shown in Figure 56, excess H<sub>2</sub>S increases significantly above a temperature of 120 ° F lean amine.

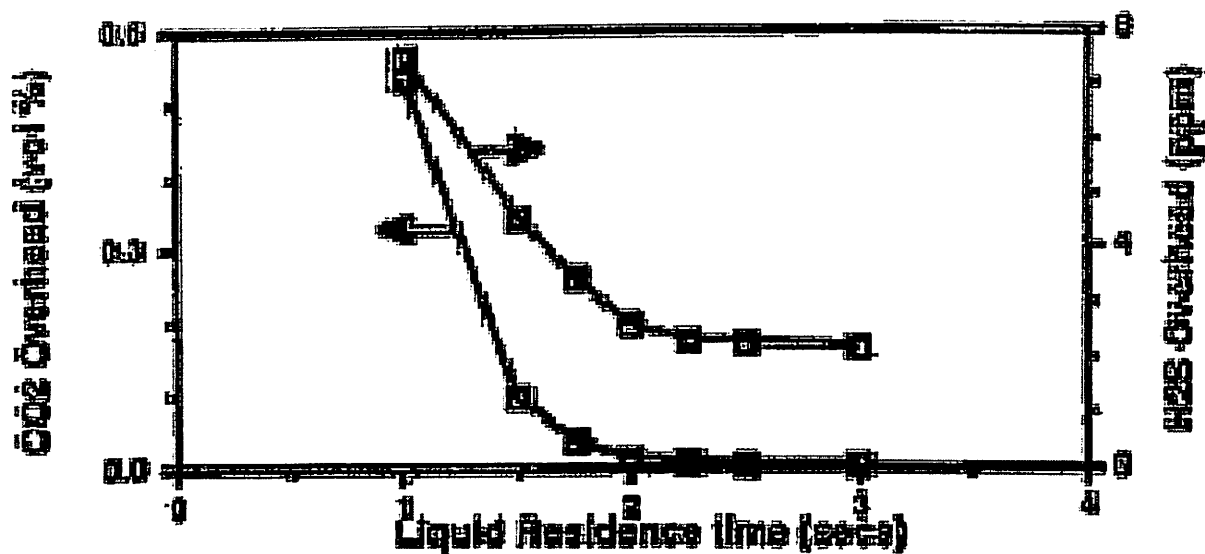


Figure 55: Effect of residence time on acid gas overhead: Case 3 (5% CO<sub>2</sub>, 5% H<sub>2</sub>S) Main Absorber.

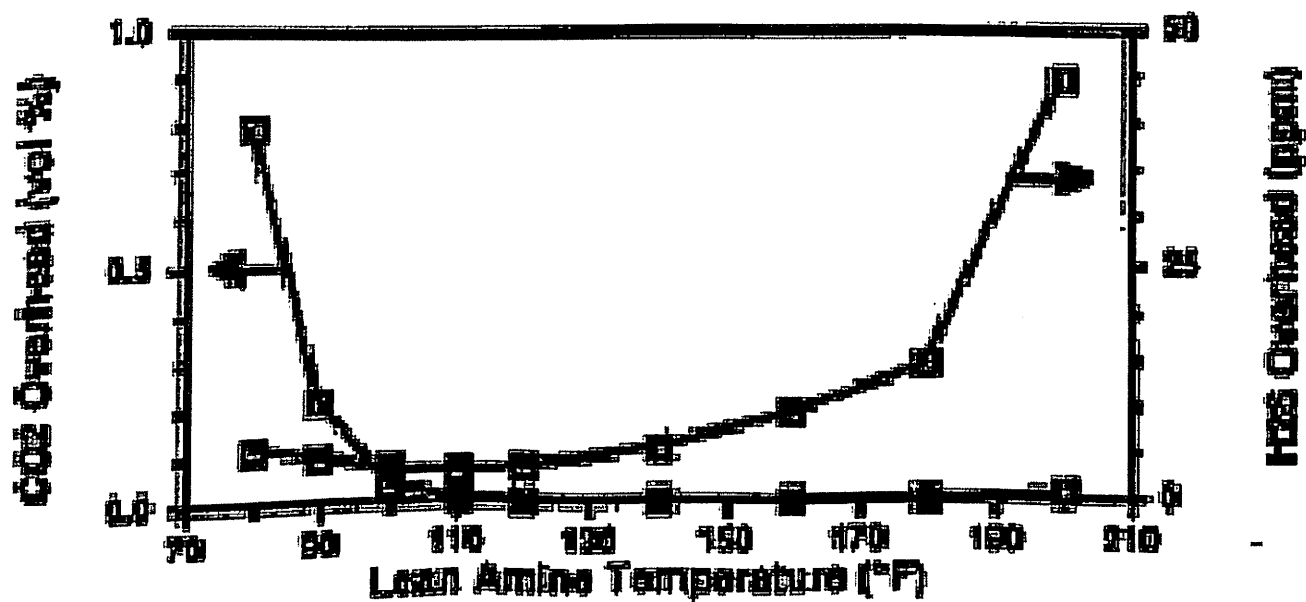


Figure 56: Effect of lean amine temperature on acid gas overhead: Case 3 (5% CO<sub>2</sub>, 5% H<sub>2</sub>S) Main Absorber.



The response of the absorber TGPU used for selective absorption provides an interesting contrast with the previous cases in bulk CO<sub>2</sub> removal. The gas to the CO<sub>2</sub> absorber was 31.6% and 0.8% H<sub>2</sub>S at a pressure of 8 bar. The base operating conditions were 50 gpm, 120 ° F temperature lean amine and 1.75 sec. residence time of the liquid. As shown in Figure 57, the CO<sub>2</sub> overhead continues to decrease with circulation rate while the H<sub>2</sub>S tends to level out at 250 ppm above 40 gpm. Figure 58 shows that the highest CO<sub>2</sub> overhead and lowest H<sub>2</sub>S is obtained at the lowest liquid residence times. As expected, the CO<sub>2</sub> overhead decreases and the H<sub>2</sub>S increases as the lean amine temperature increases as depicted in Figure 59.

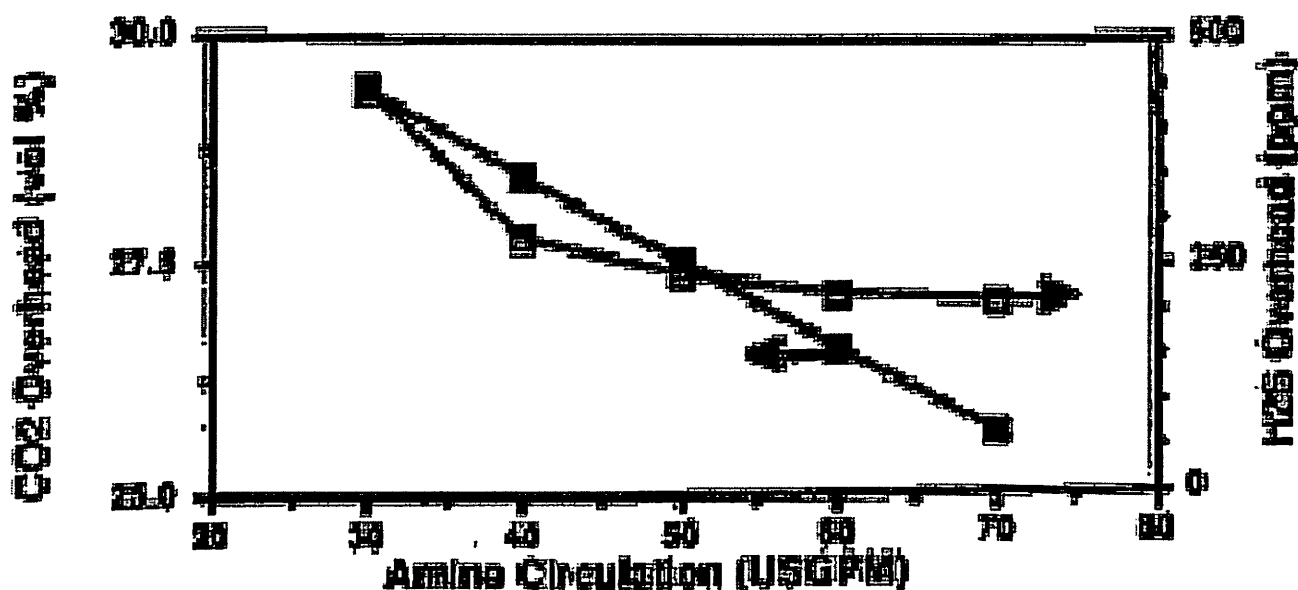


Figure 57: Effect of amine circulation on acid gas overhead: Case 3 (5% CO<sub>2</sub>, 5% H<sub>2</sub>S) TGPU Absorber.

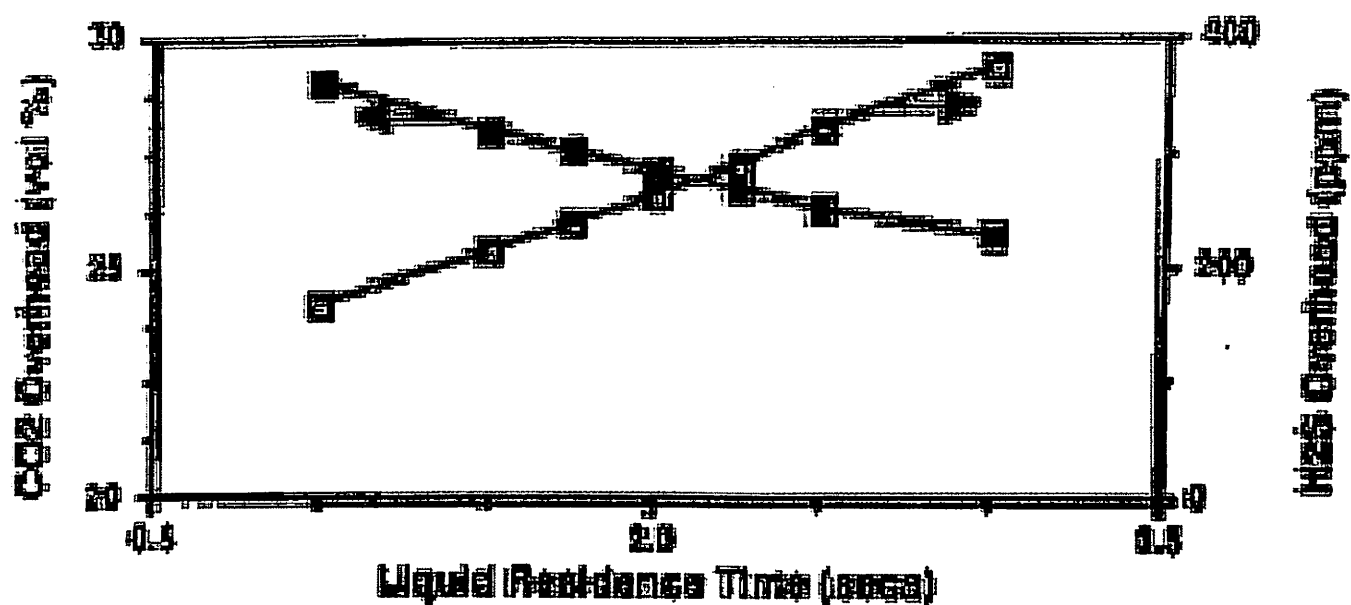


Figure 58: Effect of residence time on acid gas overhead: Case 3 (5% CO<sub>2</sub>, 5% H<sub>2</sub>S) TGCU Absorber.

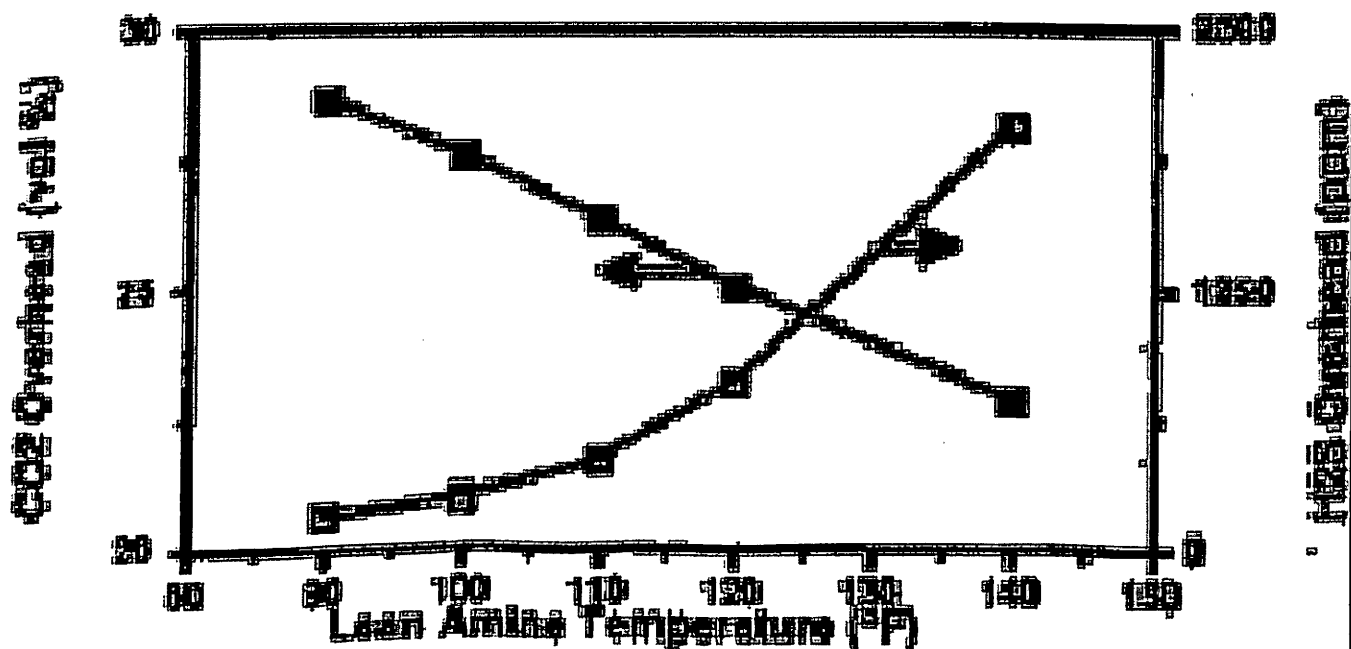


Figure 59: Effect of lean amine temperature on acid gas overhead: Case 3 (5% CO<sub>2</sub>, 5% H<sub>2</sub>S) TGCU Absorber.



## SUMMARY AND CONCLUSIONS:

The use of MDEA and mixtures of amines for CO<sub>2</sub> removal in bulk was studied for two cases of 3.5 and 15% CO<sub>2</sub> and a case with 5% CO<sub>2</sub> and 5% H<sub>2</sub>S. The first two cases involved flow conventional regimes while the second main cause of the absorber and absorber tailgas a sweetening integrated Claus unit and cleaning unit of tailgas. A simulation program called TSWEET process was used to study the effect of the amine used and important operating parameters on the performance of solutions of MDEA CO<sub>2</sub> removal in bulk.

The results showed that MDEA can be used very advantageously for the removal of CO<sub>2</sub> in bulk and for selective absorption (CO<sub>2</sub> emissions). In general, pick-up of CO<sub>2</sub> can be achieved by more residence time of liquid on the plates, higher rates of movement and higher temperatures lean amine amine up to about 120 to 140 oF. The results also show that, when using or mixtures of MDEA amines for CO<sub>2</sub> removal in bulk, the unit performance is often very sensitive to one or more operating parameters. Thus, a good parametric analysis of operating parameters must be performed in all cases.



## REFERENCES:

Kohl, Arthur L. & Nielsen, Richard B (1997). Gas Purification, Houston, Texas: Gulf Publishing Company, U.S.A.

Kidnay, Arthur J. & Parrish William R. (2006). Fundamentals Of Natural Gas Processing, Taylor & Francis Group, Boca Raton, London, U.K.

W G "Trey" Brown(2009). Selecting Gas Treating Technologies, New Point Gas, Texas, U.S.A.

Bullin, Jerry A. & Polasek, John C.(2006). The Use Of MDEA for CO<sub>2</sub> Removal: Bryan Research & Engineering, Inc., Bryan, Texas, U.S.A.



## APPENDICES:

scf = standard cubic feet of gas (60°F, 1 atm)

MMscf = million standard cubic feet of gas

s.t.p. = standard temperature and pressure (273.15 K and  $1.013 \times 10^5$  Pa)

1 grain per 100 scf = 24.19 mg/m<sup>3</sup> (s.t.p.)

1/4 grain H<sub>2</sub>S per 100 scf = 4 ppmv H<sub>2</sub>S

Volume of 1 lb mol of ideal gas at 60°F and 1 atm = 379.5 scf

Volume of 1 kmol of ideal gas at s.t.p. = 22.41 m<sup>3</sup>

Gas constant,  $R = 1.986$  Btu/lb mol °R = 8.314 J/mol K