



SLOVENSKÁ TECHNICKÁ UNIVERZITA V BRATISLAVE



Natural Gas Desulfurization

Euro Asia Partnership for Development Human Resource Capacity of
Engineering Education in Afghanistan program

Gas Sweetening/Acid Gas Removal



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Conference was very interesting for us, there were 280 participants from 27 countries of the world with 320 scientific-technical articles.

Finally, I appreciate the patience and assistance of the technical staff of Faculty of Chemical and food technology.

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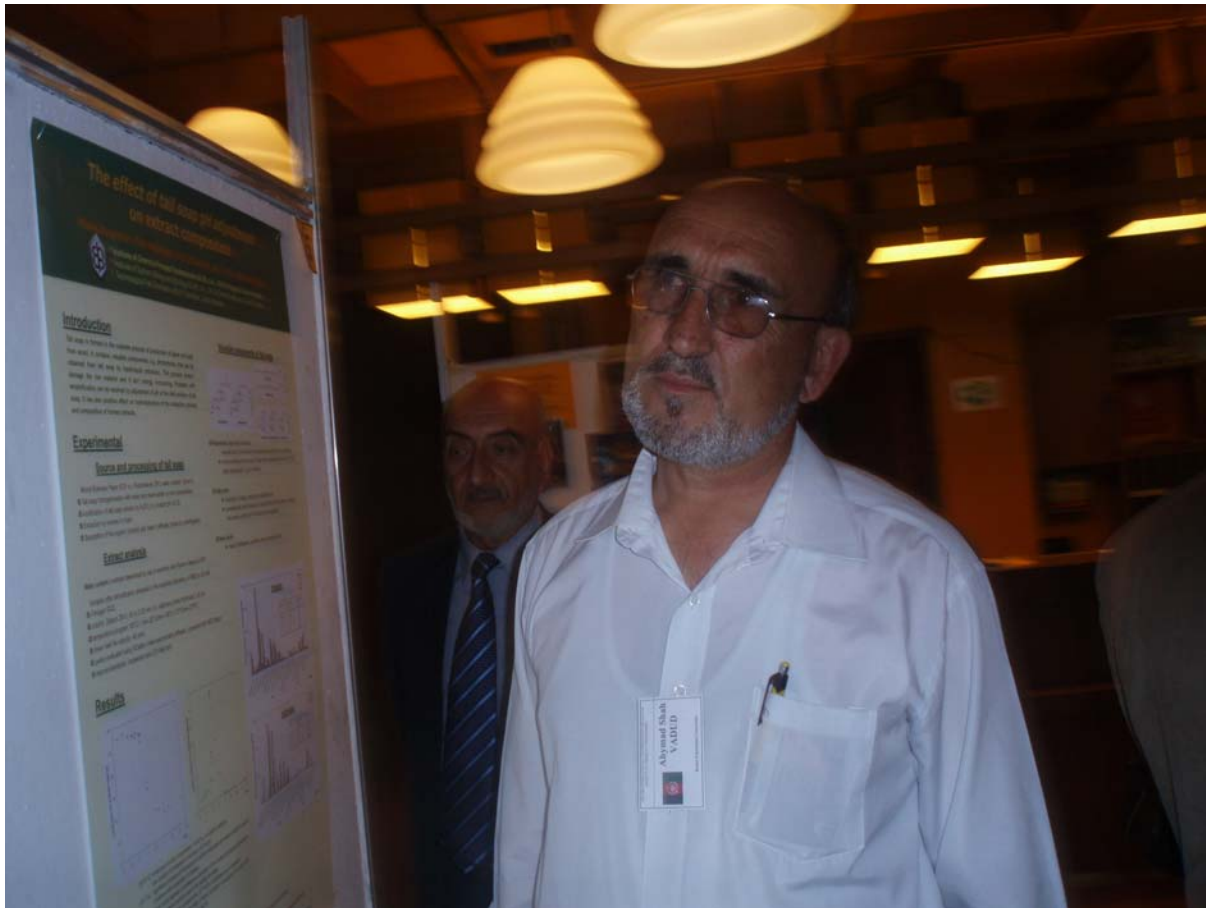


36th International Conference of Slovak Society of Chemical Engineering, Hotel Hutnik May 25-29, 2009





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Chapter 1

1.1 Introduction:

Natural gas is a subcategory of petroleum that is a naturally occurring, complex mixture of hydrocarbons, with a minor amount of inorganic compounds. Geologists and chemists agree that petroleum originates from plants and animal remains that accumulate on the sea/lake floor along with the sediments that form sedimentary rocks. The processes by which the parent organic material is converted into petroleum are not understood. The contributing factors are thought to be bacterial action; shearing pressure during compaction, heat, and natural distillation at depth; possible addition of hydrogen from deep-seated sources; presence of catalysts; and time (Allison and Palmer 1980).

Table 1 shows composition of a typical natural gas. It indicates that methane is a major component of the gas mixture. The inorganic compounds nitrogen, carbon dioxide, and hydrogen sulfide are not desirable because they are not combustible and cause corrosion and other problems in gas production and processing systems. Depending upon gas composition, especially the content of inorganic compounds, the heating value of natural gas usually varies from 700 Btu/scf to 1,600 Btu/scf.

Natural gas accumulations in geological traps can be classified as reservoir, field, or pool. A reservoir is a porous and permeable underground formation containing an individual bank of hydrocarbons confined by impermeable rock or water barriers and is characterized by a single natural pressure system. A field is an area that consists of one or more reservoirs all related to the same structural feature. A pool contains one or more reservoirs in isolated structures. Wells in the same field can be classified as gas wells, condensate wells, and oil wells. Gas wells are wells with producing gas-oil-ratio (GOR) being greater than 100,000 scf/stb;vvv temperatures.

Table 1. Composition of a Typical Natural Gas

Compound	Mole Fraction
Methane	0.8407
Ethane	0.0586
Propane	0.0220
i-Butane	0.0035
n-Butane	0.0058
i-Pentane	0.0027
n-Pentane	0.0025
Hexane	0.0028
Heptanes and Heavier	0.0076
Carbon Dioxide	0.0130
Hydrogen Sulfide	0.0063
Nitrogen	0.034
Total	1.0000

Condensate wells are those with producing GOR being less than 100,000 scf/stb but greater than 5,000 scf/stb; and wells with producing GOR being less than 5,000 scf/stb are classified as oil wells.

Because natural gas is petroleum in a gaseous state, it is always accompanied by oil that is liquid petroleum. There are three types of natural gases: nonassociated gas, associated gas, and gas condensate. Nonassociated gas is from reservoirs with minimal oil. Associated gas is the gas dissolved in oil under natural conditions in the oil reservoir. Gas condensate refers to gas with high content of liquid hydrocarbon at reduced pressures and temperatures.

The geological and geophysical studies to date indicate that all oil and gas fields existing in Afghanistan (6 oil fields and 7 gas fields) are within the Karakum oil & gas bearing basin, occupying an area of 57,000 km², situated in northern Afghanistan and constituting a south-eastern extension of the Turkmenistan basin of the same name.

At present Afghanistan is an energy-poor country. The greater part of its primary energy requirements are met by renewable but unsustainable sources such as fuel wood and charcoal. The entirety of its liquid fuel needs is imported, while the country's hydropower production is at the mercy of erratic rainfall. Unless something is done, the natural population growth and economic recovery will make the energy situation more precarious.

Major prospective structures that are blueprinted for further oil and gas exploration are also confined to this basin.

The total initial geological reserves of the 7 discovered gas fields amount to 145.1 billion m³.

Converted into western standards the remaining recoverable gas reserves would be (billion m³)

Table 2: Gas field reserves in northern Afghanistan

Gas Field	Cumulative Production 1/1/2003	Proved Recoverable Reserves	Probable Recoverable Reserves	Possible Recoverable Reserves	Proved and Probable	Proved + Probable + Possible
Khwaja Gogerdag	41.53	0.30	2.93	5.02	3.23	8.25
Jarkoduk	15.10	4.13	1.27	2.27	5.40	7.67
Yatim Tak	1.74*	2.68	0.52	0.30	3.20	3.50
Juma		10.74	0.71	6.78	11.45	18.23
Jangali Kalon		6.45	5.46	6.09	11.91	18.00
Bashi Cord		3.35	1.90	2.92	5.25	8.17
Khwaja Bulan		1.90	0.13	0.13	2.03	2.16
Total	58.47*	29.55	12.92	23.51	42.47	65.98

Note: * including 1.7 bm³ lost in blow-out



Figure 1: Oil & Gas Reserves and Potential Resources in northern Afghanistan

1.2 Natural Gas Industry

The consumption of natural gas in all end-use classifications (residential, commercial, industrial, and power generation) has increased rapidly since World War II. This growth has resulted from several factors, including development of new markets, replacement of coal as fuel for providing space and industrial process heat, use of natural gas in making petrochemicals and fertilizers, and strong demand for low-sulfur fuels.

The rapidly growing energy demands of Western Europe, Japan, and the United States could not be satisfied without importing gas from far fields. Natural gas, liquefied by a refrigeration cycle, can now be transported efficiently and rapidly across the oceans of the world by insulated tankers. The use of refrigeration to liquefy natural gas, and hence reduce its volume to the point where it becomes economically attractive to transport across oceans by tanker, was first attempted on a small scale in Hungary in 1934 and later used in the United States for moving gas in liquid form from the gas fields in Louisiana up the Mississippi River to Chicago in 1951 (Ikoku 1984).

The first use of a similar process on a large scale outside the United States was the liquefaction by a refrigerative cycle of some of the gas from the Hassi R'Mel gas field in Algeria and the export from 1964 onward of the resultant liquefied natural gas (LNG) by specially designed insulated tankers to Britain and France. Natural gas is in this way reduced to about

one six-hundredth of its original volume and the nonmethane components are largely eliminated. At the receiving terminals, the LNG is reconverted to a gaseous state by passage through a regasifying plant, whence it can be fed as required into the normal gas distribution grid of the importing country. Alternatively, it can be stored for future use in insulated tanks or subsurface storages. Apart from its obvious applications as a storable and transportable form of natural gas, LNG has many applications in its own right, particularly as a nonpolluting fuel for aircraft and ground vehicles. Current production from conventional sources is not sufficient to satisfy all demands for natural gas.

1.3 Future of the Natural Gas Industry

It is well recognized that the nineteenth century was a century of coal that supported the initiation of industrial revolution in Europe. The twentieth century was the century of oil that was the primary energy source to support the growth of global economy. Figure shows world energy consumption in the past three decades and forecast for the next two decades(DOE/EIA 2001). It indicates that the demand of the world's economy for energy is ever increasing. Simmons (2000) concluded that energy disruptions should be a "genuine concern." Simmons suggests that it will likely cause chronic energy shortage as early as 2010. It will eventually evolve into a serious energy crunch.

The way to avoid such a crunch is to expand energy supply and move from oil to natural gas and, eventually, to hydrogen. Natural gas is the fuel that is superior to other energy sources not only in economic attractiveness but also in environmental concerns. At the end of the last century, natural gas took over the position of coal as the number two energy source behind oil. In 2000, total world energy consumption was slightly below 400 quadrillion

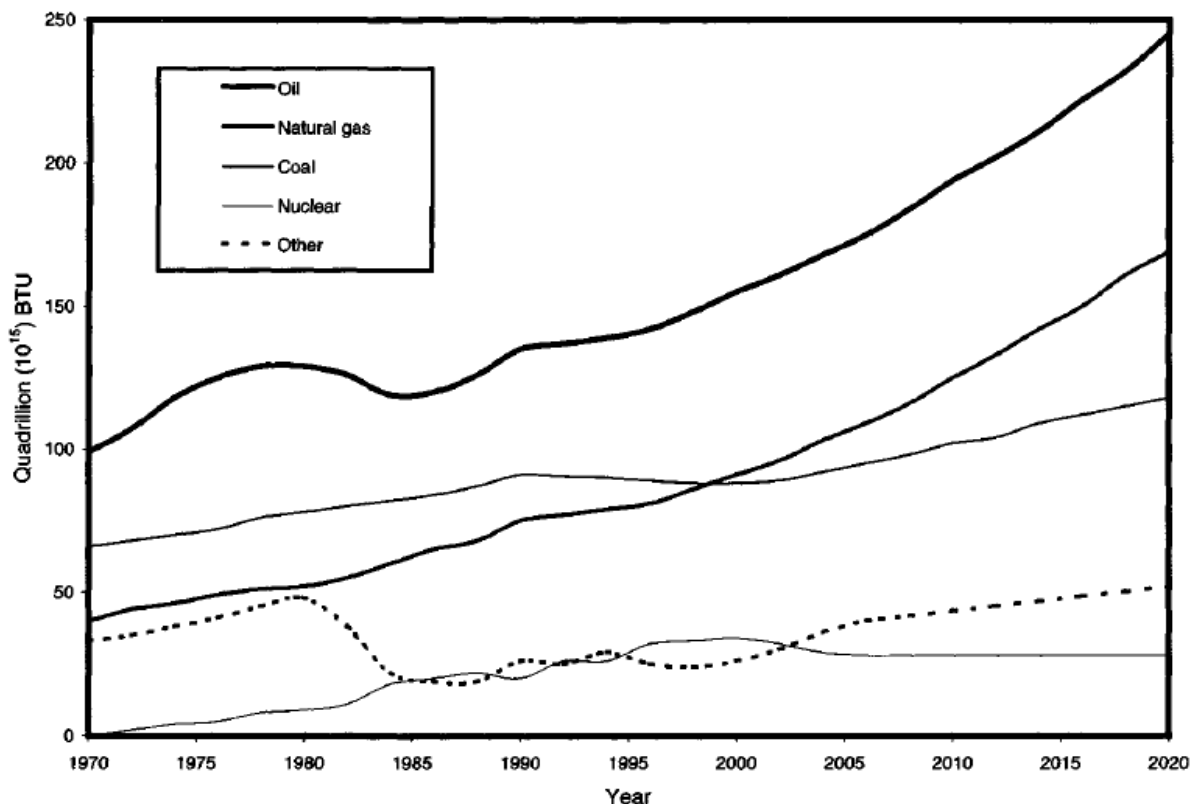


Figure 2 World energy consumption and forecast from 1970 to 2020

1.4 Natural Gas Treating

Gas treating involves reduction of the “acid gases” carbon dioxide (CO₂) and hydrogen sulfide (H₂S), along with other sulfur species, to sufficiently low levels to meet contractual specifications or permit additional processing in the plant without corrosion and plugging problems. This part focuses on acid and gases Gas treating involves reduction of the “acid gases” carbon dioxide (CO₂) and hydrogen sulfide (H₂S), along with other sulfur species, to sufficiently low levels to meet contractual specifications or permit additional processing in the plant without corrosion and plugging problems. This part focuses on acid gases

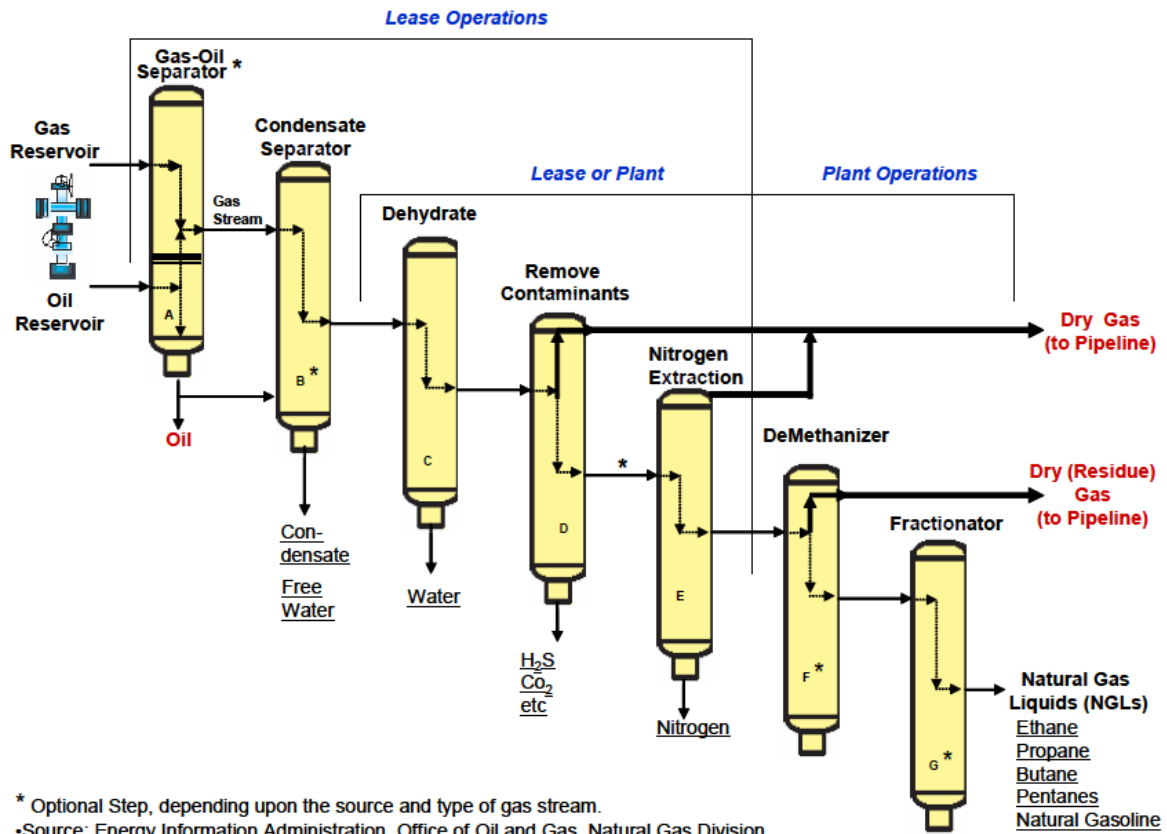


Figure 3

1.4.1 THE PROBLEM

Hydrogen sulfide is highly toxic, and in the presence of water it forms a weak, corrosive acid. The threshold limit value (TLV) for prolonged exposure is 10 ppmv and at concentrations greater than 1,000 ppmv, death occurs in minutes (Engineering Data Book, 2004b). It is readily detectable at low concentrations by its “rotten egg” odor. Unfortunately, at toxic levels, it is odorless because it deadens nerve endings in the nose in a matter of seconds.

When H₂S concentrations are well above the ppmv level, other sulfur species can be present. These compounds include carbon disulfide (CS₂), mercaptans (RSH), and sulfides (RSR), in addition to elemental sulfur. If CO₂ is present as well, the gas may contain trace amounts of carbonyl sulfide (COS). The major source of COS typically is formation during regeneration of molecular-sieve beds used in dehydration.

Carbon dioxide is non-flammable and, consequently, large quantities are undesirable in a fuel. Like H₂S, it forms a weak, corrosive acid in the presence of water.

The presence of H₂S in liquids is usually detected by use of the copper

strip test (ASTM D1838 Standard test method for copper strip corrosion by liquefied petroleum (LP) gases). This test detects the presence of materials that could corrode copper fittings. One common method of determining ppm levels of H₂S in gases is to use stain tubes, which involves gas sampling into a glass tube that changes color on the basis of H₂S concentration. This method is good for spot and field testing. A newer, continuous method measures reflectance off of a lead acetate-coated tape that darkens in the presence of H₂S. The test (ASTM D4084 Standard test method for analysis of hydrogen sulfide in gaseous fuels (Lead Acetate reaction rate method) 2005) detects H₂S down to 0.1 ppmv. It is specific to H₂S but used to detect total sulfur by hydrogenating the sulphur species in the gas before going to the detector.

The composition of natural gas in northern Afghanistan is:

Table 3. Composition of natural gas in northern Afghanistan

Compound	%, Mole Fraction
Methane	94.849
Ethane	1.0565
Propane	0.142
n-Butane	0.049
n-Pentane	0.096
Hydrogen Sulfide	0.035
Carbon Dioxide	3.19
Nitrogen	0.58

1.4.2 ACID GAS CONCENTRATIONS IN NATURAL GAS

Although many natural gases are free of objectionable amounts of H₂S and CO₂, substantial quantities of these impurities are found in both gas reserves and production in the United States. In a survey of U.S. gas resources, Meyer (2000) defined sub quality gas as that containing CO₂ ≥ 2%, N₂ ≥ 4%, or H₂S ≥ 4 ppmv. These criteria were selected because gases that contain these amounts of impurities generally require upgrading or blending. Using these criteria, Meyer (2000) estimated that 41% of proven gas reserves are subquality and 34% of 1996 gas production in the lower 48 states was subquality.

For associated gas reserves, they estimated that 13% was sub quality. It is obvious that removal of H₂S and CO₂ is a major concern in gas processing

1.4.3 PURIFICATION LEVELS

The inlet conditions at a gas processing plant are generally temperatures near ambient and pressures in the range of 300 to 1,000 psi (20 to 70 bar), so the partial pressures of the entering acid gases can be quite high. If the gas is to be purified to a level suitable for transportation in a pipeline and used as a residential or industrial fuel, then the H₂S concentration must be reduced to 0.25 gr/100 scf (6 mg/m³) (Engineering Data Book, 2004a), and the CO₂ concentration must be reduced to a maximum of 3 to 4 mol%. However, if the gas is to be processed for NGL recovery or nitrogen rejection in a cryogenic turboexpander process, CO₂ may have to be removed to prevent formation of solids. If the gas is being fed to an LNG liquefaction facility, then the maximum CO₂ level is about 50 ppmv (Klinkenbijn et al., 1999) because of potential solids formation.

1.4.4 ACID GAS DISPOSAL

What becomes of the CO₂ and H₂S after their separation from the natural gas? The answer depends to a large extent on the quantity of the acid gases.

For CO₂, if the quantities are large, it is sometimes used as an injection fluid in EOR (enhanced oil recovery) projects. Several gas plants exist to support CO₂ flooding projects; the natural gas and NGL are valuable byproducts.

If this option is unavailable, then the gas can be vented, provided it satisfies environmental regulations for impurities. Moritis (2001) gives a general discussion of the state of EOR in the United States. Although the United States has not ratified the Kyoto Treaty, which limits CO₂ emissions to the atmosphere, caps may be placed on these emissions because of the preponderance of scientific data that shows CO₂ is a significant contributor to global warming.

In the case of H₂S, four disposal options are available:

1. Incineration and venting, if environmental regulations regarding sulfur dioxide emissions can be satisfied
2. Reaction with H₂S scavengers, such as iron sponge
3. Conversion to elemental sulfur by use of the Claus or similar process
4. Disposal by injection into a suitable underground formation, as discussed by Wichert and Royan (1997) and Kopperson et al. (1998 a,b)

The first two options are applicable to trace levels of H₂S in the gas, and the last two are required if concentrations are too high to make the first two options feasible.

1.4.5 PURIFICATION PROCESSES

Four scenarios are possible for acid gas removal from natural gas:

1. CO₂ removal from a gas that contains no H₂S
2. H₂S removal from a gas that contains no CO₂
3. Simultaneous removal of both CO₂ and H₂S
4. Selective removal of H₂S from a gas that contains both CO₂ and H₂S

Because the concentrations of CO₂ and H₂S 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.

processes and groups them into the generally accepted categories. Details of processes not discussed in this chapter may be found in the handbook by Kohl and Nielsen (1997).

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, CS₂, 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 [3.4 bar] or higher) of the acid gases in the feed favor 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 by products considered hazardous chemicals.

If gas sweetening is required offshore, both size and weight are additional factors that must be considered. Whereas CO₂ removal is performed offshore, H₂S removal is rarely done unless absolutely necessary because of the problems of handling the rich acid gas stream or elemental sulfur.

Selection criteria for the solvent-based processes are discussed by Tennyson and Schaaf(1977) and Figur 1-4 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. Table below, adapted from Echterhoff (1991), presents a detailed

summary of the more widely used acid gas processes, including degree of purification attainable, selectivity for H₂S removal, and removal of the sulfur compounds COS, CS₂, and mercaptans. As a rule, these sulfur compounds exist at much lower concentrations than do H₂S, but their removal is important if product specifications have an upper limit on total sulfur. Note that in cases of deep liquids recovery, most of the COS, CS₂, and mercaptans present in the feed will stay with the liquid product (NGL). The amines are susceptible to degradation by O₂, which forms undesirable and corrosive compounds.

In this discussion, we consider only the more commonly used amine processes, an alkali salt process (hot potassium carbonate), the Selexol physical absorption process, molecular sieve adsorption, the Ryan/Holmes cryogenic fractionation process, membranes, and H₂S scavengers. For a more comprehensive discussion of acid gas purification, the reader should refer to Kohl and Nielsen (1997) and Engineering Data Book (2004b).

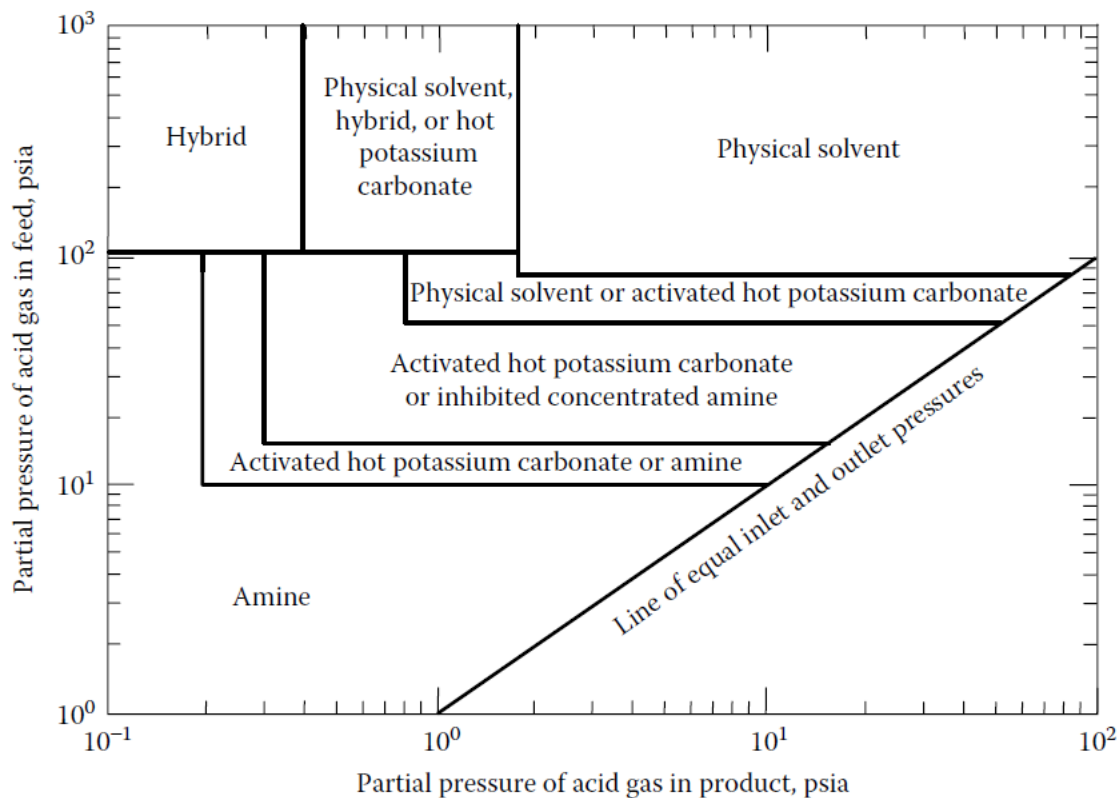


FIGURE 4 Process selection chart for CO₂ removal with no H₂S present. (Adapted from Tennyson and Schaaf, 1977.)

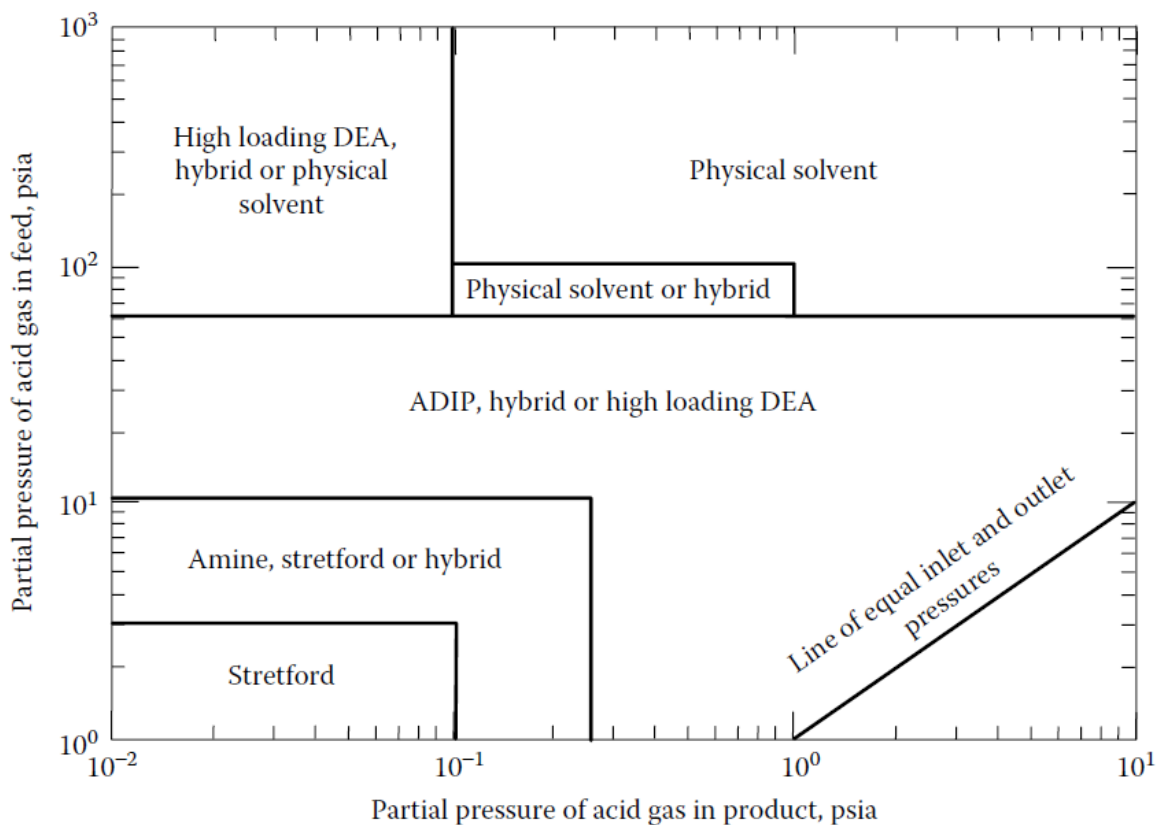


FIGURE 5 Process selection chart for H₂S removal with no CO₂ present. (Adapted from Tennyson and Schaaf, 1977.)

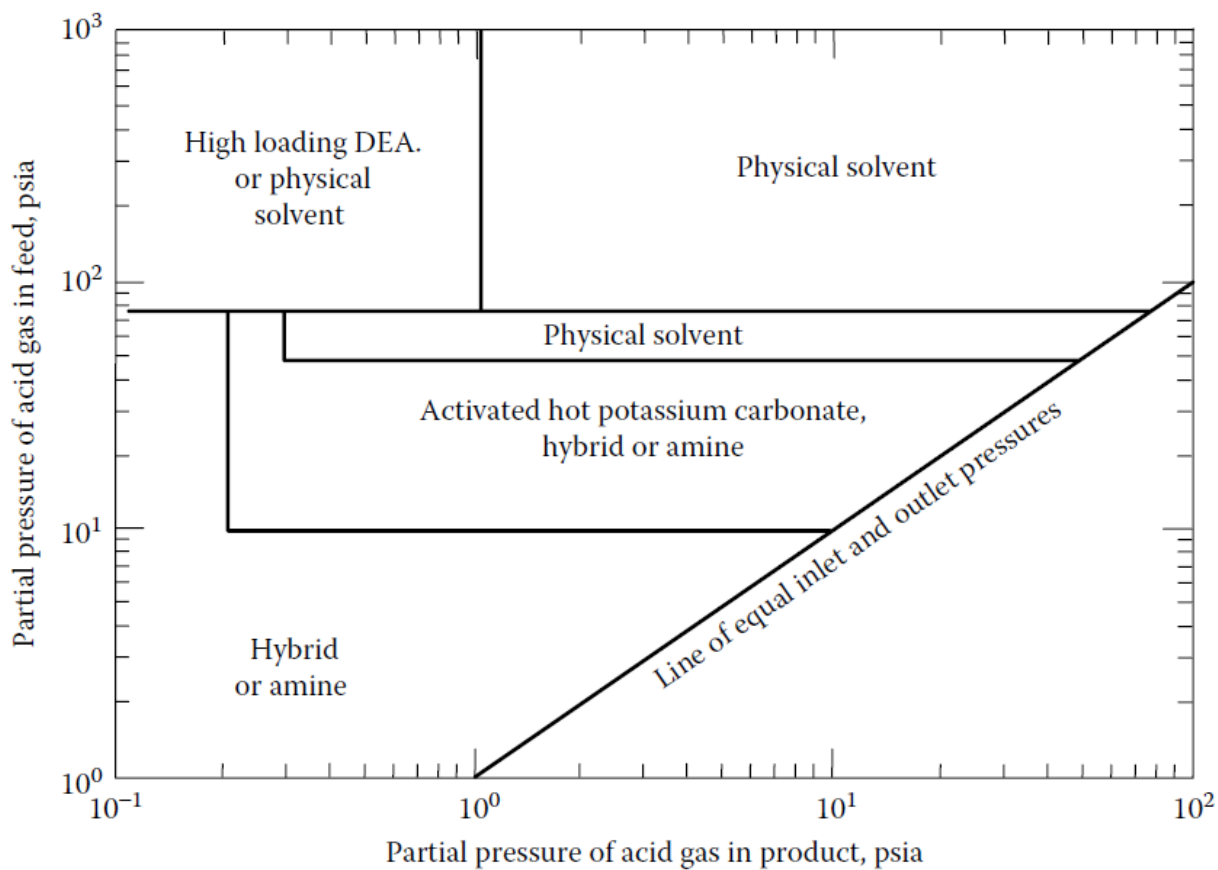


FIGURE 6 Process selection chart for simultaneous H₂S and CO₂ removal. (Adapted from Tennyson and Schaaf, 1977.)

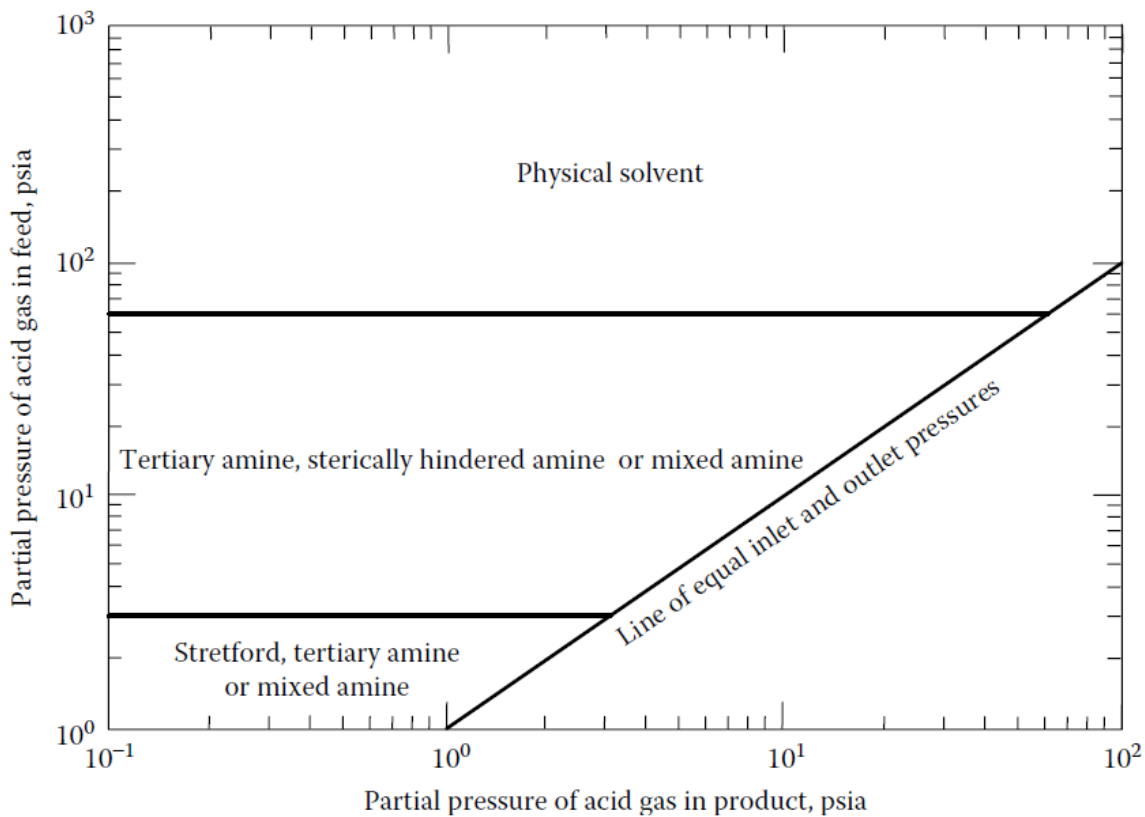


FIGURE 7 Process selection chart for selective H₂S removal with CO₂ present. (Adapted from Tennyson and Schaaf, 1977.)

1.4.6

CO₂ and H₂S Removal Processes for Gas Streams

Process	Normally Capable of Meeting H ₂ S Specification ^a	Removes COS, CS ₂ , and Mercaptans	Selective H ₂ S Removal	Minimum CO ₂ Level Obtainable	Solution Subject to Degradation? (Degrading Species)
Monoethanol-amine (MEA)	Yes	Partial	No	100 ppmv at low to moderate pressures	Yes (COS, CO ₂ , CS ₂ , SO ₂ , SO ₃ and mercaptans)
Diethanol amine (DEA)	Yes	Partial	No	50 ppmv in SNEA-DEA process	Some (COS, CO ₂ , CS ₂ , HCN and mercaptans)
Triethanol amine (TEA)	No	Slight	No	Minimum partial pressure of 0.5 psia (3 kPa)	Slight (COS, CS ₂ and mercaptans)
Methyldiethanol-amine (MDEA)	Yes	Slight	Some	Bulk removal only	No
Diglycol amine (DGA)	Yes	Partial	No	100 ppmv at moderate to high pressures	Yes (COS, CO ₂ , and CS ₂)
Diisopropanol-amine (DIPA)	Yes	COS only	Yes	Not applicable	Resistant to degradation by COS
Sulfinol	Yes	Partial	Yes (Sulfinol-M)	50 ppmv, 50% slippage while meeting H ₂ S product spec	Some (CO ₂ and CS ₂)
Hot potassium carbonate	Yes, with special design features	Partial	No	Not reported	Not reported
Stretford	Yes	No	Yes	No significant amounts of CO ₂ are removed	Yes (CO ₂ at high concentrations)

CO₂ and H₂S Removal Processes for Gas Streams

Process	Normally Capable of Meeting H ₂ S Specification ^a	Removes COS, CS ₂ , and Mercaptans	Selective H ₂ S Removal	Minimum CO ₂ Level Obtainable	Solution Subject to Degradation? (Degrading Species)
Selexol®	Yes	Slight	Some	Can be slipped or absorbed	No
Rectisol	Yes	Yes	No	1 ppmv	Not reported
Molecular sieves	Yes	Yes (excluding CS ₂)	Some	Can meet cryogenic spec when CO ₂ feed content is less than ~2%	Not applicable
Membranes	No	Slight	No	Feed concentration dependent	Not applicable

^a H₂S specification is 25% grain H₂S per 100 scf (6 mg/m³)

Source: Adapted from Echterhoff, 1991.

1.4.7 SOLVENT ABSORPTION PROCESSES

In solvent absorption, the two major cost factors are the solvent circulation rate, which affects both equipment size and operating costs, and the energy requirement for regenerating the solvent. Table (below) summarizes some of the advantages and disadvantages of chemical and physical solvents.

1.4.8

Comparison of Chemical and Physical Solvents

Chemical Solvents	
Advantages	Disadvantages
Relatively insensitive to H_2S and CO_2 partial pressure	High energy requirements for regeneration of solvent
Can reduce H_2S and CO_2 to ppm levels	Generally not selective between CO_2 and H_2S
	Amines are in a water solution, and thus the treated gas leaves saturated with water
Physical Solvents	
Advantages	Disadvantages
Low energy requirements for regeneration	May be difficult to meet H_2S specifications
Can be selective between H_2S and CO_2	Very sensitive to acid gas partial pressure

1.5 Gas Sweetening using DEA

This application brief presents the case of sweetening (purifying) a sour gas from a natural gas well. Several unit operations are employed to simulate a typical gas sweetening process configuration. Once the sour gas components have been removed, the scrubbing liquor is regenerated to remove captured sour components. These components are corrosive and metal selection can be an issue.

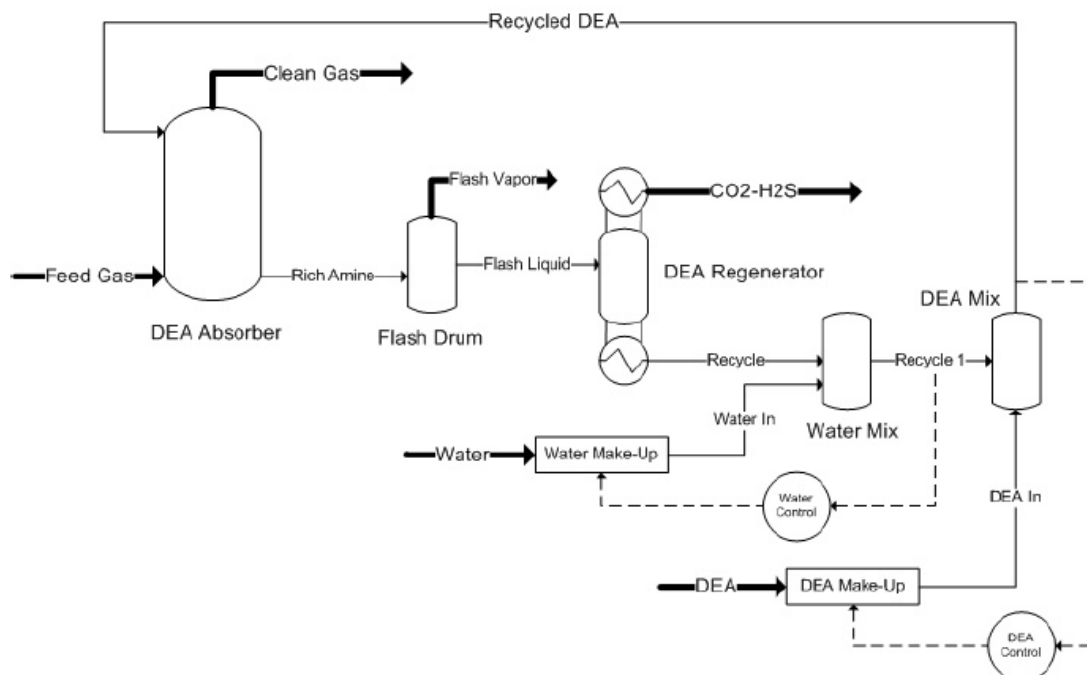


Figure8: Diethanolamine gas sweetening process flow sheet

1.5.1 The Application

A natural gas stream is approximately two mole percent (mol%) sour. This means that for every 100 moles of gas there are 2 moles of hydrogen sulfide (H₂S). In addition to H₂S, it is desirable to remove carbon dioxide (CO₂) since this constituent lowers the heating value of the gas and increases the volume of gas that must be transported. Most all alkanolamine plants are designed to maximize the removal of both of these “acid” gases.

In a typical gas cleaning plant, natural gas is fed to an absorber operating at high pressure. The gas is scrubbed using an approximately 58 weight percent (wt%) diethanolamine (DEA) solution. The scrubbed “sweet” gas is sent on for further processing or drying and transport via pipeline.

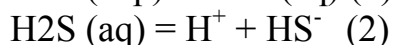
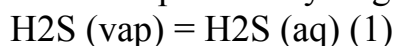
The rich DEA solution exiting the absorber is sent to a flash drum operating at a much lower pressure. This step removes any light-end hydrocarbons that were captured in the absorber. The light-end gases are sent on for further processing. Next, the hydrocarbon-free DEA solution is fed to a regeneration column. Here heat is applied to strip the acid gas components out of the DEA solution. Make-up water and DEA are added to maintain the lean 58 wt% DEA solution. This solution is then recycled to the absorber.

1.5.2 Consider the Chemistry

Why does adding DEA remove H₂S and CO₂?

Consider the vapor-liquid equilibrium and acid/base chemistry for hydrogen sulfide and carbon dioxide.

The absorption of hydrogen sulfide gas follows these equilibria:



Adding a basic reagent such as DEA increases the pH of the solution. pH is defined as:

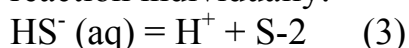
$$\text{pH} = -\log a_{\text{H}^+} \quad (4)$$

where a_{H^+} is the activity of the hydrogen ion. The activity of the hydrogen ion is defined as:

$$a_{\text{H}^+} = \gamma_{\text{H}^+} [\text{H}^+] \quad (5)$$

where γ_{H^+} is the activity coefficient for hydrogen ion and $[\text{H}^+]$ is the concentration of hydrogen ion.

As pH increases, the concentration of hydrogen ion decreases. As hydrogen ion decreases, the equilibria above shift to restore the equilibrium. Let's look at each reaction individually:

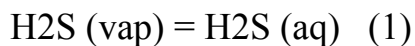


As hydrogen ion concentration decreases, this equilibrium will dissociate more

bisulfide ion (HS^-) to replace the hydrogen ion. We see that the bisulfide ion concentration will also decrease as the hydrogen ion decreases.

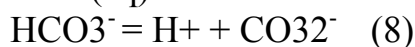
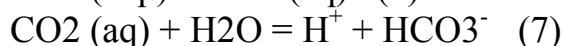
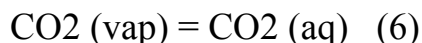


This equilibrium will also shift to the right (decreasing the hydrogen sulfide concentration) as the hydrogen ion concentration decreases. A double effect occurs since the bisulfide ion is also decreasing.



As the aqueous hydrogen sulfide concentration decreases, the amount of hydrogen sulfide remaining in the vapor phase will also decrease. This is why scrubbing of an acid gas using a basic solution works.

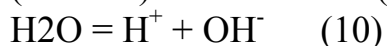
Carbon dioxide follows a similar equation path:



For similar reasons as with hydrogen sulfide, increasing the solution pH will cause more carbon dioxide to be absorbed.

1.5.3 Where does the basic reagent come from?

Adding DEA ($(\text{C}_2\text{H}_5\text{O})_2\text{NH}$) to a solution will make it more basic:



Adding DEA to the solution forces water to dissociate (Eq. 10). The hydrogen ion is complexed with the DEA molecule to create a protonated species and leaving free hydroxide ions. This increases the pH and all of the vapor-liquid equilibria described above (by Equations 1, 2, 3, 5, 6 and 7) will shift to the right.

There is a secondary equilibrium involving DEA carbamate ($(\text{C}_2\text{H}_5\text{O})_2\text{NCO}_2^-$):



This species is stable at low temperatures and helps to remove carbon dioxide from the natural gas.

1.5.4 How can DEA solution be regenerated?

One interesting feature of alkanolamine solutions in general is that the stability of the complexes are temperature dependent. The complexes tend to be less stable as the temperature increases.

We have taken a stream from the above process (**Rich Amine**) to illustrate solution temperature stability.

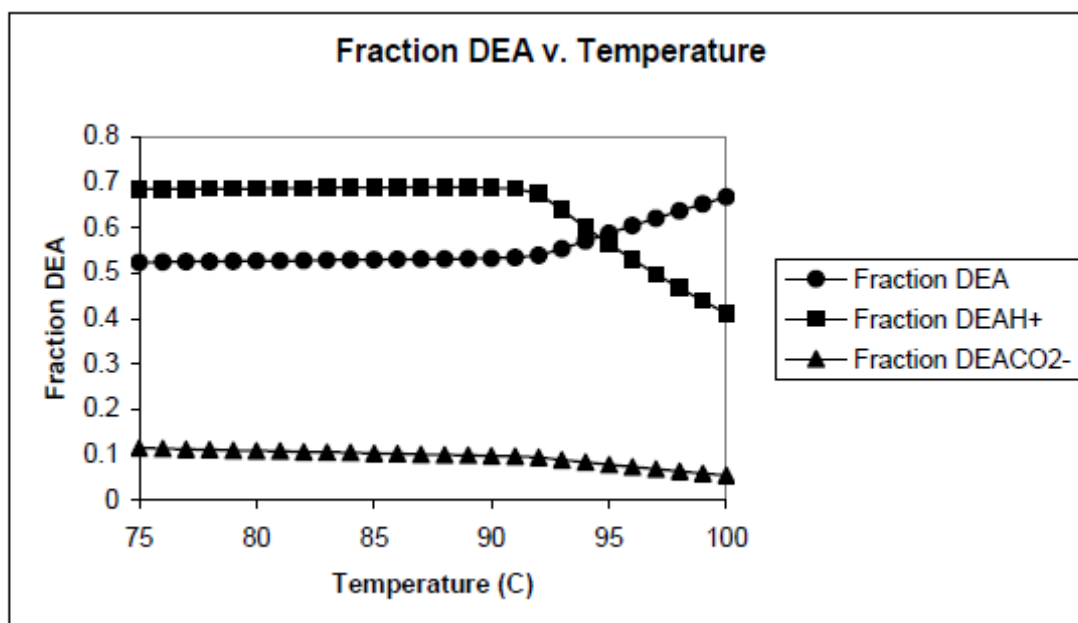


Figure 9 Temperature dependence of DEA complexes

Figure 9 illustrates the advantages of using heat to regenerate the DEA. As the temperature increases above 95 °C, the protonated form of DEA (DEAH+) rapidly decreases (the squares in Figure 9) while the neutral DEA rapidly increases (the circles in the Figure 9). The DEA carbamate species also decreases but is a much weaker function of temperature. So, we see that applying heat facilitates recovery of the amine.

An Example of natural gas sweetening by DEA and absorbent regeneration

1.5.5 Formulating the Process

DEA Absorber

This process can be simulated entirely using ESP. The natural gas stream **Feed Gas** has the following composition:

Table 4: Feed Gas composition

Temperature	30 °C
Pressure	20 atm
CH ₄	925 mole/hr
C ₂ H ₆	20 mole/hr
C ₃ H ₈	10 mole/hr
C ₄ H ₁₀	5 mole/hr
CO ₂	20 mole/hr
H ₂ S	20 mole/hr

This gas is fed to the bottom of the **DEA Absorber**. The absorber is modeled as a column with 10 theoretical stages. **Clean Gas** leaves the top of this absorber. The composition of the **Clean Gas** is:

Table 5: Clean Gas composition

Temperature	42 °C
Pressure	20 atm
CH ₄	925 mole/hr
C ₂ H ₆	20 mole/hr
C ₃ H ₈	10 mole/hr
C ₄ H ₁₀	5 mole/hr
CO ₂	7×10^{-6} mole/hr
H ₂ S	2×10^{-4} mole/hr
H ₂ O	2.9 mole/hr
DEA	5×10^{-4} mole/hr

Note that some DEA is carried up the column and lost in the overhead.

1.5.6 Flash Drum / DEA Regenerator

The **Rich Amine** solution flows to the **Flash Drum** where the pressure is reduced from 20 atm to 1.5 atm. Any remaining light-end hydrocarbons are removed at this point. The **Flash Liquid** is sent to the **DEA Regenerator** where 4.6 MMcal/hr of heat is applied to the reboiler to strip hydrogen sulfide and carbon dioxide out of the rich amine solution.

The overhead of the **DEA Regenerator (CO₂-H₂S)** contains the acid gas components. The composition of this stream is:

Table 6: CO₂-H₂S composition

Temperature	86 °C
Pressure	1.2 atm
CH ₄	0.01 mole/hr
C ₂ H ₆	2×10^{-4} mole/hr
C ₃ H ₈	5×10^{-4} mole/hr
C ₄ H ₁₀	1×10^{-4} mole/hr
CO ₂	20 mole/hr
H ₂ S	20 mole/hr
H ₂ O	40 mole/hr
DEA	3×10^{-9} mole/hr

As you can see, very little DEA is lost in the overhead product of this column. Most of the DEA is recycled back to the **DEA Absorber**. The hydrogen sulfide and carbon dioxide can now be treated separately from the hydrocarbon gas.

1.5.7 Make-up and Recycle

The **Recycle** stream leaving the bottom of the **DEA Regenerator** loses some water and amine. Both need to be replenished. Two feedback control loops are used to adjust water and DEA make-up. An additional 43 moles of water and only 5.4×10^{-4} moles of DEA are needed to maintain the **Recycled DEA** stream at a concentration of approximately 58 wt% DEA.

The **Recycled DEA** stream has the following composition (true basis) and properties:

Table 7: Recycled DEA stream

Temperature, °C	30.0
Pressure, atm	20.0
pH	11.675
Total Flow, mole/hr	620.2164
Flow Units	mole/hr
H ₂ O	500.159
C ₃ H ₈	5.77E-11
C ₄ H ₁₀	5.77E-11
CH ₄	5.79E-08
CO ₂	4.54E-09
DEA	119.206
H ₂ S	8.05E-07
OH ⁻	0.055032
(C ₂ H ₅ O) ₂ NCO ₂ ⁻	0.14022
(C ₂ H ₅ O) ₂ NH ₂ ⁺	0.453815
HCO ₃ ⁻	9.29E-04
H ⁺	2.36E-11
HS ⁻	0.145074
CO ₃ ⁻²	0.0458573
S ⁻²	0.0104223
C ₂ H ₆	0.0
Total g/hr	21621.4
Volume, m ³ /hr	0.0111339
Enthalpy, cal/hr	-4.63E+07
Density, g/m ³	1.94E+06
Osmotic Pres, atm	489.581
Ionic Strength	0.0566113

1.5.8 Corrosion Considerations

The acid gas components have been removed from the natural gas stream and stripped from the DEA solution. These gases may be treated then vented. One major concern is that piping for this overhead gas (**CO₂-H₂S**) may be subject to corrosion.

The wet gas leaving the **DEA Regenerator** is at 86.24 oC. What is the dew point of this gas? Corrosion analyzer could be used to find out corrosion characteristics.

1.5.10 Corrosion Rates

Corrosion Analyzer™ could be used to estimate the general corrosion rate for carbon steel and steel alloys:

Table 8: General corrosion rate for the CO₂-H₂S dew-point composition

Material	Corrosion, mil/yr
Carbon steel	18.9
13% chrome steel	1.0
304 stainless steel	0.3

From these results, the largest beneficial reduction in general corrosion rate seems to be to switch from carbon steel to 13% chrome steel.

Chapter 2

CALCULATION OF NATURAL GAS DESULFURIZATION UNIT BY HYSYS PROGRAM

2.1 Introduction

Natural gas is defined as gas obtained from a natural underground reservoir. It generally contains a large quantity of methane along with heavier hydrocarbons such as ethane, propane, isobutene, normal butane; also in the raw state it often contains a considerable amount of non hydrocarbons, such as nitrogen and the acid gases (carbon dioxide and hydrogen sulfide).

The acid gases must be removed from natural gas before use. One of the processes which are use in the industry to remove the acid gases from natural gas is the use of alkanolamine process.

In this present research, a simulation study for an industrial gas sweetening unit has been investigated.

The aim of the study is to investigate the effect of using diethanolamine(DEA) as solvent on the gas treatment process using the software Hysys. There are many treating processes available for removal of acid gases from natural gas.

These processes include Chemical solvents, Physical solvents, Adsorption Processes Hybrid solvents and Physical separation(Membrane) .

The chemical solvents and physical solvents or combination of these two have been used extensively in existing base load LNG facilities.

In the past few years, diethanolamine solvents for the removal of acid gases have received increased attention.

Historically, DEA has been recognized primarily for its ability to selectively absorb H₂S from a gas while leaving large amounts of CO₂ in the gas. The selective absorption characteristics of DEA have been widely reported in the literature .

DEA's selective absorption ability is due to its relatively slow reaction rate with CO₂. Until the last few years, DEA has not been associated with cases where the removal of large amounts of CO₂ is desired .

Today, computer-aided process simulation is nearly universally recognized as an essential tool in the process industries.

Indeed, simulation software plays a key role in: process Development to study process alternatives, assess feasibility, preliminary economics, interpret pilot-plant data, process design to optimize hardware and flow sheets, estimate equipment, operating cost, investigate feedstock flexibility, and plant operation to reduce energy use, increase yield and improve pollution control.

In the present research, the use of DEA employing have been investigated for a variety of cases using a process simulation program Hysys.

2.2 HYSYS SIMULATION OF AMINE PROCESS

2.2.1 Description of Process Equipment

For the acid gases removal units the following is a brief description of the major equipment necessary for successful simulation of amine unit to meet the LNG specifications and to operate environmental acceptable units.

The function of the inlet separator is to remove the entrained liquid amine carried over with the gas from the pipeline/slug catcher before getting to the absorber. The contactor allows counter-current flow of lean amine from the top and sour gas from the bottom.

The rich amine is flow to the bottom while the sweet gas is collected at the top for further processing. The throttling valve is used to expand the rich amine coming from the high pressure contactor; this is done by lowering gas pressure before entering the flash tank.

The gas from the throttling valve is flashed to remove the hydrocarbons components carried along with the rich amine, this unit serves as a recovery unit for hydrocarbons, and horizontal flash tank is used to prevent foaming.

The rich/lean exchanger is a heat conservation device where hot lean solvent preheats cooler rich solvent. Air-cooled forced draft with automatic louvers for temperature control.

Cold climate service may require air recirculation and/or preheat media on fans/coils. Condenser tubes should be made of stainless steel, as this is a wet, acid gas environment and sloped to the outlet side .

The reflux accumulator is vessel separates the reflux water and water saturated acid gases. The water is pumped back to the still and the acid gases are directed to vent, incinerator, or sulfur recovery unit.

Solvent reboiler is either a direct-fired fire tube type or cabin heater, or indirect hot oil or steam heated unit.

The lean amine solvent from the re-boiler through amineamine heat exchanger is further cool here before entering the absorber again. The reflux and booster centrifugal pump is installed to maintain the recycle lean solvent at the desired operating pressure of the absorber.

The main circulation pump choice depends upon contactor operating pressure and solvent flow rates.

2.2.2 Hysys Simulation Procedures

The first step is to select the appropriate fluid package; here amine fluid package model is selected. The component selection window is open by selecting view in the component-list as in Fig.10

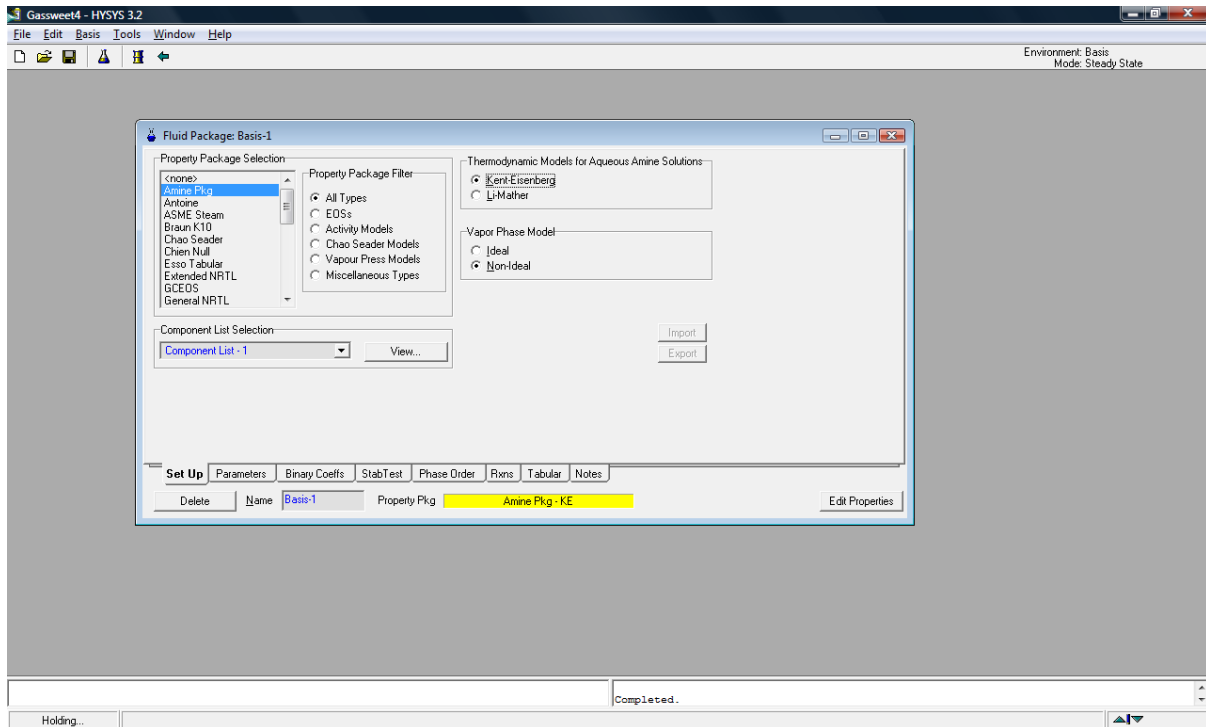
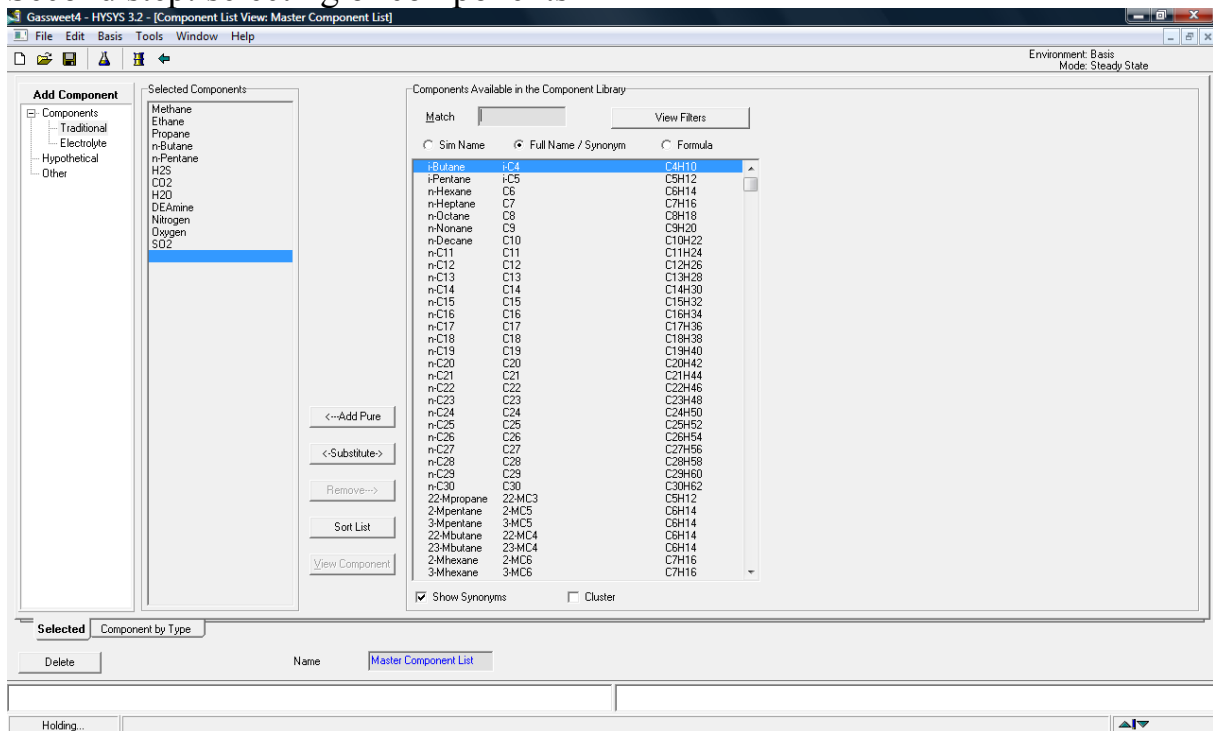


Fig.10 Fluid Package Basis (Amine fluid Package)

Second step: selecting of components



Next step: inlet stream specification (please put here pictures of inlet stream conditions and compositions)

Worksheet

	1	3	2
Methane	0.9541	0.7676	0.9541
Ethane	0.0106	0.0089	0.0106
Propane	0.0014	0.0006	0.0014
n-Butane	0.0005	0.0000	0.0005
n-Pentane	0.0010	0.0000	0.0010
H2S	0.0004	0.1376	0.0004
CO2	0.0321	0.0852	0.0321
H2O	0.0000	0.0000	0.0000
DEAmine	0.0000	0.0000	0.0000
Oxygen	0.0000	0.0000	0.0000
SO2	0.0000	0.0000	0.0000

Design Reactions Rating **Worksheet** Dynamics

Delete OK Ignored

Worksheet

	Mole Fractions	Vapour Phase
Methane	0.954052	0.954052
Ethane	0.010622	0.010622
Propane	0.001428	0.001428
n-Butane	0.000493	0.000493
n-Pentane	0.000966	0.000966
H2S	0.000352	0.000352
CO2	0.032087	0.032087
H2O	0.000000	0.000000
DEAmine	0.000000	0.000000
Oxygen	0.000000	0.000000
SO2	0.000000	0.000000

Total 1.00000

Edit... Edit Properties... Basis...

Worksheet Attachments Dynamics

Delete Define from Other Stream... OK

Other streams specifications made are DEA to Contactor temperature pressure and flow rate, make up water temperature and DEA to recycle temperature, the regenerated feed out of the amine-amine heat exchanger.

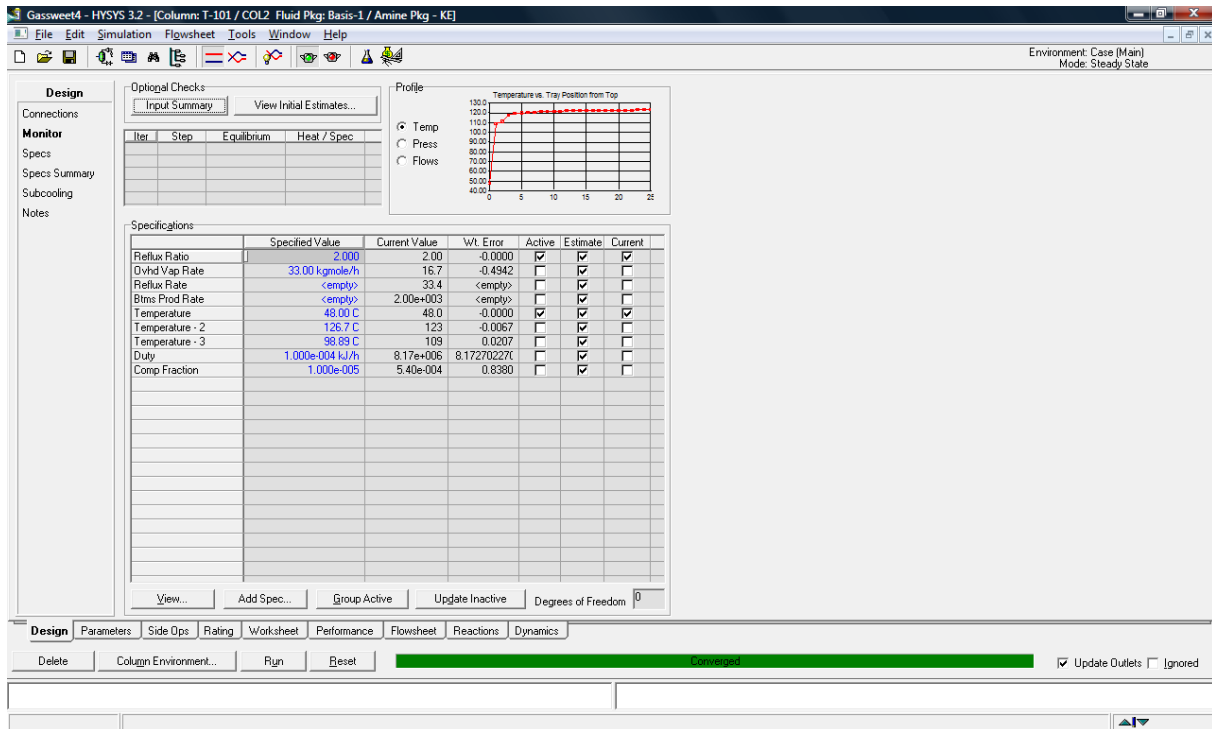
One of the rigorous tasks is the convergence of the absorber and the regenerator, to converge the absorber top and bottom temperature and pressure was specified and run.

The regenerator is converged by specifying the condenser and re-boiler pressure, the reflux ratio and the vent rate, the column is then run.

Next step: simulation of Absorber, Regenerator and other unit.

The screenshot displays the HYSYS 3.2 interface for the design of a distillation column (T-100). The column is configured with 24 stages and a top-down numbering scheme. The top stage inlet is set to 4, and the bottom stage inlet is set to 2. The top pressure (P1) and bottom pressure (Pn) are both set to 2000 kPa. The top product is Dyhd Vapour Outlet (5), and the bottom product is Bottoms Liquid Outlet (6). The simulation status is 'Converged'.

The screenshot displays the HYSYS 3.2 interface for the design of a distillation column (T-101) with a condenser and reboiler. The column is configured with 24 stages and a top-down numbering scheme. The condenser is set to Full Reflux, and the reboiler is set to Delta P = 0.0000 kPa. The top pressure (P cond) is 189.6 kPa, and the bottom pressure (P reb) is 217.2 kPa. The simulation status is 'Converged'.



After selecting the component of the fluid, the simulation environment can enter where the process flow diagram is built.

The aim of the study is to investigate the effect of using diethanolamine (DEA) on the natural gas treatment process using the process simulation program Hysys.

As a simulation result shows the fig.7 the effect of different percent of mixing amines upon the amount of CO₂ in mol fraction in the absorber column in different circulation rate, DEA best result in the absorption processes of CO₂ from the natural gas.

With the convergence of the absorber and the regenerator units a complete amine simulation for the base case was established as shown in above.

Gasweet4 - HYSYS 3.2 - [Workbook - Case (Main)]

File Edit Simulation Flowsheet Workbook Tools Window Help

Environment: Case (Main)
Mode: Steady State

Name	1	2	3	4	5	6	7	8	9	10	11	12
Vapour Fraction	1.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0003	0.0001	1.0000	0.0000	0.0000	0.0000
Temperature [C]	25.00	25.00	25.00	35.00	35.08	41.11	41.11	93.00	48.02	123.3	90.93	25.00
Pressure [kPa]	6400	6400	6400	6350	2000	2000	620.5	600.5	189.6	217.2	207.2	197.2
Molar Flow [kgmole/h]	520.0	520.0	0.0000	2000	504.2	2016	2016	2015	16.89	1399	1937	2.538
Mass Flow [kg/h]	3950	3950	0.0000	4.169e+004	8239	4.240e+004	4.240e+004	4.239e+004	700.1	4.169e+004	4.164e+004	45.73
Liquid Volume Flow [m3/h]	28.10	28.10	0.0000	41.17	27.20	42.06	42.06	42.03	0.9533	41.18	41.12	4.582e+002
Heat Flow [kJ/h]	6.606e+006	6.606e+006	0.0000	-6.083e+007	6.652e+006	-6.088e+007	-6.088e+007	-5.201e+007	1.724e+005	-4.956e+007	-5.128e+007	-8.657e+004
Name	13	14	15	7a	7b	10a	10b	7c	11a	2c	3b	** New **
Vapour Fraction	0.0000	0.4241	0.0000	1.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	
Temperature [C]	72.64	Calculated by: 1	35.00	41.11	41.11	47.00	122.9	60.00	72.70	100.0	80.00	
Pressure [kPa]	197.2	197.2	6350	620.5	620.5	217.2	217.2	610.5	197.2	101.3	304.0	
Molar Flow [kgmole/h]	2000	2000	0.0000	0.5135	2015	1.091	1.997	2015	1997	27.12	136.2	
Mass Flow [kg/h]	4.169e+004	4.169e+004	4.169e+004	8.363	4.239e+004	47.89	4.164e+004	4.239e+004	4.164e+004	1029	2454	
Liquid Volume Flow [m3/h]	41.17	41.17	41.17	2.749e+002	42.03	5.805e+002	41.12	42.03	41.12	1.143	2.459	
Heat Flow [kJ/h]	-5.452e+007	-6.117e+007	-6.083e+007	6854	-6.088e+007	1.115e+004	-4.557e+007	-5.772e+007	-5.444e+007	3.227e+005	-4.068e+006	

Material Streams Compositions Energy Streams Unit Ops

FeederBlock_1
V-100
Horizontal Matrix

Fluid Pkg: All
Include Sub-Flowsheets:
Show Name Only:
Number of Hidden Objects: 0

Gasweet4 - HYSYS 3.2 - [Workbook - Case (Main)]

File Edit Simulation Flowsheet Workbook Tools Window Help

Environment: Case (Main)
Mode: Steady State

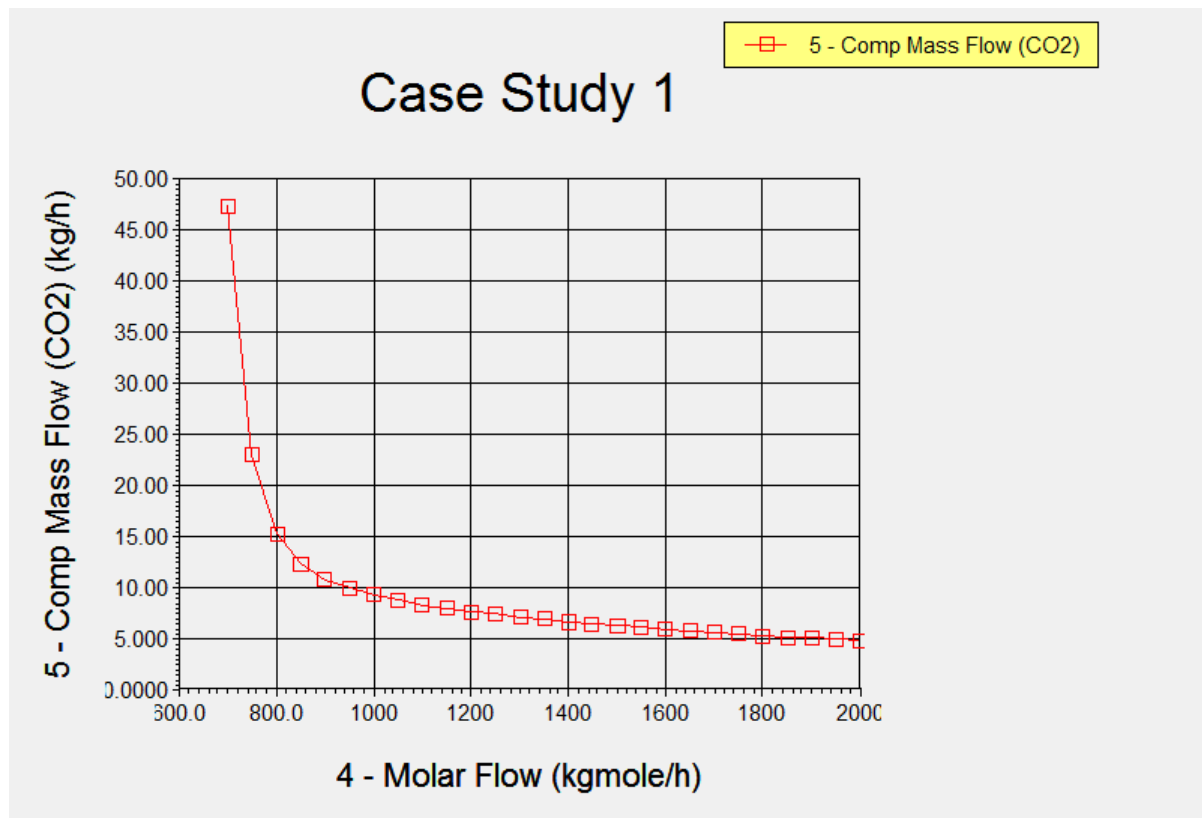
Name	1	2	3	4	5	6	7	8	9	10	11	12
Comp Mole Frac (Methane)	0.9541	0.9541	0.7676	0.0000	0.9824	0.0004	0.0004	0.0001	0.0144	0.0000	0.0000	0.0000
Comp Mole Frac (Ethane)	0.0106	0.0106	0.0089	0.0000	0.0109	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000
Comp Mole Frac (Propane)	0.0014	0.0014	0.0006	0.0000	0.0015	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (n-Butane)	0.0005	0.0005	0.0000	0.0000	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (n-Pentane)	0.0010	0.0010	0.0000	0.0000	0.0010	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (H2S)	0.0004	0.0004	0.1376	0.0000	0.0000	0.0001	0.0001	0.0001	0.0102	0.0000	0.0000	0.0000
Comp Mole Frac (CO2)	0.0321	0.0321	0.0852	0.0000	0.0007	0.0081	0.0081	0.0081	0.9154	0.0005	0.0000	0.0000
Comp Mole Frac (H2O)	0.0000	0.0000	0.9675	0.0030	0.9592	0.9592	0.9594	0.9594	0.0598	0.9669	0.9675	1.0000
Comp Mole Frac (DEAmine)	0.0000	0.0000	0.0000	0.0325	0.0000	0.0322	0.0322	0.0322	0.0000	0.0325	0.0325	0.0000
Comp Mole Frac (Nitrogen)	***	***	***	***	***	***	***	***	***	***	***	***
Comp Mole Frac (Oxygen)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mole Frac (SO2)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Name	3	14	15	7a	7b	10a	10b	7c	11a	2c	3b	** New **
Comp Mole Frac (Methane)	0.0000	0.0000	0.0000	0.9745	0.0001	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	
Comp Mole Frac (Ethane)	0.0000	0.0000	0.0000	0.0109	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
Comp Mole Frac (Propane)	0.0000	0.0000	0.0000	0.0012	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
Comp Mole Frac (n-Butane)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
Comp Mole Frac (n-Pentane)	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
Comp Mole Frac (H2S)	0.0000	0.0000	0.0000	0.0000	0.0001	0.0116	0.0000	0.0001	0.0000	0.0000	0.0000	
Comp Mole Frac (CO2)	0.0000	0.0000	0.0000	0.0009	0.0081	0.9884	0.0000	0.0081	0.0000	0.5914	0.0000	
Comp Mole Frac (H2O)	0.9675	0.9675	0.0124	0.9594	0.0000	0.9675	0.9594	0.9675	0.0390	0.9990	1.0000	
Comp Mole Frac (DEAmine)	0.0325	0.0325	0.0325	0.0000	0.0322	0.0000	0.0325	0.0322	0.0325	0.0000	0.0000	
Comp Mole Frac (Nitrogen)	***	***	***	***	***	***	***	***	***	***	***	
Comp Mole Frac (Oxygen)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.3033	
Comp Mole Frac (SO2)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0063	0.0000	

Material Streams Compositions Energy Streams Unit Ops

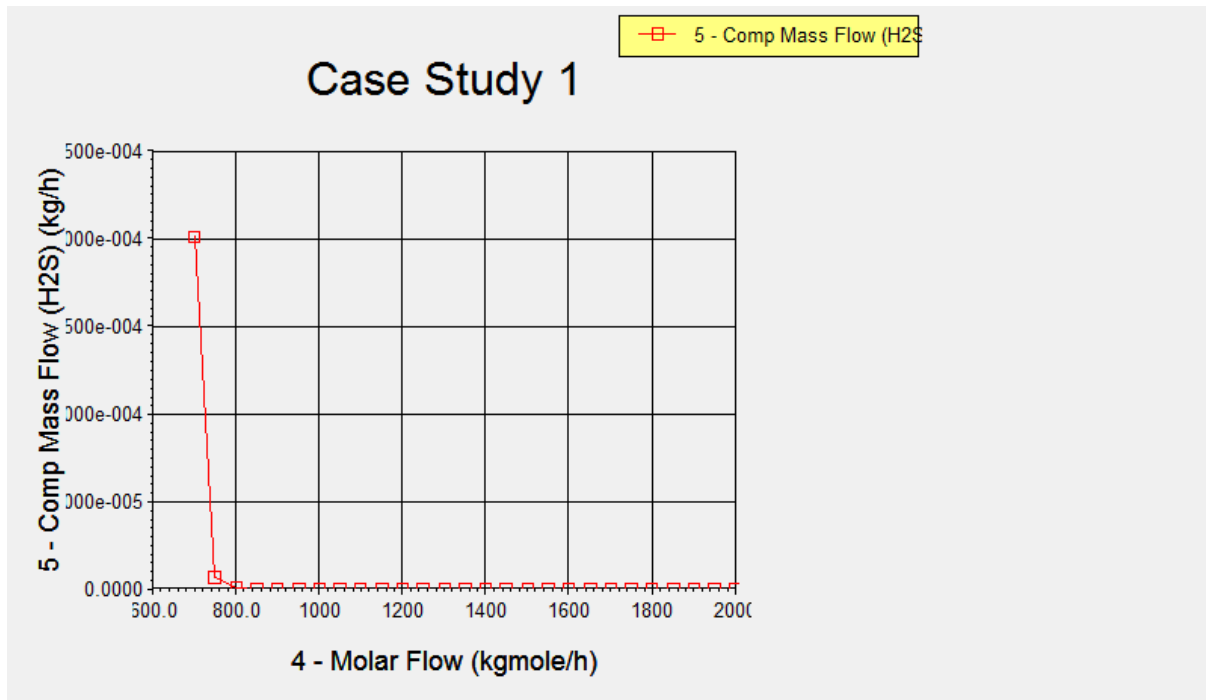
FeederBlock_1
V-100
Horizontal Matrix

Fluid Pkg: All
Include Sub-Flowsheets:
Show Name Only:
Number of Hidden Objects: 0

2.3



Next figure shows the effect of different percent of DEA upon the amount of H₂S in mol fraction in the absorber column in different circulation rate, as shown is the best result in the absorption processes of H₂S from the natural gas.



2.4 CONCLUSION

The principle investigation was directed to study the effect of using diethanolamine (DEA), as solvent on the gas treatment process using the software Hysys. In all cases, DEA was the best result in the absorption processes of CO₂ and H₂S from the natural gas.

The simulation result show that, by using of the 1000(kg mole /h) DEA with T=35-40 °C and P=6350 (kPa) were the best result in the absorption processes of CO₂ (0.00175,mole fraction) and H₂S (0.000000,mole fraction) from the natural gas of northern Afghanistan.

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