Chapter 14

Physical Solvents for Acid Gas Removal

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BACKGROUND

When the acid gas impurities make up an appreciable fraction of the total gas stream, the cost of removing them by heat regenerable solvents may be out of proportion to the value of the treated gas. This has provided the major impetus for the development of processes that employ nonreactive organic solvents as the treating agents. These materials physically dissolve the acid gases, which are then stripped without the application of heat by merely reducing the pressure.

Early efforts to employ water as a physical solvent met with limited success (see Chapter 6), but the solubilities of CO_2 and H_2S in water are too low for water wash to be a practical commercial process. The earliest commercial process based on an organic physical solvent, methanol, was the Rectisol Process, which has been used for synthesis gas applications where the removal of other impurities in addition to CO_2 and H_2S and the production of treated gas containing only ppm levels of CO_2 and H_2S is required. This process operates at very low temperatures (to minus 100°F) and is quite complex compared to other physical solvent processes. As a result, the Rectisol process is not considered applicable to most gas treating services, although it continues to find application in purifying synthesis gases derived from the gasification of heavy oil and coal.

This trend to physical solvents accelerated in 1960 with the introduction of the Fluor Solvent Process, which was followed by several other physical solvent processes. More recently, a new class of process based on the use of a mixed absorbent, containing both a physical and a chemical solvent, has been commercialized. Both simple physical solvent and mixed solvent processes are described in this chapter.

A listing of the major physical solvent gas purification processes that have been or are currently offered for commercial use and the solvents used by each is provided in **Table 14-1.** Many more solvents have been proposed and evaluated in the past, and the search for superior solvents is continuing. A screening study to optimize physical solvent processes for the purification of gases at high pressure has been presented by Zawacki et al. (1981). In this work a large number of physical solvents were screened and, after selection of two solvents (the dimethyl ether of tetraethylene glycol and N-formyl morpholine), process schemes were proposed for a variety of applications.

A key parameter in the screening of potential solvents is the solubility of the gaseous impurities to be absorbed. Techniques for evaluating the solubilities of gases in polar solvents of the type used as physical solvents are described by England (1986) and Sweeney et al. (1988). The latter authors propose a technique which is particularly effective for evaluating a series of functionally related solvents. The need for experimentation is not eliminated, but is greatly reduced. A comparison of calculated versus experimental data for six solvents and three gases presented by Sweeney et al. is summarized in **Table 14-2.**

The calculated values for the first five solvents in the table are based on experimental data for n-Methyl-2-pyrrolidone (NMP), a solvent used in the Purisol process. Calculated values for the Selexol solvent are based on experimental data for the compound tetraethylene glycol dimethyl ether ($CH_3O(CH_2CH_2O)_4CH_3$). The Selexol solvent is reported to be a mixture of polyethylene glycol dimethyl ethers ($CH_3O(CH_2CH_2O)_XCH_3$), where x ranges from 3 to 9, with an average molecular weight of about 272 (Sweeney et al., 1988).

Although many organic solvents appear to be suitable for use as physical solvents, their actual number is limited by certain criteria that must be fulfilled to make them acceptable for economic operation. In order to be practical, the solvents must have an equilibrium capacity for acid gases several times that of water, coupled with a low capacity for the primary con-

Table 14-1
Physical Solvent Processes

Process Name	Solvent	Process Licensor
Simple Physical Solvents		
Fluor Solvent	Propylene carbonate (PC)	Fluor Daniel
SELEXOL	Dimethyl ether of polyethylene glycol (DMPEG)	Union Carbide
Sepasolv MPE	Methyl isopropyl ether of polyethylene glycol (MPE)	Badische (BASF)
Purisol	N-Methyl-2-pyrrolidone (NMP)	Lurgi
Rectisol	Methanol	Lurgi and Linde AG
Ifpexol	Methanol	Institut Français du Pétrole (IFP)
Estasolvan	Tributyl phosphate	IFP/Uhde
Methylcyanoacetate	Methylcyanoacetate	Unocal
Mixed Physical/Chemical Solvents		
Sulfinol	Sulfolane and DIPA or MDEA	Shell Oil/SIPM
Amisol	Methanol and secondary alkylamine	Lurgi
Selefining	Undisclosed physical solvent and tertiary amine	Snamprogetti

Table 14-2
Comparison of Calculated with Experimental Solubility Data

	Solubility, Mol% at 1 atm and 298°K					
	CO_2		H_2S		COS	
Solvent	**Calc.**	**Exp.**	**Calc.**	**Exp.**	**Calc.**	**Exp.**
Dimethyl-2-pyrrolidone	2.31	1.99	22.7	21.1	7.30	5.85
n-Methyl-2-piperidone	2.39	1.68	24.0	22.5	7.52	5.95
n-Methyl-caprolactam	1.88	1.62	21.3	21.7	6.13	5.26
n-Methyl-4-piperidone	2.83	2.25	24.6	24.4	8.62	7.11
n-Ethyl-pyrrolidone	1.91	1.30	21.2	15.6	2.02	3.98
Selexol solvent	3.39	3.56	29.6	22.4	10.3	9.65

Data of Sweeney et al. (1988)

stituents of the gas stream, e.g., hydrocarbons and hydrogen. In addition, they must have low viscosity and low or moderate hygroscopicity. They must be noncorrosive to common metals as well as nonreactive with all components in the gas and, preferably, have a very low vapor pressure at ambient temperature. Finally, they must be available commercially at a reasonable cost.

The simplest version of a physical solvent process involves the regeneration of the solvent by flashing to atmospheric pressure or vacuum, or by inert gas stripping. This approach produces a treated gas that still contains small amounts of acid gas. If H_2S is present at only very low concentrations or is entirely absent, this flow scheme is usually applicable since CO_2 concentrations as high as 2 or 3% can often be tolerated in the product gas. Where H_2S is present in significant amounts, however, thermal regeneration has generally been necessary to accomplish the thorough stripping of the solvent needed to reach stringent H_2S purity requirements. Heat requirements are usually far less for physical solvents than for reactive solvents, such as amines, since the heat of desorption of the acid gas for the physical solvent is only a fraction of that for reactive solvents. The circulation rate of the physical solvent may also be less, particularly when the acid gas partial pressure is high.

Physical solvent processes are used primarily for acid-gas removal from high-pressure natural-gas streams and for carbon dioxide removal from crude hydrogen and ammonia synthesis gases produced both by partial oxidation and steam-hydrocarbon reforming. Since solvent processes are most efficient when operated at the highest possible pressure, carbon dioxide removal from reformer effluents is best carried out after compression of the process gas to the ultimate pressure required for such processes as ammonia synthesis or hydrocracking. Under these circumstances, the molecular weight of the CO_2-rich gas is sufficiently high to permit use of relatively inexpensive centrifugal compressors to reach the required discharge pressure.

As shown in Table 14-2, most organic solvents have an appreciably higher solubility for hydrogen sulfide than for carbon dioxide, and a certain degree of selective hydrogen sulfide removal can be attained. This feature is of special significance when the ratio of carbon dioxide to hydrogen sulfide in the crude gas is so high that the acid gas stream resulting from complete removal cannot be processed in a Claus sulfur recovery unit. By removing essentially all of the hydrogen sulfide and only a portion of the carbon dioxide, this ratio can often be lowered sufficiently to permit normal processing in a Claus plant. The selectivity displayed by physical solvents has been applied to excellent advantage in many instances and is described in more detail later in the chapter.

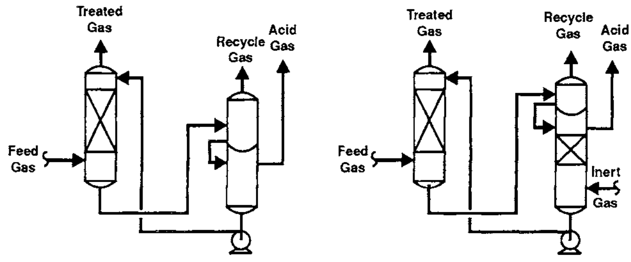
Minor gas impurities such as carbonyl sulfide, carbon disulfide, and mercaptans are quite soluble in most organic solvents, and these compounds are removed to a large extent together with the acid gases. The solubility of hydrocarbons in organic solvents increases with the molecular weight of the hydrocarbon. Consequently, hydrocarbons above ethane are also removed to a large extent and flashed from the solvent together with the acid gas. Although special designs for the recovery of these compounds have been proposed, physical solvent processes are generally not economical for the treatment of hydrocarbon streams that contain a substantial amount of pentane-plus hydrocarbons. Aromatic hydrocarbons are especially difficult to deal with. Even in trace amounts they require a special step to separate them from the solvent because they are very strongly absorbed by most of the solvents used in these processes and tend to accumulate in the solvent.

In another class of process usually referred to as mixed solvent processes, an amine is blended with a physical solvent so that the bulk removal capabilities of the physical solvent are combined with the amine's ability to achieve very low residual acid-gas specifications in a single treating step. These processes are typified by Shell's Sulfinol Process.

PROCESS DESCRIPTION

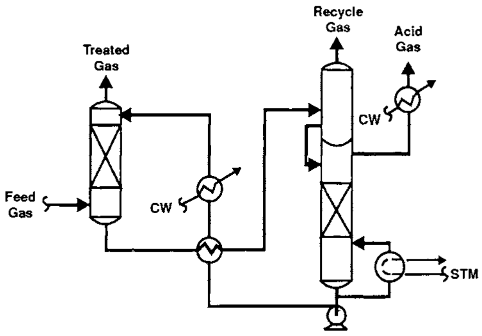
In their simplest form, physical solvent processes require little more than an absorber, an atmospheric flash vessel, and a recycle pump. No steam or other heat source is required. After the absorbed gases are desorbed from the solution by flashing at atmospheric pressure, the lean solution contains acid gas in an amount corresponding to equilibrium at 1 atm acid-gas partial pressure; and this, therefore, represents the theoretical minimum partial pressure of acid gas in the purified-gas stream. To obtain a higher degree of purification, vacuum or inert gas stripping or heating of the solvent must be employed. Other process modifications are used to minimize loss of valuable gas components, provide a relatively low temperature of operation, and otherwise improve process economics.

Figure 14-1 presents three different configurations of physical solvent processes differing in the method by which the solvent is stripped. The first illustrates regeneration by simple flashing. One or more flash steps may be employed. **Figure 1(A)** shows a two stage flash system with the final flash to atmospheric pressure. An alternate to this case that is not shown is to conduct the final flash at vacuum conditions. **Figure 1(B)** shows the use of inert gas stripping to lower the acid gas content of the lean solvent. Nitrogen and fuel gas have been used as stripping agents. Air may also be used, but is not feasible in systems where sulfur species occur due to the formation and accumulation of elemental sulfur and to other side reactions. **Figure 1(C)** shows thermal regeneration of the solvent, a method that is widely practiced with physical solvents to achieve pipeline quality gas.



A. Flash Regeneration

B. Inert Gas Stripping



C. Thermal Regeneration

Figure 14-1. Simplified flow diagrams of physical solvent processes showing three basic methods of solvent regeneration.

The absorption step is the same with all three types of regeneration. The gas enters the bottom of the absorber, which contains either packing or trays, and is washed by a descending stream of regenerated solvent. The rich solvent leaves the bottom of the absorber and flows to the regeneration system. When multiple flashes are used, the gases flashed at the highest pressure level will contain most of the dissolved non-acidic gases, and are usually recompressed and returned to the absorber inlet to minimize losses of product gas. Quite frequently, solvent regeneration by pressure reduction is adequate for attaining the required gas purity, and the solvent leaving the lowest pressure flash is directly recycled to the top of the absorber. If product gas of higher purity is required, the residual acid-gas content of the solvent can be further reduced by stripping with an inert gas. Complete removal of the last remaining acid gas can be effected by heat regeneration and reboiling of the solvent as shown in **Figure 14-1(C).**

Although not shown in **Figure 14-1,** the rich solvent is frequently expanded through hydraulic turbines that are used to supply about half of the lean solvent pump horsepower. This has the dual purpose of reducing energy requirements and cooling the regenerated solvent before reuse, since less net shaft work is introduced into the system through the lean solvent pump. Since the absorption capacity of the solvents for acid gases increases as the temperature is lowered, it is advantageous to operate at the lowest possible temperature. Often, sufficient autorefrigeration is available in the system to make outside refrigeration unnecessary. In other cases the inclusion of auxiliary mechanical (or absorption) refrigeration results in a more efficient and less costly plant.

With most processes, solvent recovery from the effluent streams is not required since the vapor pressures of the solvents are sufficiently low at operating conditions. With some processes, however, such as the Purisol process, effluent streams are water washed.

Most commercially used solvents are very stable and reclaiming is not required. However, water removal by distillation is sometimes necessary to maintain the water concentration of the solvent at low levels. Alternatively, the feed gas can be dehydrated by glycol injection or other means to keep water out of the system.

PROCESS DESIGN

The design of absorption and stripping columns for physical solvents is relatively straightforward (compared to reactive absorbents) because no chemical reactions occur in the liquid phase. Design equations and simulation models commonly used for hydrocarbon separations are generally applicable to physical solvent gas purification. The key requirement is adequate liquid/vapor equilibrium data covering all components and conditions encountered in the process. Thermal and physical property data are also necessary for complete designs.

Computer models based on a tray-by-tray heat and material balance are the best approach for final designs; however, preliminary studies can make use of the Kremser equation which is described in Chapter 1 (equation 1-20). An application of this equation to the design of a Selexol system for selectively absorbing H_2S in the presence of CO_2 is described by Sweny (1985).

The Kremser equation correlates three factors: (1) the fraction of a given gas component that is absorbed, (2) the number of theoretical plates in the column, N, and (3) the absorption factor, A. A is defined as L/KV, where L and V are the liquid and gas flow rates in moles per unit time, and K is the equilibrium constant for the given component, y/x. The symbols y and x have their usual meaning of mole fraction of the given component in the gas and in the liquid, respectively, at equilibrium.

For any compound, the fraction absorbed increases as A is increased or as the number of trays is increased. However, complete removal of a component from the gas cannot be attained unless A is greater than 1, no matter how many trays are used. Any desired removal efficiency can be obtained over a wide range of values for A and N. For example, the Kremser equation shows that 98% removal of a given component is possible with either 25 trays at A = 1.25 or 7 trays at A = 1.5.

These considerations are very important in the design of physical solvent absorbers because the conditions selected to meet the requirements for the key component (e.g., H_2S) may have a major effect on column performance with regard to other, less soluble components (e.g., CO_2, COS, and CH_4). If maximum selectivity is desired, a large number of trays should be used, with the lowest possible value of A that will permit attainment of the desired removal efficiency for the key component. "A" will then be slightly over 1.0 for H_2S and much lower than 1 for the less soluble gases, which will, therefore, not be efficiently removed. On the other hand, if it is desired to remove a selected less soluble component (e.g., COS) more efficiently, it is necessary to increase A for that component (normally by increasing the liquid rate). At values of A significantly below 1.0, increasing A has a much greater effect on the fraction removed than increasing the number of trays. As a result, it is often possible to meet the requirements for both H_2S and COS removal with a high liquid rate and a relatively short column.

The selectivity of a physical absorption process can be enhanced by the use of more than one stripping and absorption stage. For example, if H_2S is absorbed selectively relative to CO_2, the rich solution from the primary absorber will contain a higher H_2S/CO_2 ratio than the feed gas. If the rich solution is stripped (or partially stripped), and the released gas is subjected to selective reabsorption, the rich solution from the reabsorber will contain an even higher H_2S/CO_2 ratio. This type of flow scheme can be useful in providing an acid gas stream with a high enough H_2S content for use in a standard Claus plant. Many other flow schemes have been developed to meet specific requirements and take advantage of the properties of specific solvents. Several of these alternative flow schemes are described in subsequent sections of this chapter in connection with commercial physical solvent processes.

Since the equilibrium constant is a function of temperature, absorber and stripper designs must take into account temperature changes that occur as a result of absorption (or desorption) of components. Zawacki et al. (1981) report using heats of absorption values of 150, 180, and 1,000 Btu/lb for CO_2, H_2S, and H_2O, respectively, for calculating the temperature rise due to absorption in two different solvents (N-formyl morpholine and the dimethyl ether of tetraethylene glycol). They also assumed tray efficiencies of 15 to 20% for absorption in these solvents, and estimated that 50 to 60 actual trays would represent practical column heights.

Solvent Circulation Rate

As in other types of gas treating processes, probably the most important process factor that dictates capital cost of the plant is the solvent circulation rate. This is particularly true for bulk removal plants, but also applies to those plants that use thermal regeneration of the solvent. The reason for this is obvious, since circulation rate affects the size and the cost of virtually every piece of equipment, including the absorber, piping, circulation pumps, and flash drums.

Every effort should be made to minimize solvent circulation rate. For a given solvent this can be accomplished most readily by reducing the contact temperature since the solvent's capacity for absorbing acid gases increases as the temperature is decreased. Factors which reduce solvent temperature include the following:

- The Joule-Thomson cooling effect of expanding CO_2 through the plant—from feed gas pressure to atmospheric pressure—cools the solvent. No additional equipment is required to realize this benefit.
- The use of heat exchangers to recover refrigeration from process streams such as the absorber overhead and flash gas streams is a common practice.
- A cooling effect is achieved if the rich solvent is directed through hydraulic turbines to provide part (up to almost 50%) of the solvent pumping energy. Without these turbines, motor or steam driven turbines would be needed and additional shaft work would be added to the system.
- In plants where the feed gas is very high in CO_2 content, i.e., 30% or higher, a portion of the absorbed CO_2 can be flashed from the solvent at an intermediate pressure, then directed through expansion turbines which are used to drive circulation pumps. The flashed gas is cooled during expansion through the turbine and can then be used in a heat exchanger to remove heat from the circulating solvent.
- The use of external mechanical or absorption refrigeration to further reduce solvent temperature has often been used. For bulk removal plants where the lean solvent is not heated, applying the refrigeration at the warmest point in the cycle (the rich solvent leaving the absorber) is preferred since the capital and energy requirements for the refrigeration system are the lowest. In plants where thermal regeneration is used, the refrigeration is applied to the lean solvent leaving the stripper.

An additional benefit derived from chilling the solvent and reducing its flow rate is that the amount of light hydrocarbon (or $H_2 + CO$ in a syngas application) absorbed in the solvent may be significantly reduced. This benefit is possible because the solubilities of CO_2 and H_2S generally increase significantly when the operating temperature is reduced, while the solubilities of CH_4, H_2, and CO show little change with temperature. **Figure 14-2** illustrates this phenomenon for methanol and the Sepasolv MPE solvent. The solubility of CH_4 in these solvents is seen to change much less with temperature than the solubilities of H_2S, COS, and CO_2. In some solvents, CH_4, H_2, and CO may actually become less soluble as the temperature is reduced. The dimethyl ether of tetraethylene glycol is an example of such a solvent as indicated by the data in **Table 14-3** from Zawacki et al. (1981).

The temperature to which a solvent may be cooled is limited primarily by its increased viscosity and the resulting decrease in solvent heat and mass transport capabilities. The cost of providing the required cooling is, of course, also a factor. The minimum acceptable temperature depends on the solvent used. Methanol, for example, can be used at temperatures as low as –95°F (Knapp, 1968), while propylene carbonate is limited to temperatures above 0°F (Freireich and Tennyson, 1977).

Recycle Gas Rate

In every physical solvent process, a portion of the most valuable constituent of the process gas—ordinarily either CH_4 or H_2—is unavoidably dissolved in the rich solvent. With CH_4 this potential loss can be as high as 10% of the total CH_4. Standard practice is to flash the rich solvent to an intermediate pressure, ½ to ⅓ of the absorber pressure, and to recompress the flash gas and recycle it to the feed gas. This additional step can reduce CH_4 losses to typically 2 or 3% of the CH_4 present in the feed gas. The CH_4 (or H_2) loss is clearly a function of the pressure at which the flash is conducted and standard optimization procedures can be followed to determine this pressure. In some cases, several intermediate flashes, rather than a single flash, are used to reduce compression horsepower. Another method of reducing compression horsepower that has been proposed is to scrub CO_2 from the flash gas in a "reab-

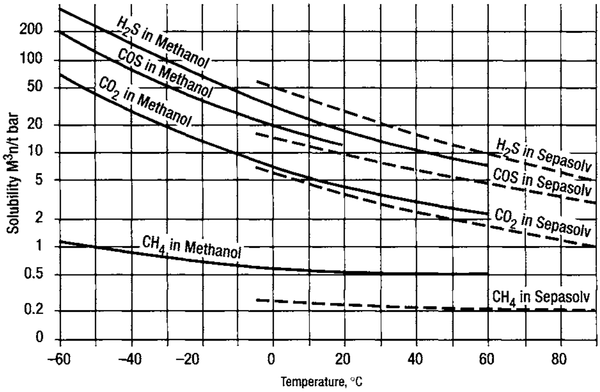


Figure 14-2. Effect of temperature on the solubility of gases in methanol and Sepasolv MPE solvent (*Ranke and Mohr, 1985; Wölfer, 1982*). *Reproduced with permission from "Acid and Sour Gas Treating Processes," S. A. Newman, Ed., copyright 1985, Gulf Publishing Company*

Table 14-3

Effect of Temperature on the Solubility of Various Gases in the Dimethyl Ether of Tetraethylene Glycol

Gas	Solubility at:	
	80°F	40°F
Methane	0.43	0.37
Carbon monoxide	0.12	0.05
Hydrogen	0.08	0.05
Carbon dioxide	3.61	4.15
Hydrogen sulfide	20.67	25.85

Solubility values are in the units of volumes of gas (60°F, 1 atm) per volume of solvent (60°F, 1 atm).

Data source: Zawacki et al. (1981)

sorber." This is especially applicable when the feed gas contains a high concentration of CO_2, since the flash gas will be even more concentrated with CO_2.

Water Disposition

The feed gas, whether it is natural or synthesis gas, will almost always contain water. Typically, the gas will be water-saturated at feed gas conditions. Another source of water entering the system may be stripping gas used to regenerate the solvent. Some water will be discharged from the plant in the gas streams leaving the system; however, water will accumulate in the solvent until the amounts entering and leaving the system are equal. Although most processes can tolerate several percent water in the solvent, it is sometimes necessary to control water buildup. This can be accomplished by distilling water from a solvent slipstream or dehydrating the feed gas and/or stripping gas.

PROCESS SELECTION

A number of proven physical solvent processes are available for most applications. In addition to capital cost, the following factors must be included in any comparison:

- Process performance in terms of treated gas purity, and acid gas composition (e.g., suitability as Claus plant feed)
- Loss of light and heavy hydrocarbon (or other valuable constituents)
- Experience and ingenuity of the designer in adapting the process to the case at hand
- Experience and method of dealing with impurities that may be present, such as COS, NH_3, aromatic hydrocarbons, etc.
- Experience with regard to corrosion, foaming, or other operating problems
- Cost of initial solvent charge
- Cost of replacement solvent—as influenced by process temperatures, vapor pressure of solvent, solvent stability, and fugitive losses
- Energy and/or stripping gas requirements
- Process royalty cost

Depending upon the extent of process data available, a comparison may be made of the carrying capacities of the various solvents. **Table 14-4,** which is based on the data of Bucklin and Schendel (1985), presents gas solubility data for three different processes: Fluor Solvent (propylene carbonate), Selexol (polyethylene glycol dimethyl ether), and Purisol (n-methyl-2-pyrrolidone). Solubilities of CO_2 and H_2S as well as hydrocarbons and other gases are shown, with all data collected at 25°C. The solubilities shown are single component data. In real systems there can be substantial interactions between the solutes, the net effect of which is usually to decrease the CO_2 and H_2S solubilities and to increase the hydrocarbon solubilities. Also, since all processes do not operate at the same temperature, the relationship between solubility and temperature must also be included in the evaluation.

The comparative data in **Table 14-4** show that, at equal temperatures, all three solvents have nearly the same CO_2 capacity. For H_2S, however, Selexol and Purisol have capacities about three times that of Fluor Solvent. For this reason, it is clear that Selexol or Purisol would be preferred to Fluor Solvent for cases where the feed gas contains a substantial concentration of H_2S or where selective H_2S removal is required. However, when CO_2 dictates the design, i.e., when H_2S is absent or present only in trace amounts, Fluor Solvent has an inherent advantage since hydrocarbon solubilities are substantially less in it than in the other two solvents.

Table 14-5 provides some key physical property data for DMPEG, NMP, PC, and methanol. Vapor pressure versus temperature data for DMPEG, NMP, methanol, and MPE are plotted in **Figure 14-3.** Methanol has by far the highest vapor pressure and requires very low temperature operation. NMP has a much higher vapor pressure than DMPEG, PC, or MPE and normally requires water washing of the process offgases to limit solvent losses. The Selexol, Fluor Solvent, and Sepasolv MPE processes require no water wash steps. The

Table 14-4
Gas Solubility Data for Selexol, Purisol, and Fluor Solvent Process Absorbents. Volume Gas/Volume Liquid @ 25°C and 1 Atm.

Gas	Selexol (DMPEG)	Purisol (NMP)	Fluor Solvent (Propylene Carbonate)
H_2	0.047	0.020	0.027
N_2	—	—	0.029
CO	0.10	0.075	0.072
C_1	0.24	0.26	0.13
C_2	1.52	1.36	0.58
CO_2	3.63	3.57	3.41
C_3	3.70	3.82	1.74
iC_4	6.79	7.89	3.85
nC_4	8.46	12.4	5.97
COS	8.46	9.73	6.41
iC_5	16.2	—	11.9
NH_3	17.7	—	—
nC_5	20.1	—	17.0
H_2S	32.4	36.4	11.2
nC_6	39.9	—	46.0
CH_3SH	82.4	121	92.7

Data from Bucklin and Schendel (1985)

Table 14-5
Solvent Comparative Data

Process Solvent	Selexol (DMPEG)	Purisol (NMP)	Fluor Solvent (PC)	Rectisol (Methanol)
Vapor Pressure, mm Hg @ 25°C	$.073 \times 10^{-2}$	40×10^{-2}	8.5×10^{-2}	—
Viscosity, cp @ 25°C	5.8	1.65	3.0	0.6
Maximum feasible operating temperature, °C	175	—	65	—
Density, kg/m^3 @ 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, Btu/(lb)(°F)	0.49	0.40	0.339	0.556
Thermal conductivity, Btu/(hr)(ft^2)(°F/ft)	0.11	0.095	0.12	0.122

Data from Bucklin and Schendel (1985) and Ranke and Mohr (1985)

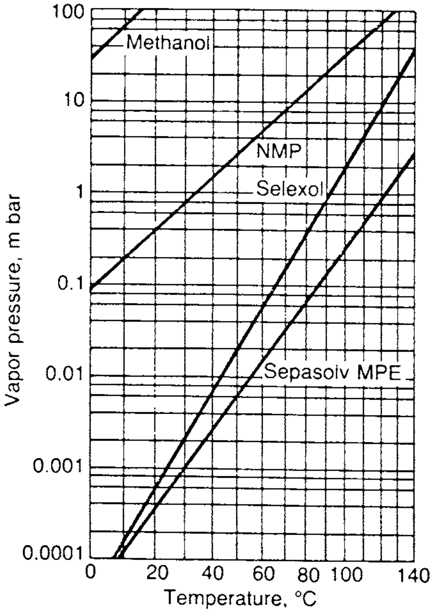


Figure 14-3. Vapor pressure of various physical solvents (*Wölfer, 1982*). *Courtesy of Hydrocarbon Processing*

Selexol solvent has the highest viscosity, which can significantly affect mass and heat transfer as the solvent temperature is reduced. Selexol, however, is suitable for operation at temperatures up to 175°C, while, for stability reasons, Fluor Solvent (propylene carbonate) is limited to a maximum operating temperature of about 65°C.

SIMPLE PHYSICAL SOLVENT PROCESSES

Fluor Solvent Process

The Fluor Solvent process, which is licensed by Fluor Daniel, Inc., was introduced in 1960 (Kohl and Buckingham, 1960). Although several solvents were covered by U.S. patents, only propylene carbonate has been used commercially. The process has been applied in 13 commercial installations—nine processing natural gas, two ammonia synthesis gas, and two hydrogen.

Basic Data

Selected physical properties of propylene carbonate are tabulated in **Tables 14-5** and **14-6.** Data on the solubility of various gases in propylene carbonate have been reported by several investigators (Dow Chemical Company, 1962; Schmack and Bittrich, 1966; Makranczy et al., 1965; Bucklin and Schendel, 1985). The equilibrium solubilities of hydrogen sulfide and carbon dioxide as a function of pressure are shown in **Figure 14-4.** Although there is some scattering of points, it is evident that the solubilities of both acid gases follow Henry's law

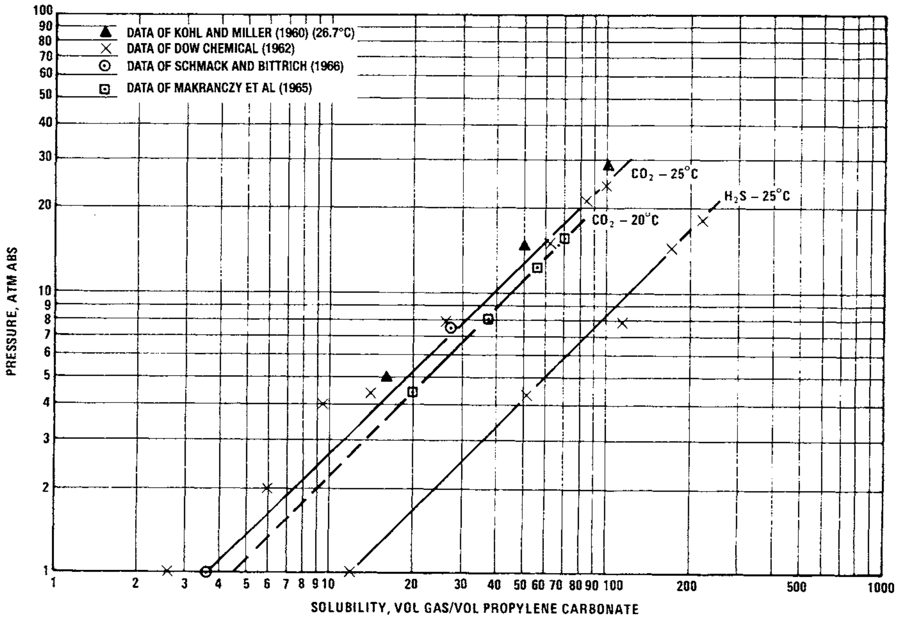


Figure 14-4. Effect of pressure on the solubility of carbon dioxide and hydrogen sulfide in propylene carbonate (gas volumes at 0°C and 760 mm Hg).

Table 14-6
Physical Properties of Propylene Carbonate

Empirical formula	$C_4H_6O_3$
Molecular weight	102.09
Vapor Pressure at 60°F	0.046 mm Hg
Viscosity at 60°F	2.6 centistokes
at 0°F	6.4 centistokes
Water Solubility in Solvent @ 25°C	94 g/l
Solvent solubility in water @ 25°C	236 g/l
CO_2 solubility in solvent @ 25°C, 1 atm	0.455 ft^3/US gal

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

up to a pressure of about 20 atm. The effect of temperature is shown for carbon dioxide and hydrogen in **Figure 14-5.** It is interesting to note that the solubility of hydrogen increases with increasing temperature.

No data appear to be available in the open literature on the specific effects of dissolved carbon dioxide, hydrogen sulfide, and other gases on the solubility of the individual compo-

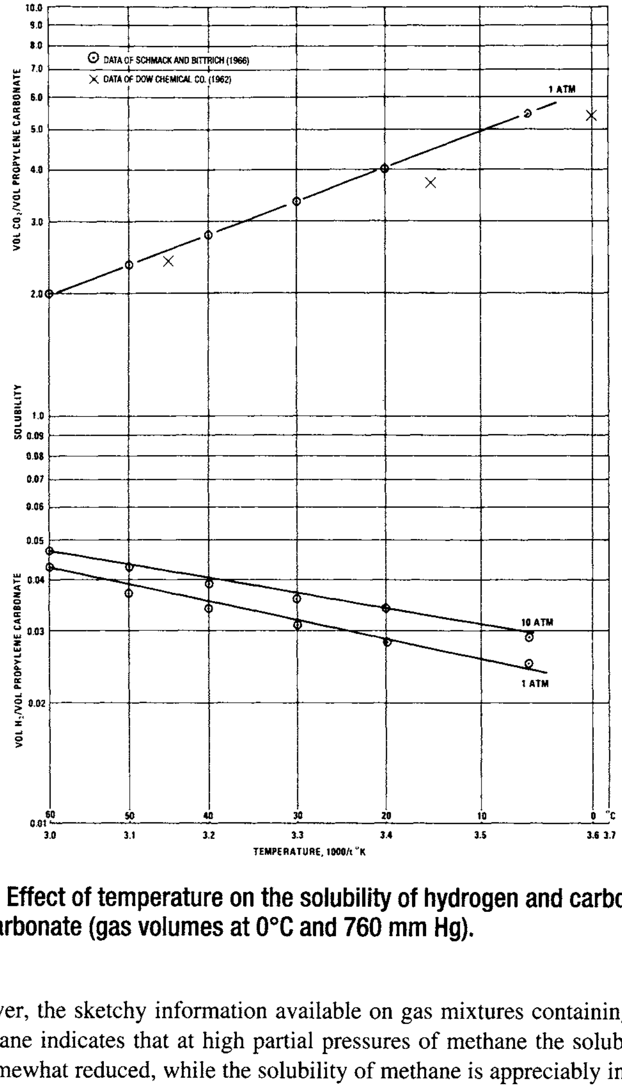


Figure 14-5. Effect of temperature on the solubility of hydrogen and carbon dioxide in propylene carbonate (gas volumes at 0°C and 760 mm Hg).

nents. However, the sketchy information available on gas mixtures containing carbon dioxide and methane indicates that at high partial pressures of methane the solubility of carbon dioxide is somewhat reduced, while the solubility of methane is appreciably increased by the presence of dissolved carbon dioxide (Dow Chemical, 1962; Makranczy et al., 1965). In view of the low solubility of hydrogen in propylene carbonate, it is reasonable to assume that its presence has no significant effect on the solubility of carbon dioxide or hydrogen sulfide. Solubilities of several gases, in terms of Bunsen coefficients (volume of gas at 0°C and 760 mm Hg per volume of liquid), are shown in **Table 14-7.** Additional solubility data are included in **Table 14-4.**

Process Design and Operation

The Fluor Solvent process uses flash regeneration as depicted in **Figure 14-1(A).** Commercial plants utilize several flashes of the rich solvent at decreasing pressure levels with recycling of the gas evolved in the high pressure flash. Lean solvent temperatures as low as

Table 14-7
Solubility of Gases in Propylene Carbonate

Solute	Bunsen Coefficient	Reference
H_2	0.03	A
O_2	0.09	B
N_2	0.09	B
CO	0.06	B
COS	6.25	B
C_2H_2	8.6	C
CH_4	0.13	B
C_2H_6	0.58	B
CO_2	3.22	D
H_2S	10.6	D

Data sources: A) Schmack and Bittrich (1966); B) Fluor Daniel (1993); C) Dow Chemical Co. (1962); D) Bucklin and Schendel (1985)

0°F have been used in this process. A modification of the process resulting in an appreciable reduction of hydrocarbon gas loss has been described by Freireich and Tennyson (1977). In this scheme, the gas from the second intermediate pressure flash is washed with solvent in a small absorber. The overhead from this absorber is recompressed and recycled to the plant inlet. It is claimed that the value of the recovered gas amply compensates for the cost of the additional equipment, and that a payout as low as three months is realized with a fuel cost of $2 per MMbtu.

The operation of the Fluor Solvent process in the initial commercial plant has been described by Buckingham (1961). This author has also reported performance data for four plants treating natural gas (Buckingham, 1964). Data from these plants are given in **Table 14-8.**

An economic study comparing the Fluor Solvent process with the activated hot potassium carbonate process for the removal of carbon dioxide from synthesis gas for the production of ammonia and urea has been reported by Cook and Tennyson (1969). The authors concluded that the process is more economical than activated hot potassium carbonate in all cases stud-

Table 14-8
Operating Data of Fluor Solvent Process Plants

Plant	Design feed gas rate MMscfd	Feed gas composition		Absorption pressure, psig	Acid gas partial pressure in feed, psia	Sales gas specification	
		CO_2	H_2S			CO_2	H_2S
A	220	53%	3 gr/100 scf	850	CO_2: 458	2%	0.25 gr/100 sc
B	10	17%	—	450	CO_2: 79	5%	—
C	20	22.8%	—	800	CO_2: 186	1%	—
D	28	10–30%	5–15%	1,000	$CO_2 + H_2S$: 250–300	0.1%	0.8 gr/100 scf

Source: Buckingham (1964)

ied, which included production of ammonia and urea by steam reforming of natural gas and naphtha and by partial oxidation.

A comparison of Fluor Solvent to other physical solvent processes (Bucklin and Schendel, 1985) illustrates that for cases where CO_2 removal requirements dictate the plant design, i.e., where little or no H_2S is present, the Fluor Solvent process enjoys a significant advantage over the other processes due to lower solubilities of the gas being purified, light hydrocarbons in the case of natural gas and H_2 in the case of synthesis gas. This advantage is evidenced by either a higher percent hydrocarbon or hydrogen recovery or by lower compression requirements for gas flashed from the rich solvent at intermediate pressures.

A photograph of a Fluor Solvent plant processing natural gas is shown in **Figure 14-6.**

Selexol Process

The Selexol process uses a physical solvent and, as a result, is generally similar to other processes discussed in this chapter. The process was originally developed by Allied Chemical Corporation. In 1982, the Norton Company purchased the rights to the process; in 1990,

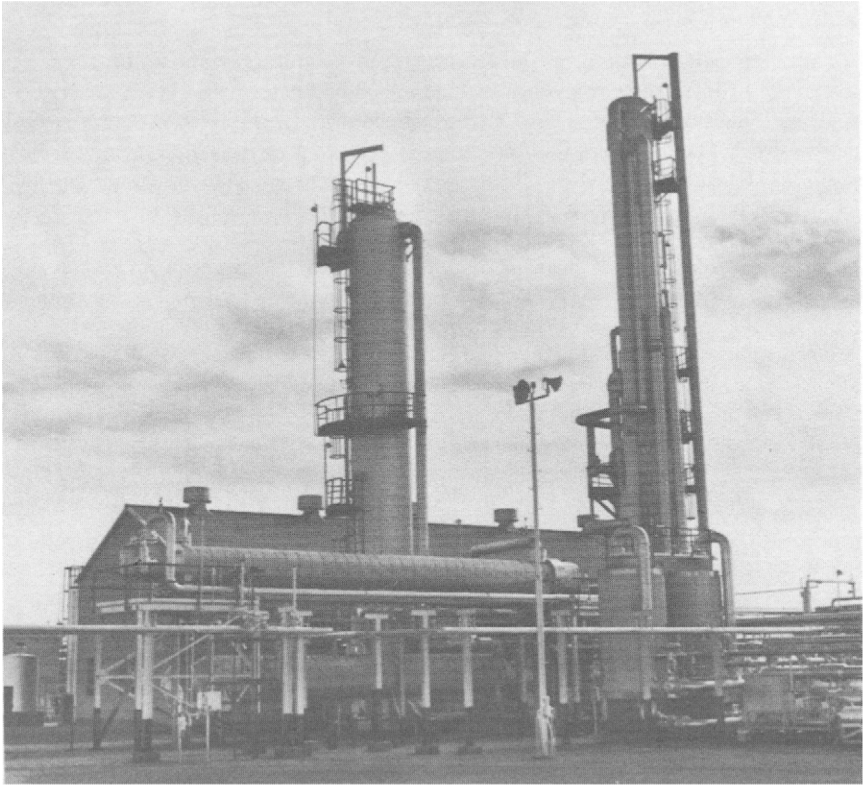


Figure 14-6. Fluor Solvent process plant treating high pressure natural gas. ***Fluor Daniel and El Paso Natural Gas Company***

Union Carbide acquired the process from Norton; and, in 1993, UOP acquired the rights to the Selexol process and is now responsible for process licensing.

The Selexol process has found a very wide range of applications. It was originally used to remove CO_2 from an ammonia plant in Nebraska, followed soon after by H_2S and CO_2 removal from natural gas in the U.S. and in Europe. Other applications include desulfurization and CO_2 removal from synthesis gas derived from the partial oxidation of heavy petroleum stocks and from coal gasification. Natural gas treating applications include several, where in addition to production of pipeline specification gas, a relatively pure stream of carbon dioxide is produced for reinjection into oil formations, so-called enhanced oil recovery or EOR. A relatively new use for the process dating back to 1979 is the purification of landfill gas drawn from the biological degradation of municipal waste in sanitary landfills. This application is characterized by the occurrence of chlorinated and aromatic hydrocarbons as impurities in the landfill gas.

Union Carbide reported that as of 1992, a total of 53 Selexol plants had been installed. These comprise 10 for CO_2 removal from various synthesis gases, 12 for CO_2 removal from natural gas, 15 for selective H_2S removal (with or without CO_2 removal), 8 for desulfurization of synthesis gas, and 8 for landfill gas purification (Epps, 1992A).

This process has been described quite extensively in the literature (Hegwer and Harris, 1970; Sweny and Valentine, 1970; Sweny, 1973; Valentine, 1974; Clare and Valentine, 1975; Valentine, 1975; Sweny, 1976; Raney, 1976; Van Deraerschot and Valentine, 1976; Judd, 1978; Swanson, 1978; Sweny, 1980; Hernandez and Huurdeman, 1989; Epps, 1992B).

Basic Data

The treating solution used in the Selexol process is a mixture of homologues of the dimethylether of polyethylene glycol. This material has been shown to be chemically stable as well as non-toxic and biodegradable. It has a very low vapor pressure as well as a high capacity for various impurities, including H_2S, CO_2, COS, mercaptans, and others.

The relative solubilities of various gases in Selexol solvent as compared to methane are shown in **Table 14-9** (Shah and McFarland, 1988; Epps, 1992B). The data in this table indicate that H_2S is almost 9 times as soluble as CO_2. This high ratio facilitates the use of Selexol for the selective removal of H_2S from gas streams also containing CO_2. The data also show that hydrocarbons are quite soluble and their solubility increases with increasing molecular weight. Propane, for example, has a relative solubility of about 15.4, which is similar to that of CO_2; while hexane, with a relative solubility of 167, is somewhat more soluble than H_2S. Water is more soluble than any of the listed compounds except HCN, and liquid water is miscible with the Selexol solvent. These solubility characteristics have led to the development of Selexol solvent applications for removing hydrocarbons and/or water from natural gas, e.g., simultaneous hydrocarbon and water dew point control (Epps, 1994). Actual solubility values for a number of components in the Selexol solvent (and in two other solvents) are given in **Table 14-4** in terms of volume of gas per volume of liquid at 25°C and 1 atm partial pressure. The effect of partial pressure on solubility is shown in **Figure 14-7** for several gases. Physical properties of the Selexol solvent are given in **Table 14-5.** The solvent's flash point is reported to be about 304°F (Sweny and Valentine, 1970).

Process Design and Operation

The basic flow scheme of the process is very simple, requiring only an absorption stage and regeneration by flashing at successively decreasing pressure levels as depicted in **Figure**

Table 14-9
Relative Solubilities of Various Gases in SELEXOL Solvent

Component	R = K′ Methane / K′ Component	Component	R = K′ Methane / K′ Component
H_2	0.20	NH_3	73
N_2	0.30	nC_5	83
CO	0.43	H_2S	134
C_1	1.0	C_6	167
C_2	6.5	CH_3SH	340
C_2H_4	7.2	C_7	360
CO_2	15.2	CS_2	360
C_3	15.4	SO_2	1,400
iC_4	28	C_6H_6	3,800
COS	35	CH_2Cl_3	5,000
nC_4	36	C_4H_4S	8,200
iC_5	68	H_2O	11,000
C_2H_2	68	HCN	19,000

$K' = y/x'$ where y is the mole fraction of the component in the vapor phase and x′ is the mole fraction of the component in the liquid phase considering only the solvent and the component.
Sources: Shah and McFarland (1988); Epps (1992B)

14-1(A). If the objective is bulk removal of carbon dioxide from a gas stream, successive flashes are all that is required for regenerating the solution. More extensive regeneration can be achieved by vacuum flashing, by stripping with air or an inert gas, or by application of heat. In the case of hydrogen sulfide removal, stripping with inert gas or heat is the usual procedure.

If selective removal of sulfur compounds is required, the Selexol plant consists of an absorber, a flash, and a steam-heated stripping column [see **Figure 14-1(C)**]. The flashed gas is compressed and recycled to the absorber inlet, and the regenerator effluent is processed for the production of elemental sulfur.

In cases where both selective sulfur removal and complete carbon dioxide removal are required, such as with coal-derived substitute natural gases, two successive independent absorption-regeneration cycles are used as shown in **Figure 14-8.** Various flow schemes are discussed in some detail by Van Deraerschot and Valentine (1976) and Sweny (1980). These authors claim that, with proper plant design, removal of sulfur compounds to concentrations as low as a few parts per million can be achieved with relatively low co-absorption of carbon dioxide.

Operating results from three plants treating natural gas containing various amounts of hydrogen sulfide and carbon dioxide (Hegwer and Harris, 1973) are summarized in **Table 14-10.**

In Plant A, the bulk of the solvent is regenerated by flashing at three pressure levels (400 psig, 200 psig, and atmospheric), and a side stream is further regenerated by an additional atmospheric flash at elevated temperature. A split-flow circuit is used, with the semistripped solvent and the completely stripped solvent being fed to the absorber at different points.

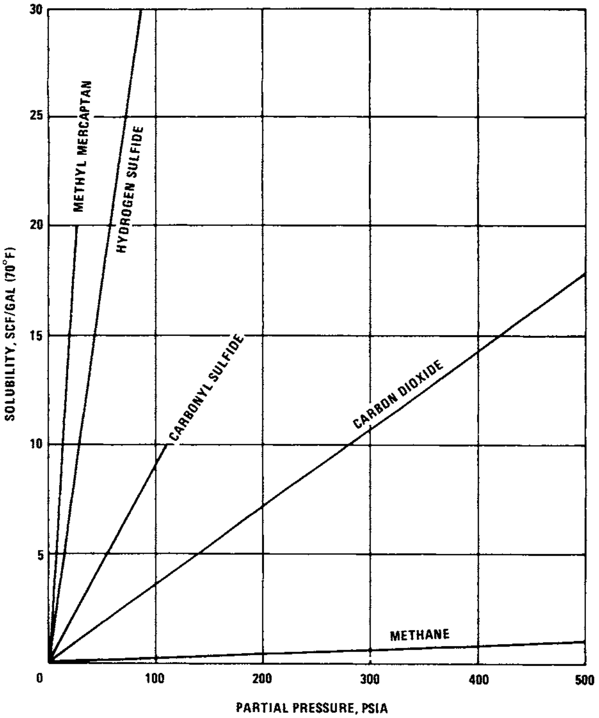


Figure 14-7. Solubility of gases in SELEXOL solvent. *Data of Sweny and Valentine (1970)*

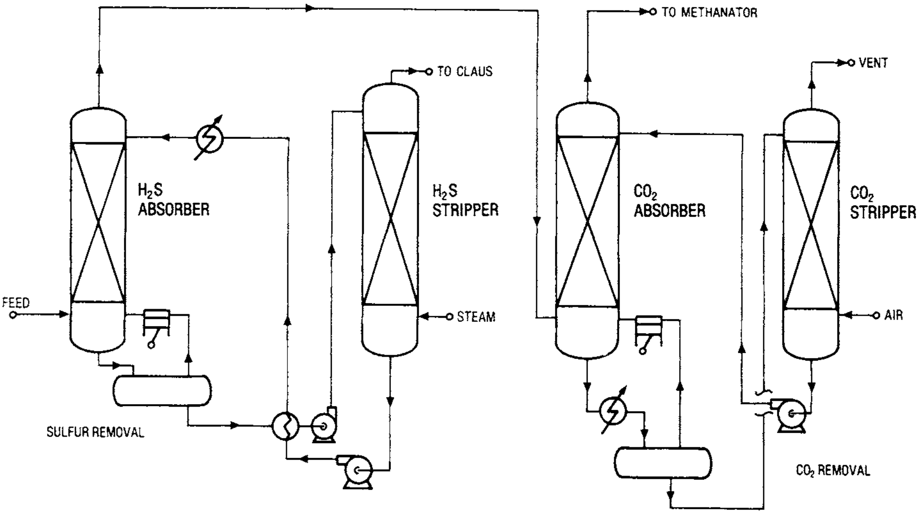


Figure 14-8. Flow diagram of SELEXOL process for selective hydrogen sulfide removal and complete carbon dioxide removal.

Table 14-10
Operating Data of SELEXOL Plants Processing Natural Gas

Plant	A	B	C
Feed gas:			
Volume, MMscfd	275	250	130
Pressure, psig	1,000	1,000	1,000
CO_2,%	43	3.5	18
H_2S, gr/100 scf	1	8	8
Treated gas:			
CO_2,%	3.5	3.0	2.5
H_2S, gr/100 scf	0.25	0.25	0.25

Data of Hegwer and Harris (1970)

Extensive power recovery by hydraulic turbines and gas expanders supplies the total pumping energy required. A single stream circuit is employed in Plant B. The solvent is regenerated by flashing at 300 psig, 175 psig, and atmospheric pressure and then by stripping with air at elevated temperature. The flow scheme of Plant C is similar to that of Plant B, except that a split-flow cycle for semistripped and completely stripped solvent is used. Solvent flashing is carried out at 250 psig, 190 psig, and atmospheric pressure. Power recovery is also practiced in Plants B and C.

A Selexol unit that is integrated into the design of an ammonia plant located in the Netherlands is described by Hernandez and Huurdeman (1989). Since minimum steam consumption is a key requirement, air stripping of the Selexol solvent is employed. The flow diagram is depicted in **Figure 14-9.** In this arrangement, three stages of flashing, including one at subatmospheric pressure, are used prior to air stripping. Lean solution from the stripper is cooled by heat exchange with a refrigerant before it is pumped to the absorber. The air feed to the stripper is cooled using a portion of the partially stripped solvent. The warmed solvent heats the stripper vent gas which increases its enthalpy, thereby conserving refrigeration. Some data on plant operation are provided in **Table 14-11.**

Commercial applications of the Selexol solvent for simultaneous hydrocarbon dew-point control and natural gas dehydration are described by Epps (1994). A plant design used in several European installations pretreats natural gas before it enters a molecular sieve unit. The design is intended to meet a treated gas specification of a maximum of 0.50 mole% CO_2 and a maximum of 6.5 mole% ethane and heavier components. A plant is designed to treat 26 MMscfd of gas at 32°F and 603 psia. Operating data for this plant, given in **Table 14-12,** show that it meets the CO_2 and ethane-plus removal specifications. The plant also reduces the water content of the gas from 75 ppmv to 12 ppmv, decreasing the load on the molecular sieve unit, and removes a major fraction of the sulfur components.

Commercial experience with the Selexol technology as applied to the treatment of landfill gas is described by Epps (1992B). This gas is derived from municipal landfills and, after removal of potentially harmful impurities, the gas is used as a fuel or in some cases is sold to natural gas distributors.

Typical landfill gas compositions cited by Epps (1992B) are shown in **Table 14-13.** Oxygen is present because air is drawn into the landfill due to the slight vacuum that occurs

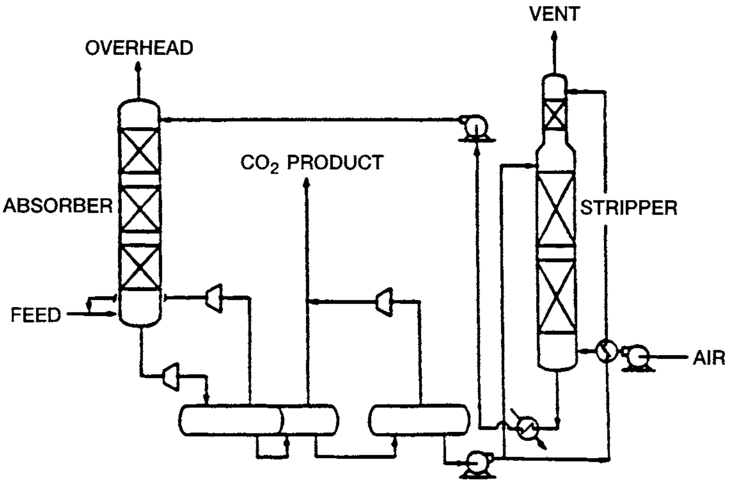


Figure 14-9. Flow diagram of SELEXOL process for ammonia synthesis gas treating (*Hernandez and Huurdeman, 1991*)

Table 14-11
Ammonia Plant SELEXOL Unit Operating Data

	Design	Operating
Plant capacity, NH_3 t/d	1,360	1,440
Feed gas CO_2 content, mol%	18.2	18.1
Treated gas CO_2 content, ppmv	1,000	440
CO_2 product recovery, % of feed	81	82
CO_2 product purity, mol%	99.0	99.4
CO_2 product temperature, °F	63	43
CO_2 product pressure, psia	21.6	23.3
Solvent losses, lbs/year		11,000

Data of Hernandez and Huurdeman (1989)

within the gas gathering system. The primary breakdown products of the municipal waste, largely paper, cardboard, and other organic materials, are methane and carbon dioxide. Small but significant amounts of H_2S are also formed.

Heavy and aromatic hydrocarbons as well as chlorinated hydrocarbons are generated by the municipal waste due to biodegradation and vaporization. If not removed from the landfill gas, these impurities can result in corrosion, scaling, and other problems and would also present environmental problems if discharged to the atmosphere.

As depicted in **Figures 14-10** and **14-11,** the Selexol process used for landfill gas purification consists of two stages. In Stage 1 all impurities except CO_2 are removed completely and medium BTU gas is produced. This gas is suitable for local use as fuel for boilers or gas tur-

Table 14-12
Inlet and Outlet Gas Compositions for SELEXOL Unit Pretreating Natural Gas

Component	Gas Composition, Mole%	
	Inlet	Outlet
H_2S	0.00020	0.00003
CH_3SH	0.00050	0.00012
CO_2	2.44	0.29
N_2	0.785	0.88
Methane	88.317	93.02
Ethane	7.539	5.33
Propane	2.403	0.35
i-Butane	0.119	0.02
Butane	0.303	0.07
i-Pentane	0.0080	0.002
Pentane	0.059	0.016
Hexane	0.008	0.003
Heptane	0.005	0.003
n-Decane	0.002	0.000
Water	0.008	0.001

Data of Epps (1994)

Table 14-13
Typical Landfill Gas Composition

Component	Range	Median
Methane, Mole%	41.2–60	53.4
Carbon Dioxide, Mole%	30.9–46.1	40.7
Nitrogen, Mole%	0.2–22.6	4.5
Oxygen, Mole%	0.01–5.2	0.35
Hydrogen Sulfide, ppmv	4.0–99	30.0
Impurities*, ppmv	72.0–2,000	181.0

***Impurities**

Methylmercaptan
Ethylmercaptan
Carbonyl Sulfide
Carbon Disulfide
Methylene Chloride
Ethane
Propane
Butene
Pentanes
Hexane
Heptane
Octane
Nonane
Decane
Undecane
Dodecane
1, 1 - Dichloroethylene
Trichloroethylene
Perchloroethylene
Tetrachloroethylene
Chlorobenzene
Ethylbenzene
Vinyl Chloride
Ethylene Dibromide
o,m,p - Dichlorobenzene
1,1 - Dichloroethane
1,2 - Dichloroethane
Benzene
Toluene
o,m,p - Xylene
Acetonitrile
1,2 - Dibromomethane
Benzyl Chloride
Chloromethane
1,2 - Dichloroethane
1,1,1 - Trichloroethane

Data of Epps (1992B)

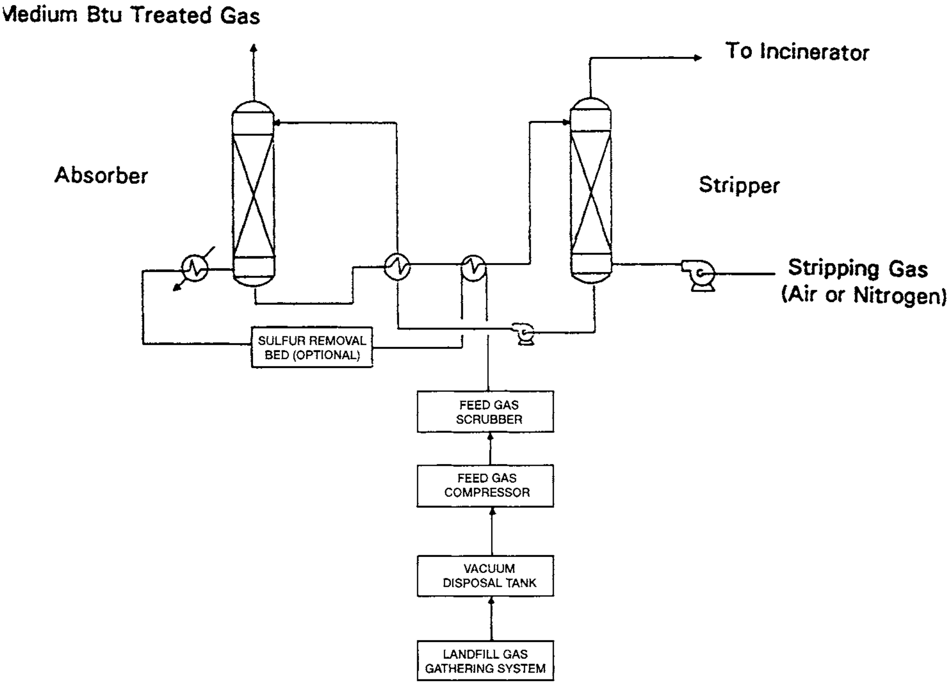


Figure 14-10. SELEXOL process flow diagram, landfill gas treatment; stage 1, medium Btu gas production. (*Epps, 1992B*)

bines. If high-BTU gas is required to meet pipeline specifications, it is necessary to remove the CO_2 as well as the other impurities. This is accomplished in Stage 2.

Figure 14-10, which represents Stage 1 purification, shows an optional fixed bed sulfur removal unit, such as iron sponge, to remove H_2S from the gas before it contacts the Selexol solvent. The solvent removes the heavy and chlorinated hydrocarbons since their solubilities in the solvent are exceedingly high, in some cases over an order of magnitude higher than the H_2S solubility. Air is used to strip absorbed hydrocarbons from the solvent and the resulting impure air is incinerated. If the H_2S is not removed ahead of the absorber, it will dissolve in the solvent and be oxidized in the air stripper, producing elemental sulfur and causing operating problems within the system. If steam stripping is used instead of air, it is possible to eliminate the fixed bed H_2S removal step, in which case most of the H_2S is stripped from the solvent by the steam and must be disposed of by incineration or other means. If the feed gas contains oxygen, some of the H_2S may be oxidized to elemental sulfur, even when steam is used for stripping. The first stage serves to remove H_2S, heavy hydrocarbons, and chlorinated compounds from the feed gas. When medium BTU gas is desired, no further treatment is required.

When high BTU gas is required, the gas is usually compressed to a pressure in the range of 150 to 350 psig and subjected to a second stage of absorption for CO_2 removal. This is a conventional Selexol unit in which solvent regeneration is accomplished by flashing, using a final vacuum flash if required to achieve higher CO_2 removal. Direct discharge to the atmosphere of the CO_2 from the second stage is ordinarily practiced. Flash gas from the highest

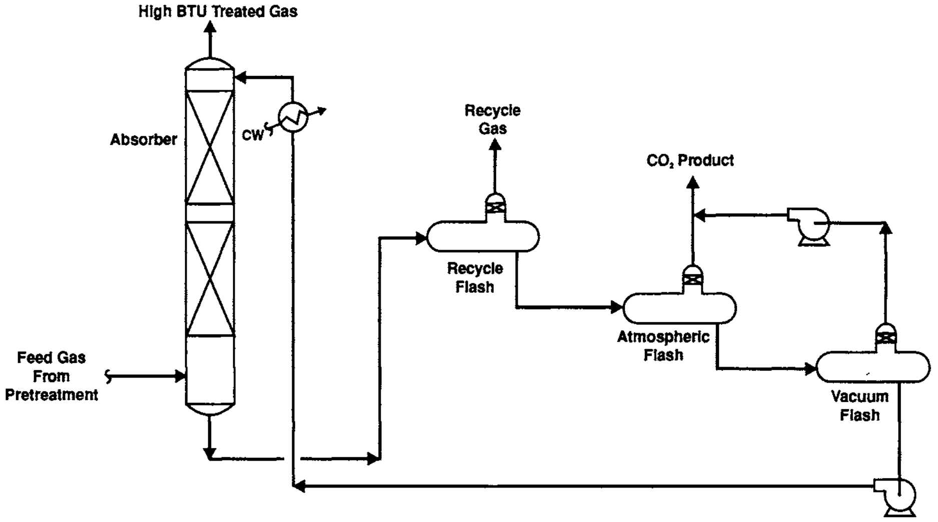


Figure 14-11. SELEXOL process flow diagram, landfill gas treatment; stage 2, high Btu gas production. (*Epps, 1992B*)

pressure flash step is recycled to improve overall methane recovery. This scheme is shown in **Figure 14-11.**

Sepasolv MPE Process

This process, which was developed by BASF of West Germany, is quite similar to the Selexol process, both with respect to the solvent used and the mode of operation. It was initially developed primarily for the selective removal of H_2S from natural gas, but reportedly is also suitable for CO_2 removal from synthesis gases. Two commercial Sepasolv MPE operating plants are described in the literature (Wölfer et al., 1980), but BASF (1992) reports that this process is no longer licensed.

The Sepasolv MPE solvent is described as a mixture of polyethylene glycol methyl isopropyl ethers with a mean molecular weight of about 316. Physical properties of the solvent are given in **Table 14-14.** Bucklin and Schendel (1985) and Wölfer et al. (1980) present gas solubility data that show MPE gas solubilities are similar to those of the Selexol solution.

Purisol Process

This process has been developed and commercialized by Lurgi GmbH of Frankfurt, Germany, and as of 1996 seven units were in operation or under construction (Lurgi Öl-Gas-Chemie GmbH, 1996). Discussions of the basic features of the process and of its application to the purification of natural gas, hydrogen, and synthesis gases are provided in several references: (Hochgesand, 1968; Hochgesand, 1970; Stein, 1969; Kapp, 1970; Beavon and Roszkowski, 1969; Lurgi, 1978; Lurgi, 1988A; Kriebel, 1989).

The solvent used in the Purisol process is N-methyl-2-pyrrolidone (NMP), a high boiling liquid, which has an exceptionally high solubility for hydrogen sulfide. NMP is particularly

Table 14-14
Physical Properties of Sepasolv MPE

Molecular Weight	316
Density, 20°C, g/cc	1.002
Specific Heat, 0°C, KJ/kgK	1.94
Specific Heat, 100°C, KJ/kgK	2.18
Viscosity, 20°C, in Pa. S	7.2
Viscosity, 0°C, in Pa. S	15.0
Freezing Point, °C	–25

Data of Wölfer (1982)

suitable for selective hydrogen sulfide absorption in the presence of carbon dioxide, since, as shown in **Table 14-4,** H_2S solubility is almost 9 times that of CO_2. NMP is also used in a number of other chemical processing applications, including acetylene recovery from pyrolysis gases, butadiene recovery from C_4 fractions, and as an extractive agent for aromatics recovery from oil refinery stocks. The Purisol process is reportedly capable of yielding gas streams containing less than 0.1 percent carbon dioxide and a few parts per million of hydrogen sulfide (Lurgi, 1978).

Basic Data

Physical properties of NMP are given in **Table 14-5** and in **Figure 14-12.** Equilibrium solubility data for carbon dioxide, hydrogen sulfide, methane, and propane are presented in **Table 14-15.** The data of Boston and Schneider (1971) were obtained with a gas mixture containing 97.10% methane, 1.02% propane, 1.17% carbon dioxide, and 0.71% hydrogen sulfide at a total pressure of 850 psia and a temperature of 74°F. Additional gas solubility data are given in **Table 14-4.**

Process Operation

As with other physical solvents, the optimum method for regenerating the solvent depends upon the purity required for the treated gas. In order of increasing severity, the applicable regeneration methods are flashing to atmospheric pressure, vacuum flashing, inert gas stripping, and regeneration by heating.

Grünewald (1989) reports that Purisol is effective in removing COS and that the removal can be enhanced by raising the absorption temperature and increasing the water concentration in the solvent. Both of these measures serve to promote the hydrolysis of COS to CO_2 and H_2S. The highest COS removal is obtained by the use of an undisclosed catalyst dispersed in the solvent and by increasing the residence time of the solvent in the absorber to further promote COS hydrolysis. NMP is somewhat more volatile than other physical solvents so water washing of gaseous effluents is required to minimize solvent losses.

The Purisol process is particularly well suited to the purification of high-pressure, high CO_2 synthesis gas for gas turbine integrated gasification combined cycle (IGCC) systems because of Purisol's high selectivity for H_2S. Extreme purity with regard to sulfur com-

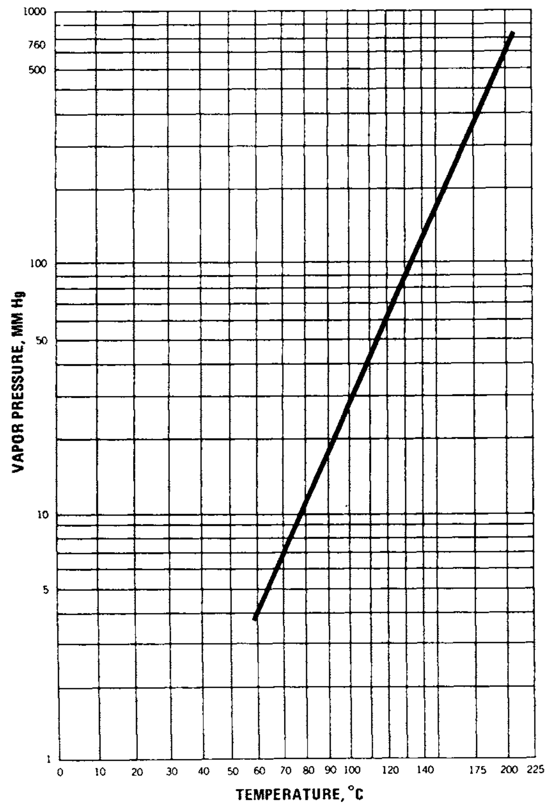


Figure 14-12. Vapor pressure of N-methyl-2-pyrrolidone. ***Data of General Aniline and Film Corp.***

pounds is not normally required for such fuel gas, and carbon dioxide in the purified gas expands through the gas turbine to provide additional power.

Grünewald (1989) suggests the flow arrangement shown in **Figure 14-13** as optimum for the processing of gas turbine fuel gas for IGCC applications. Hydrogen sulfide and some carbon dioxide are removed from the raw gas in the H_2S absorber. The rich solution is flashed to a lower pressure and the flashed gas is passed through a reabsorber (for selective removal of H_2S) before it is recompressed and recycled to the main gas stream. The solution is then completely stripped of acid gas by a second (hot) flash step followed by a reboiled stripping operation. Gas from the hot flash step is purified and recycled, while the reboiled stripper offgas, which has a high H_2S concentration, is sent to an oxygen-blown Claus unit. The Claus unit is operated so that its tail gas contains H_2 and CO, as well as H_2O and CO_2 and any unconverted H_2S and SO_2. The tail gas is passed through a hydrogenation reactor where all sulfur compounds are converted to H_2S. It is then cooled to remove water and the remaining gas, consisting primarily of CO_2 with small amounts of H_2 and H_2S, is recycled through the reabsorber to the fuel gas stream. The net result of the process is selective hydrogen sulfide removal from the fuel gas and conversion of the H_2S to elemental sulfur without

Table 14-15
Equilibrium Solubility of Gases in N-Methyl-2-Pyrrolidone

Gas	Temperature, °C	Partial pressure, atm. abs.	Solubility, vol/vol*	Reference
CO_2	20	1.0	3.95	A
CO_2	23.5	0.67	2.0	C
CO_2	35	1.0	3.0	B
CO_2	35	10.0	32.0	B
H_2S	20	1.0	48.8	A
H_2S	23.5	0.41	14.3	C
H_2S	35	1.0	25.0	B
CH_4	20	1.0	0.28	A
CH_4	23.5	56	12.2	C
C_3H_8	23.5	0.59	1.9	C

**Gas volume at 0°C and 760 mm Hg.*
Data sources: A) Stein (1969); B) Hochgesand (1970); C) Boston and Schneider (1971)

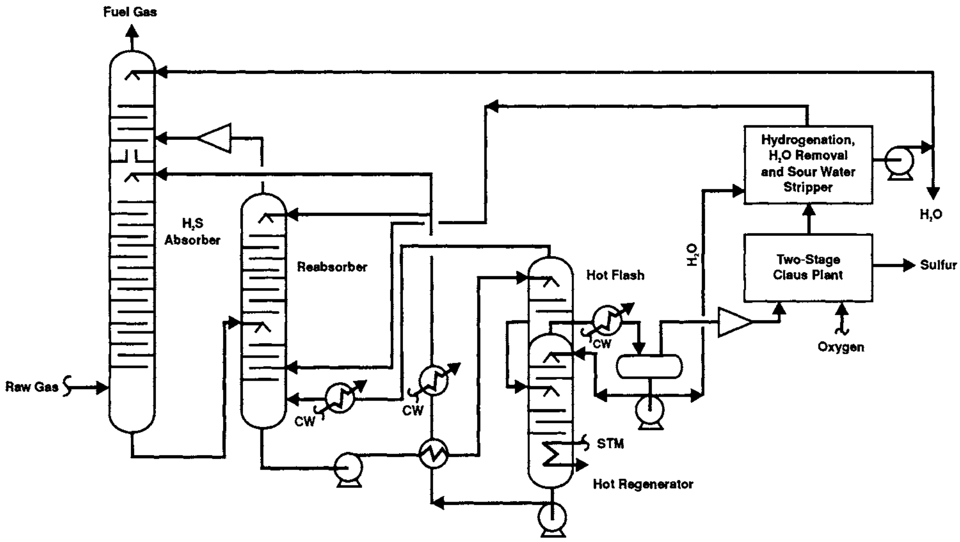


Figure 14-13. Proposed optimum configuration for combined cycle fuel gas desulfurization, incorporating a Purisol unit, a two-stage oxygen-blown Claus unit, and a Claus tail gas hydrogenation unit. (*Grünewald, 1989*)

the production of a Claus plant offgas stream or the use of a Claus tail gas unit with its associated tail gas incinerator.

Operation of a Purisol plant processing about 40 MMscfd of natural gas containing hydrogen sulfide and carbon dioxide has been described by Stein (1969). The principal objective in this installation is to remove a maximum of hydrogen sulfide with only partial removal of carbon dioxide. Absorption of the acid gases is carried out in two columns, operating in series, the first provided with trays and the second with packing. The solvent passes from the second to the first absorber and is then regenerated by flashing at three different pressure levels, augmented by stripping with inert gas at elevated temperature in the last flash. Cooling of the solvent is required between the two absorption columns and, of course, after regeneration. The gas released in the first flash is recompressed and returned to the inlet of the first absorber. The acid gases are processed in a Claus type sulfur recovery unit. Typical operating data from this installation are given in **Table 14-16.**

Examples of process conditions proposed by Lurgi (1978) for three cases involving (a) essentially complete carbon dioxide removal from high-pressure gases with high carbon dioxide content, (b) bulk removal of hydrogen sulfide from natural gas, and (c) selective removal of hydrogen sulfide from natural gas are presented in **Table 14-17.** The first case involves solvent regeneration by flashing and inert-gas stripping, see **Figure 14-1(B).** In the second case, the solvent is simply flashed at three pressure levels. In the third case, requiring complete solvent regeneration, flashing and high temperature regeneration with reboiling are employed, see **Figure 14-1(C).**

Table 14-16
Operating Data for Purisol Plant Treating Natural Gas

	Inlet Gas	Outlet Gas
H_2S, vol %	1–10	0.02–0.2
CO_2, vol %	8–26	6–20
N_2, vol %	4–5	4–5
CH_4, vol %	70–80	75–90
Temperature, °F	32–59	77
Pressure, psig	720	570
Temperature, °F:		
Solvent to first absorber	70	
Solvent from first absorber	86	
Solvent to second absorber	75–82	
Solvent from second absorber	104–111	
Solvent to flash	266	
Pressure, psig:		
First flash	500	
Second flash	210	
Third flash	7.5	

Data from Stein (1969)

Table 14-17
Typical Process Conditions for Acid-Gas Removal with Purisol Process

Case:				
Feed gas:		1	2	3
Volume, MMscfd		100	100	100
Pressure, psig		1,070	510	1,070
Temperature, °F		110	80	80
H_2	vol.%	64.53	—	—
CO_2	vol.%	33.15	1.0	15.0
H_2S	vol.%	—	34.0	6.0
CO	vol.%	1.50	—	—
CH_4	vol.%	0.44	63.7	75.0
C_2H_6-C_4H_{10}	vol.%	—	1.1	—
$C_6H_{12}^+$	vol.%	—	0.2	—
N_2	vol.%	0.38	—	4.0
Treated gas:				
H_2	vol.%	96.44	—	—
CO_2	vol.%	0.10	1.2	13.6
H_2S	vol.%	—	2.0	2 ppm
CO	vol.%	2.24	—	—
CH_4	vol.%	0.59	95.4	82.0
C_2H_8-C_4H_{10}	vol.%	—	1.4	—
$C_6H_{12}^+$	vol.%	—	—	—
N_2	vol.%		0.63	4.4
Utilities:				
Power, kW*		2,100	1,600	1,100
Steam, (45 psig), lb/hr		3,750	1,500	13,000 (60 psig)
Cooling water (75°F), gpm		1,300	750	820
Condensate, lb/hr		2,850	2,000	2,200
NMP loss, lb/hr		6.5	11	9

**Without power recovery.*
Data source: Lurgi GmbH (1978)

Rectisol Process

The Rectisol process, which uses methanol as its solvent, was the first physical organic solvent process. Although it is a true physical solvent process, it has a number of features that set it apart from the other physical solvent processes. First, Rectisol has the demonstrated ability to separate troublesome impurities that are produced in the gasification of coal or heavy oil, including hydrogen cyanide, aromatics, organic sulfur compounds, and gum-forming hydrocarbons. The use of methanol also facilitates dehydration and the prevention of ice and hydrate formation at the low temperatures used in the process. The second distinguishing feature is that the Rectisol process operates at much lower temperatures than other physical solvent processes—with operating temperatures as low as –75° to –100°F. At these temperatures, methanol still has a low viscosity so that mass and heat transfer are not significantly impaired, and the solvent's carrying capacity for both CO_2 and H_2S becomes very high, considerably higher than that of other physical solvents at their typical operating temperatures. These features lead to the ability to achieve very sharp separations, with H_2S concentrations of typically 0.1 ppm and CO_2 concentrations of just a few ppm in the treated gas. Likewise, Rectisol can achieve concentrated H_2S streams suitable for Claus plant feeds and CO_2 offgases essentially free of H_2S.

Operation at very low temperatures with very sharp separations results in relatively complex flow schemes. This, combined with the need for low level refrigeration, leads to high plant costs. As a result, most applications of the Rectisol process represent relatively difficult gas treating conditions where other gas treating processes are not suitable for one reason or another. Typical applications are the purification of gas streams in the heavy oil partial oxidation processes of Shell and Texaco and the Lurgi coal gasification process, as used at the Sasol plants in South Africa.

The Rectisol process was initially developed in Germany by Lurgi GmbH. It was developed further jointly with Linde AG (Kriebel, 1989) and is now offered by both firms. The major use of the process is in coal- and heavy oil-based facilities to produce ammonia, methanol, hydrogen, SNG, Fischer-Tropsch liquids, and oxo alcohols. In 1996 it was reported that more than 100 units were in operation or under construction (Lurgi Öl-Gas-Chemie GmbH and Linde AG, 1996).

A large industrial Rectisol plant used for the purification of gas obtained by coal gasification in Lurgi gasifiers at the first Fischer-Tropsch plant of South African Oil, Coal, and Gas Corporation (SASOL) in South Africa has been described (Hoogendoorn and Solomon, 1957; Ranke, 1973). This plant, which was installed in the 1950s, consists of three identical purification units with a total capacity of 164 MMscfd of gas and a common regeneration section. In the 1970s, two much larger coal gasification facilities were installed by Sasol, with each Rectisol purification system treating over 1 billion standard cubic feet per day of gas. Each of these Rectisol facilities consists of four independent trains. Another large Rectisol facility was installed at the Great Plains gasification plant in North Dakota and was designed to produce 137.5 MMscfd of substitute natural gas (SNG) from lignite.

Basic Data

Physical property data for methanol are given in **Table 14-5.** The solubility of carbon dioxide in methanol as a function of temperature at a partial pressure of one atmosphere is shown in **Figure 14-14** (Herbert, 1956). The effect of partial pressure on the equilibrium solubility at two temperatures is shown in **Figure 14-15** (Hochgesand, 1968). Equilibrium solubilities of H_2S and CO_2 at two temperatures are reported by Hochgesand (1970) and are presented in **Table 14-18.** Additional data on the effects of temperature on the solubilities of gases in methanol are provided by **Figure 14-2.** The vapor pressure of methanol (Dreisbach, 1952) is given in **Figure 14-16.** The high vapor pressure of methanol results in relatively high vapor pressure losses and correspondingly high methanol makeup requirements.

Process Description and Operation

The Rectisol process is available in a wide variety of configurations to meet specific requirements and feed conditions. Systems can be designed to (1) remove all impurities, pro-

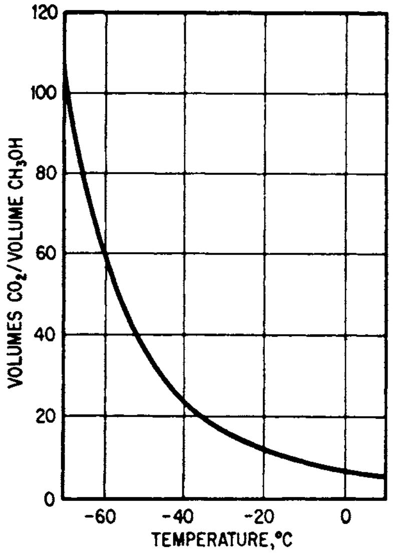


Figure 14-14. Solubility of carbon dioxide in methanol, partial pressure of carbon dioxide = 1 atm. *Data of Herbert (1956)*

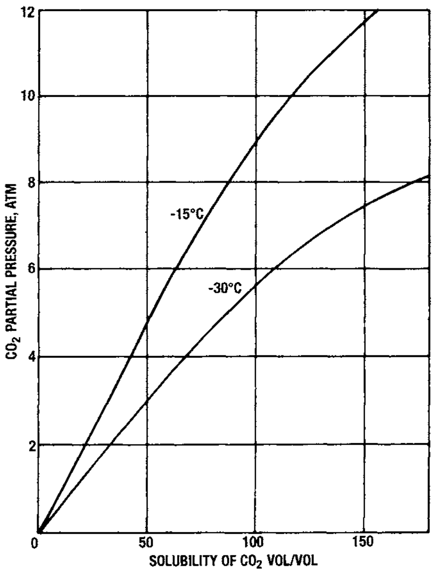


Figure 14-15. Effect of partial pressure on solubility of carbon dioxide in methanol. *Data of Hochgesand (1968)*

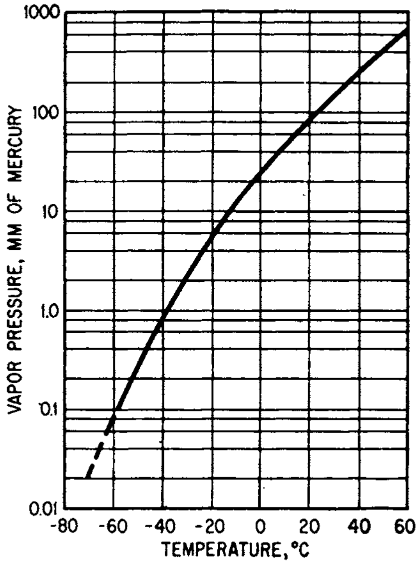


Figure 14-16. Vapor pressure of methanol. ***Data of Dreisbach (1952)***

Table 14-18
Equilibrium Solubilities of H_2S and CO_2 in Methanol

Temperature, °C	Solubility, vol/vol		Selectivity H_2S/CO_2
	H_2S	CO_2	
−10	41	8	5.1
−30	92	15	6.1

Source: Data of Hochgesand (1970)

ducing a treated gas that is essentially free of both CO_2 and sulfur compounds; (2) remove H_2S and other sulfur compounds selectively, leaving a portion of the CO_2 in the treated gas; and (3) remove and recover CO_2, and H_2S separately producing three product streams (purified gas, CO_2, and H_2S). Typical objectives of the different configurations include the production of a highly purified gas stream; the production of a hydrogen sulfide-rich gas stream suitable as feed to a Claus plant; and the production of a pure CO_2 stream that can be used in the synthesis of urea.

A Rectisol unit designed for the production of synthesis gas and carbon dioxide, which are suitable as feeds to a urea plant, has been described by Linde AG and Lurgi GmbH (1992). The material balance for this type of plant and a summary of utility requirements based on a 1,000 tons/day ammonia unit are provided in **Table 14-19.**

Two basic configurations of the Rectisol process are the nonselective standard process and the selective version. In the nonselective or single-step process the CO_2 and H_2S are

Table 14-19
Rectisol Process Material Balance and Utility Requirements

Material Balance, Mol%	Feed	Purif. Gas	CO_2	Tail Gas	H_2S Stream
H_2	62.47	95.27	0.84	0.07	0.31
$N_2 + Ar$	0.51	0.76	0.08	25.32	4.36
$CO + CH_4$	2.67	3.97	0.33	0.04	0.08
CO_2	34.10	20 ppm	98.75	74.57	68.01
$H_2S + COS$	0.25	0.1 ppm	2 ppm	5 ppm	27.24
Conditions					
Flow, kmol/h	6,021.1	3,936.1	1,283.9	1,003.6	54.2
Pressure, bar	78	76	1.8	1.1	2.5

Utility Requirements	
Power (shaft, without power recovery), kW	1,100
Steam (6 bar), lb/h	14,300
Refrigerant (at 235°K), Btu/h	6.75×10^6
Cooling water ($\Delta t = 10°C$), gpm	1,320
Stripping gas (4 bar), kmol/h	256.7
Methanol loss, lb/h	66

Basis: 1,000 ton/d ammonia plant (Linde AG and Lurgi GmbH, 1992)

absorbed simultaneously; whereas, in the selective or two-step design H_2S is removed in the first step followed by CO_2 removal in the second step. The majority of commercial applications employ the standard configuration.

Many of the operating details of the commercial facilities are held confidential by the licensors. However, good general descriptions are available in the previously cited articles, and in a non-confidential DOE document (Miller and Lang, 1985) describing the Great Plains SNG-from-coal plant in North Dakota. The description which follows is taken from this latter reference.

Standard Rectisol Plant

In the North Dakota plant, lignite is gasified using Lurgi technology. After removal of heavy impurities such as coal tar and particulate solids from the gasifier effluent and a water gas shift conversion step, the Rectisol process is used to remove naphtha, H_2S, CO_2, and other contaminants such as HCN, mercaptans, COS, and organic sulfur impurities. The process gas then undergoes methanation, which produces methane from H_2 and carbon oxides to yield pipeline specification gas referred to as SNG (synthetic or, alternatively, substitute natural gas).

The Great Plains Rectisol unit consists of two identical absorption and regeneration trains with a common naphtha extraction and methanol recovery train. The basic flow scheme is shown in **Figure 14-17.** The composition of the feed gas to the Rectisol plant at the Great Plains plant is 39% CO_2 and 0.35% H_2S. Feed gas pressure to the Rectisol unit is close to 400 psig, while the combined feed gas flow for both Rectisol trains is 556 MMscfd.

The feed gas is first chilled by heat exchange with process off-gas streams and then by ammonia refrigeration to a temperature between −30° and −55°F. The feed gas then passes to the prewash and absorber column. The prewash and absorber column is divided into three major sections: the bottom prewash, the middle main absorption, and the top final absorption sections. The middle main absorption section is divided into upper and lower segments by a chimney tray. The bottom or prewash section removes naphtha and other relatively heavy impurities, while H_2S, CO_2, and most of the lighter impurities are absorbed in the middle main absorption sections. The top final absorption section removes the residual traces of CO_2 and H_2S from the product gas. Methanol is used in all three sections to accomplish these separations.

The leanest methanol, from the hot regenerator column, is fed to the top final absorption section of the prewash and absorber column. Most of the methanol from the flash regenerator is returned to the upper main absorption section. Methanol from this upper main absorption section is withdrawn from the prewash and absorber column and chilled by ammonia refrigeration. Most of this methanol is recycled back to the top tray of the lower main absorption section. This removes the heat of absorption and permits higher solution loadings. A small slipstream of the rich, chilled methanol is used for heavy impurity removal in the bottom prewash section.

The treated gas with H_2S and CO_2 concentrations reduced to 0.2 ppm and 1.5 volume percent, respectively, is used to precool the feed gas, and then passes to the battery limits enroute to methanation. With the design feed gas, both Rectisol trains produce 355 MMscfd of product gas which, after methanation, yields 137 MMscfd of SNG. The rich methanol from the main absorption section of the prewash and absorber column is chilled by ammonia refrigeration and flows to a series of six flash regeneration steps, A through F. In these six flash regeneration stages, the rich solvent is flashed at successively lower pressures with the final flash at vacuum conditions. Offgas from the first flash, containing significant amounts of H_2, CO, and CH_4, is recycled to recompression facilities for eventual recovery of these valuable components. Flash gas from the other flashes is sent to a Stretford unit for removal of H_2S. Gas from the three lowest pressure flashes requires compression to 8 psig before Stretford treating.

Some of the methanol from the flash regenerator is regenerated in the hot regenerator column where H_2S is stripped to very low residual levels. This tower is reboiled with low pressure steam; while the overhead gas stream containing acid gases is washed with steam condensate for methanol removal, then combined with the flash regenerator offgas, and directed to the Stretford plant for H_2S removal.

Methanol from the prewash section of the prewash and absorber column, which contains naphtha and other impurities, is flashed in the prewash flash vessel for removal of dissolved gases, which also pass to the Stretford unit. The flashed methanol then flows to the naphtha extractor along with several aqueous streams. When the aqueous streams and the prewash methanol are mixed, the methanol preferentially dissolves in the aqueous phase and the naphtha is recovered as an immiscible layer in the extractor. The naphtha is then distilled in the naphtha stripper for removal of dissolved gases and small amounts of water.

The methanol-water cut from the naphtha extractor is distilled in the azeotrope column where a methanol-water-naphtha azeotrope is taken overhead and then recycled to the naphtha extractor. The bottom product from the azeotrope column contains methanol and water

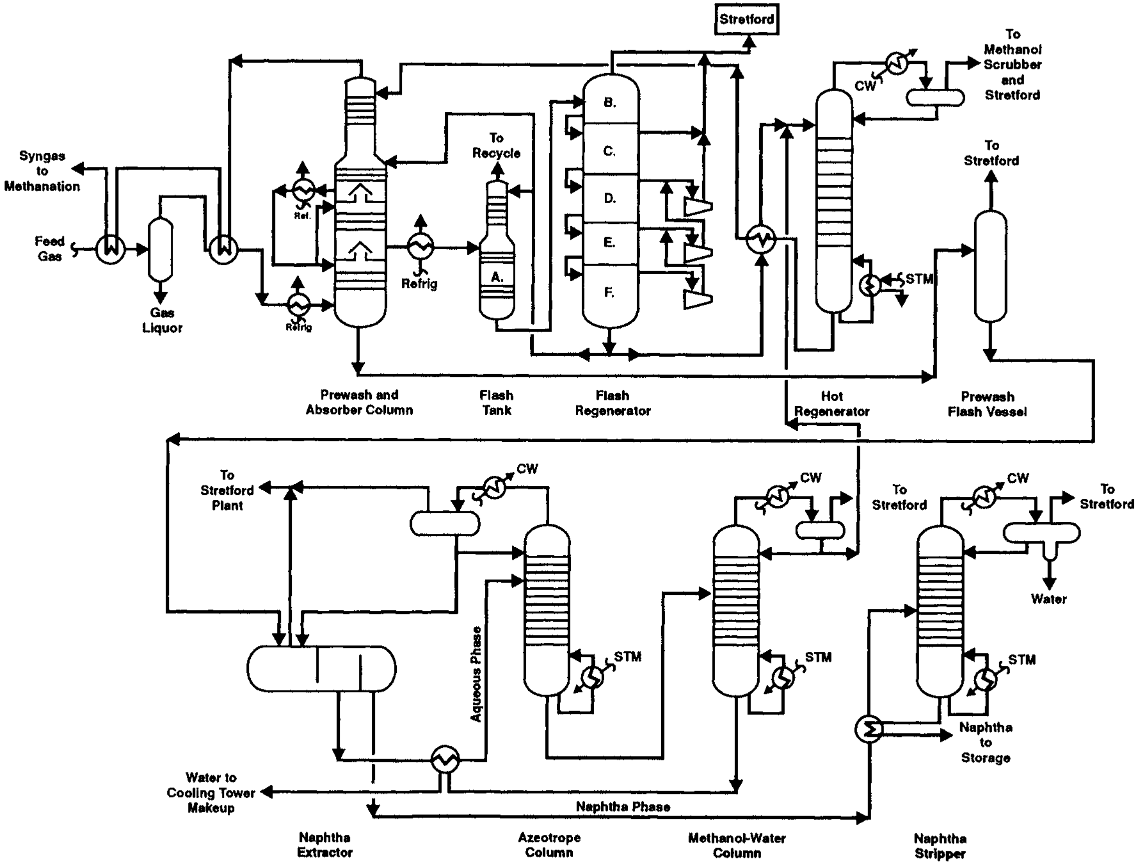


Figure 14-17. Simplified process flow diagram of Rectisol process system at the SNG-from-coal plant in North Dakota. (*Miller and Lang, 1985*)

and is sent to the methanol-water column. In this tower, the water is rejected from the bottom and used off-site for cooling tower makeup. The methanol overhead stream is recycled to the hot regenerator column for eventual reuse in the final absorption section of the prewash and absorber column.

Many of these steps are made necessary by the presence of naphtha and other troublesome contaminants in the gas stream and are not normally included in plants that treat gas streams derived from sources other than the Lurgi coal gasification process.

Selective Rectisol Plant

Hochgesand (1968, 1970) and Kriebel (1989) present essentially identical flow diagrams for a selective Rectisol unit treating high-pressure partial oxidation gas. See **Figure 14-18** for details.

In the selective Rectisol process, the H_2S is removed in the first absorber using a relatively small flow of methanol while the CO_2 is removed in the second absorber with the main methanol flow. A flash regenerator is used to expel some of the dissolved CO_2 from the rich methanol. Nitrogen stripping is then used to remove additional CO_2 and further concentrate the H_2S in the methanol. Finally, H_2S is stripped from the methanol in the hot regenerator,

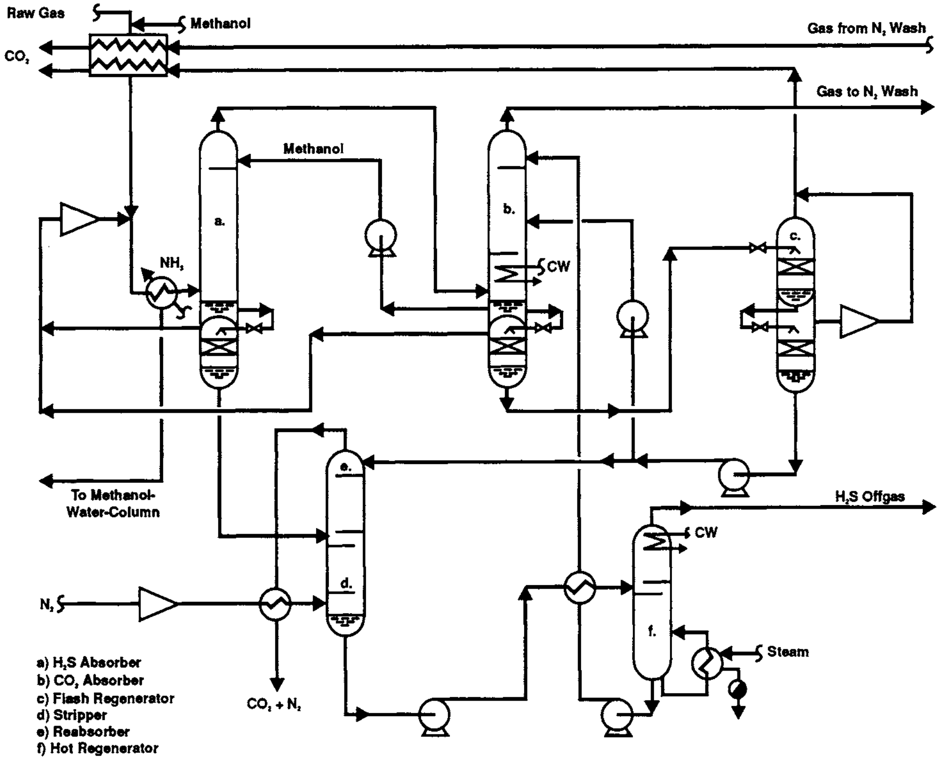


Figure 14-18. Simplified process flow diagram of selective Rectisol process. (*Kriebel, 1989*)

which is a conventional trayed distillation tower with reboiler and condenser. An additional tower, which is not shown, is also used to remove water accumulating in the circulating methanol stream.

Ifpexol Process

This process has recently been introduced by Institut Français du Pétrole (IFP). The process employs methanol as the sole agent for treating natural gas to achieve (1) dehydration, (2) natural gas liquids recovery, and (3) acid gas removal. These steps are integrated into an overall processing system. The first Ifpexol unit was constructed in 1992. In 1996, it was reported that six Ifpexol process plants were in operation and five more were in various stages of design. Capacities range from 10 to 350 MMscfd (Institut Français du Pétrole, 1996). The technology is described by Minkkinen and Levier (1992). The overall system involves two separate processes that may be used independently or in combination. IFPEX-1 removes condensable hydrocarbons from the feed gas, while IFPEX-2 accomplishes acid gas removal and recovery.

Figure 14-19 is a flow diagram of the combined Ifpexol concept. In the first step water is separated from the natural gas to allow low-temperature processing in the subsequent steps. This is accomplished by contacting the natural gas feed with a methanol-rich stream in a conventional countercurrent contactor. Methanol, since it is more volatile than water, is vaporized and taken overhead, while the water stream containing as little as 50 ppm of methanol is withdrawn as bottoms. Control of this column to achieve the desired splits of water and methanol while minimizing methanol losses in the water stream is critical to proper operation.

Liquid hydrocarbons and a water-methanol liquid stream are condensed from the gas as it is chilled for low temperature acid gas removal by the IFPEX-2 process with the water-methanol cut being recycled to the dehydration step. The chilled mixture is passed through a separator from which the liquid water-methanol cut is recycled to the dehydration column, the liquid hydrocarbon cut is removed for recovery, and the gas phase is sent to the IFPEX-2

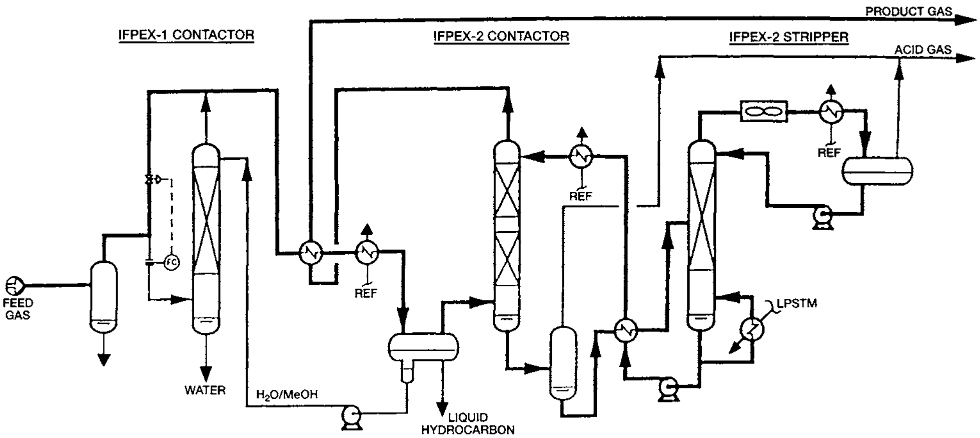


Figure 14-19. Flow diagram of Ifpexol process, consisting of IFPEX-1 and IFPEX-2 units in series. (*Menkkinen and Levier, 1992*)

process absorber. In the IFPEX-2 section, acid gases are removed from the natural gas stream in a conventional absorber-stripper system, much as in the Rectisol process. IFP states that hydrocarbon removal in this acid gas removal step can be controlled within limits by adjusting absorption parameters, primarily the water content of the methanol.

Selective removal of H_2S or removal of essentially all the acid gas can be achieved. Pipeline H_2S specifications of 0.25 grains per 100 SCF and CO_2 levels of 1% are claimed to be feasible (Institut Français du Pétrole, 1992).

Estasolvan Process

The Estasolvan process was announced jointly by Institut Français du Pétrole of France and Friedrich Uhde GmbH of West Germany (Franckowiak and Nitschke, 1970). The process was demonstrated in two pilot plants, but it has recently been reported that further promotion of the process has been halted, and the process is now commercially unavailable (Uhde, 1992).

The Estasolvan process was based on the use of tri-n-butyl phosphate as a solvent. Selected physical properties of this material are listed in **Table 14-20.** The process development work focused primarily upon the selective removal of H_2S from natural gas that also contained CO_2. The solubility of CO_2 in the solvent is significantly lower than in most other physical solvents used for gas treating, but this, of course, is beneficial in accomplishing selective removal of H_2S.

One proposed variation of the process incorporated simultaneous absorption of acid gases and liquefied petroleum gases (LPG) in the solvent, followed by separation of the absorbed components by fractional distillation. High percentage removal of both COS and mercaptans was also claimed.

Table 14-20
Physical Properties of Tributylphosphate

Formula		$(C_4H_8)_3PO_4$
Molecular weight		266.32
Specific gravity (25°C)		0.973 gram/ml
Melting point		−80°C
Boiling point (30 mm Hg)		180°C
Viscosity		
	20°C	3.19 cp
	40°C	2.15 cp
	100°C	1 cp
Vapor pressure	20°C	0.0037 mm Hg
	40°C	0.018 mm Hg
	100°C	1 mm Hg
Solubility		
TBP in water (25°C)		0.42 gram/liter
Water in TBP (25°C)		65 grams/liter

Data source: Franckowiak and Nitschke (1970)

Methylcyanoacetate Process

The Methylcyanoacetate process, disclosed by the Union Oil Company of California (Woertz, 1971), was tested in a pilot plant, but has not been used commercially. The solvent, methylcyanoacetate (MCA), is reported to be stable and to have high capacity for acid gases. An interesting feature of the process is that the solvent is appreciably more selective for acid gases contained in hydrocarbon gas streams than the solvents used in commercial processes of this type. For example, it is reported by Woertz (1975) that under comparable operating conditions, propylene carbonate removes about 50% of the propane and 100% of the butanes present in a hydrocarbon feed gas, while MCA removes only about 30% of the propane and 75% of the butanes. Vapor-liquid equilibrium data for a number of gases in methylcyanoacetate have been reported (Woertz, 1975).

MIXED PHYSICAL/CHEMICAL SOLVENT PROCESSES

Sulfinol Process

In contrast to the processes described previously in this chapter, the Sulfinol process employs a mixture of a chemical and a physical solvent. This is often referred to as a "mixed solvent process." In a mixed solvent process, the physical solvent removes the bulk of the acid gas while the chemical solvent (an alkanolamine in the Sulfinol process) purifies the process gas to stringent levels, all in a single step. Although the process flow sheet resembles that of a conventional amine treating unit, the presence of the physical solvent enhances the solution capacity, especially when the gas stream to be treated is at high pressure and the acidic components are present in high concentrations. The Sulfinol process also has demonstrated its ability to achieve high efficiency removal of other impurities, namely COS, mercaptans, and other organic sulfur compounds.

The Sulfinol process is licensed by the Shell Oil Company in the U.S. and by Shell International Petroleum Maatschappij (SIPM) in the Netherlands. The process has found wide application in the treatment of natural, refinery, and synthesis gases. The Sulfinol process can meet the requirement for deep CO_2 removal to 50 ppm for LNG plants, as well as the opposite extreme of bulk CO_2 removal using flash regeneration. **Table 14-21** shows the ranges of feed gas composition and conditions and of treated gas purity specifications of licensed Sulfinol plants (Shell, 1992). In 1996, more than 180 commercial units were reported to be in operation or under construction (Shell, 1996).

Basic Data

The Sulfinol solvent consists of sulfolane (tetrahydrothiophene dioxide) and an alkanolamine, usually diisopropanolamine (DIPA) or methyldiethanolamine (MDEA), and water. The solvent with DIPA is referred to as Sulfinol-D or simply as Sulfinol, and the solvent with MDEA is referred to as Sulfinol-M. Typically, Sulfinol-D is used when essentially complete removal of both hydrogen sulfide and carbon dioxide and deep removal of carbonyl sulfide is desired. Sulfinol-M is used for the selective removal of hydrogen sulfide over carbon dioxide and the partial removal of carbonyl sulfide (Nasir, 1990). Both Sulfinol solvents are reported to be capable of removing mercaptans and alkyl sulfides to very low levels.

The equilibrium solubility of hydrogen sulfide in sulfolane and in the Sulfinol-D solvent, as a function of partial pressure, is shown in **Figure 14-20** (Dunn et al., 1964). For compari-

Table 14-21
Ranges of Feed Gas Compositions, Conditions, and Treated Gas Purity For Licensed Sulfinol Plants

	Feed Gas	Treated Gas Purity
Pressure, psia	22 to 1,330	
Acid Gas Content, %vol		
H_2S	0 to 53.6	1 to 8 ppmv
CO_2	2.6 to 43.5	50 ppmv to 3.7%m+
COS	0 to 1,000 ppmv	3 to 160 ppmv
RSH	0 to 3,000 ppmv	4 to 160 ppmv
Acid Gas Partial Press, psia		
H_2S	0 to 713	
CO_2	2.7 to 396	
$H_2S + CO_2$	12 to 748	
H_2S/CO_2 Ratio, Volume	0 to 20.4	

Source: (Shell, 1992)

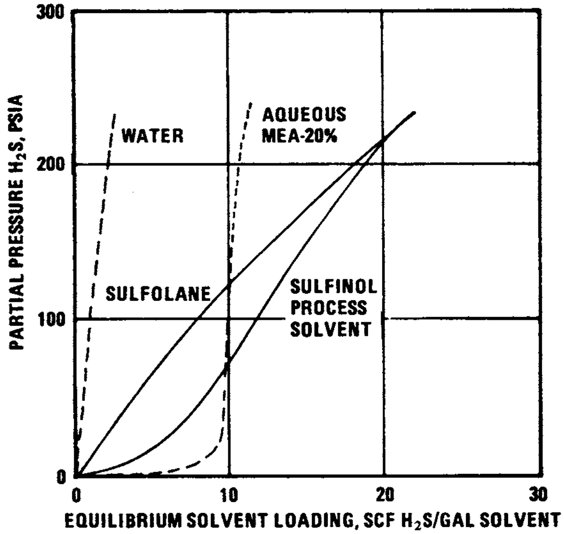


Figure 14-20. Solubility of hydrogen sulfide in Sulfinol solvent. *(Dunn et al., 1964)*

son, the solubility of hydrogen sulfide in water and in 20% aqueous monoethanolamine solution is also shown. It should be noted that, from the standpoint of solvent capacity, the Sulfinol solvent is inferior to aqueous monoethanolamine at low hydrogen sulfide partial pressures. However, as the partial pressure of hydrogen sulfide becomes higher, the capacity of the Sulfinol solvent continues to increase, while that of the monoethanolamine solution remains almost constant because the stoichiometry of the chemical reaction between hydrogen sulfide and the amine limits the capacity of the monoethanolamine solution.

Process Description

A typical flow diagram of a Sulfinol unit is shown in **Figure 14-21.** The scheme is identical to that of a typical alkanolamine system as discussed in Chapter 2, with the exception of the flash tank, which is optional in aqueous ethanolamine systems treating low pressure gases, but almost a necessity in a Sulfinol unit. Because of the relatively high solubility of hydrocarbons in the solvents, omission of the flash tank would lead to high concentrations of hydrocarbons in the acid gas and possibly to operational difficulties in Claus units where the hydrogen sulfide is converted to elemental sulfur. The flash gas from the flash tank can either be recompressed and recycled to the absorber inlet, or, as usually practiced in natural gas-treating plants, treated and used as plant fuel.

Process Operation

Operating data from commercial units using Sulfinol-D as reported by Dunn et al. (1965) and Frazier (1970) are presented in **Table 14-22.** Pilot-plant data obtained with an East Texas natural gas are shown in **Table 14-23** (Dunn et al., 1964). For comparison, performance data of the same pilot plant with an aqueous 20% monoethanolamine solution are also given. Additional pilot-plant data obtained in processing four different Canadian natural-gas streams are given in **Table 14-24** (Dunn et al., 1964).

A Sulfinol-M plant in Rankin County, Mississippi, which treats 100 MMscfd of natural gas containing 34% H_2S and produces pipeline quality gas and 1,275 LT/d of elemental sulfur, is described by Christensen (1979). The plant also removes 97% of the COS, which is present in the feed gas at a concentration of 705 ppm.

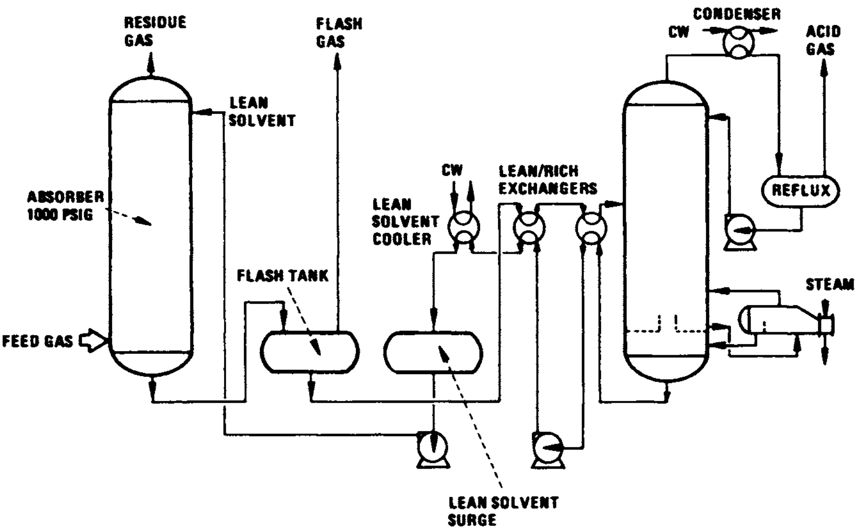


Figure 14-21. Typical flow diagram of Sulfinol process.

Table 14-22
Commercial Operating Data for the Sulfinol-D Process

Plant	A	B	C	D
Feed gas:				
Volume, MMscf/d	32	150	50	150
Pressure, psig	1,000	1,000	1,000	1,000
H_2S, gr/100 scf	1.60(%)	6.35	27.00	19.00
CO_2, %	6.90	3.30	9.16	6.81
COS, ppm	7	—	—	—
RSH, gr/100 scf	19(ppm)	0.75	0.20	—
Total hydrocarbon, %	91.00	96.33	89.88	91.40
Treated gas:				
CO_2, %	—	0.30	0.30	0.30
H_2S, gr/100 scf	<0.1–0.6	0.25	0.25	0.25
RSH, gr/100 scf	—	0.25	—	—
Solvent rate, gpm	315–335	—	—	—
Solvent loading, scf/gal	6.0	—	—	—
Reboiler duty, MMBtu/MMscf gas	10.1	—	—	—

Data sources: Plant A–Frazier (1970); Plants B, C, and D–Dunn et al. (1965)

Table 14-23
Pilot-Plant Data for Sulfinol-D Process and Aqueous MEA
(East Texas Natural Gas)

	Sulfinol	20% MEA
Absorber pressure, psig	1,000	1,000
Feed gas rate, scf/min	40.7	23.6
Solvent rate, gpm	1.0	1.0
Solvent loading, scf/gal	8.5	4.9
Total steam, lb/lb acid gas*	1.42	3.80
Feed gas:		
H_2S, %	15.00	
CO_2, %	6.00	
COS, ppm	60	
N_2, %	7.50	
CH_4, %	57.69	
C_2H_6, %	6.24	
C_3H_8 +, %	7.57	
Treated gas:		
H_2S, gr/100 scf	<1	<1

**Combined duty of preheater and reboiler*
Data of Dunn et al. (1964)

Table 14-24
Pilot-Plant Data for Sulfinol-D Process
(Canadian Natural Gas)

Gas Stream	A	B	C	D
Pressure, psia	995	935	935	715
Feed gas:				
H_2S, %	26.40	16.20	15.60	3.40
CO_2, %	5.20	5.40	5.50	1.30
COS, %	0.03	0.01	0.01	—
RSH, gr/100 scf	0.75	0.14	0.14	—
Treated gas:				
H_2S, gr/100 scf	0.4	0.13	0.1	0.15
CO_2, gr/100 scf	<1	<1	<1	<1
RSH, gr/100 scf	<0.01	—	—	—
COS, ppm	2.0	1.0	1.0	—
Acid gas:				
Hydrocarbon, %	1.9	0.8	0.7	3.6
Steam, lb/lb acid gas	0.9	1.0	1.0	1.3

Data of Dunn et al. (1964)

A summary of plant operation is given in **Table 14-25.** The operation of a Sulfinol-M plant in The Netherlands that treats 300 MMscfd of natural gas containing 0.15 to 0.44% H_2S and 2.87 to 4.25% CO_2 is described by Taylor and Hugill (1991). This plant is designed to reject CO_2 during the absorption step and also to increase the H_2S content of the feed to the Claus unit by a "flash enrichment" step. **Figure 14-22** is a simplified flow diagram showing the integration of the Claus plant and its tail gas treater and a molecular sieve dryer with the Sulfinol unit. Also shown is the flash enrichment step. **Table 14-26** summarizes the overall performance of the plant.

Studies of hydrocarbon solubility in the Sulfinol solvent conducted during the early pilot plant tests indicate that aliphatic hydrocarbons up to pentane are largely rejected by the solvent. However, aromatics are absorbed quite efficiently (Dunn et al., 1964). Sulfinol solvent has proved to be very stable. For Sulfinol-D, losses due to degradation are generally less than 5 lb per MMscf of raw gas. No significant losses or degradation of the solvent have been experienced with Sulfinol-M. Corrosion is, in general, no problem in Sulfinol units, and carbon steel is a satisfactory material of construction (Dunn et al., 1964). However, isolated cases of absorber corrosion, particularly in the lower section of the vessel, have been reported (Schmeal et al., 1978). Blisters and "ring pits" were observed on trays, downcomers, and vessel walls. The corrosion was ascribed to boiling and flashing of acid gas. It was especially pronounced in units processing gases where the acid gases are present in low ratios of carbon dioxide to hydrogen sulfide. Lowering of temperatures in the absorber bottom and protection of that area with stainless steel liners were found to be effective remedies.

In addition to its effectiveness for acid-gas removal, the Sulfinol solvent shows excellent capability for the removal of carbonyl sulfide and mercaptans. In one test, about 96% removal

Table 14-25
Operating Data from Rankin County, Mississippi Sulfinol-M Plant

	Design	Actual
Feed Gas Flow Rate, MMscfd	100	5 to 106
Temperature, °F	100	135–150
H_2S, mol %	34	34.4
CO_2, mol %	9	7.7
COS, ppm	500	705
Residue Gas		
H_2S, ppm	8	1
CO_2, mol %	Nil	0.02
COS, ppm	70	15
Sulfur		
Production, LT/d	1,275	120–1,434
Recovery efficiency, %	97.7	98.6–96.5

Data source: Christensen (1979)

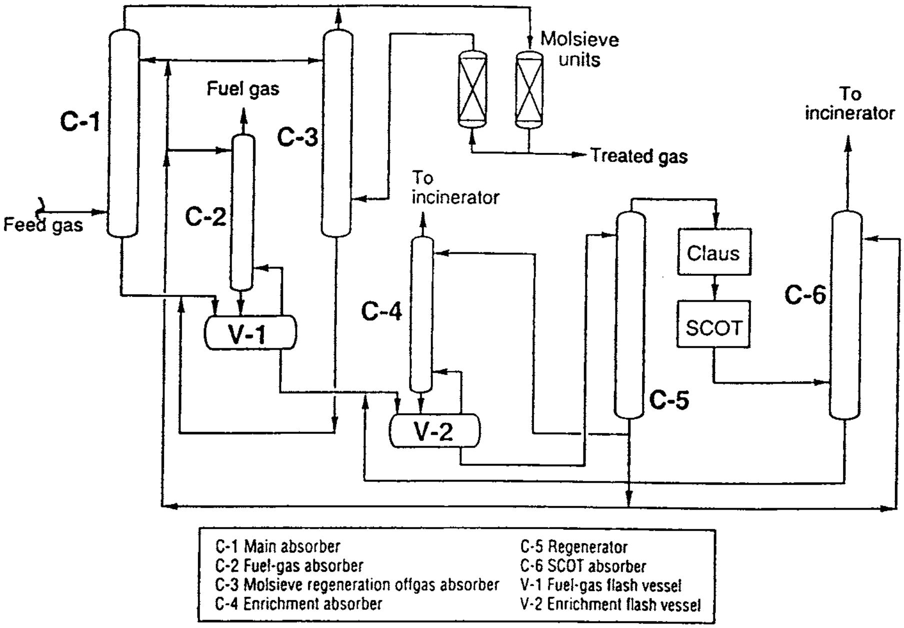


Figure 14-22. Simplified flow diagram of Sulfinol unit integrated into an overall process including a Claus sulfur recovery unit and a tail gas treatment system. (*Taylor and Hugill, 1991*)

Table 14-26
Performance of Sulfinol-M Desulfurization Unit at Emmen, The Netherlands

	Design	Actual Performance	
		High H_2S	Low H_2S
Feed Gas, MMscfd	150*	150	150
H_2S, mol %		0.44	0.15
CO_2, mol %		4.25	2.87
Pipeline Gas			
H_2S, ppm	<3.5	2.6	2.2
CO_2 slip, %	>60	62.4	60.8
Reboiler Duty, MMBtu/h	<51	49	46

**All data are for one of two trains.*
Data source: Taylor and Hugill (1991)

of methyl mercaptan was reported (Dunn et al., 1964). When a Sulfinol absorber is designed to reduce the H_2S concentration in the gas to 4 ppm, it will typically remove about 70% of the other sulfur compounds (Shell Oil Co., 1992). The removal efficiency for other sulfur compounds in a given column can, of course, be increased by increasing the solvent flow rate.

Amisol Process

The Amisol process is similar to the Sulfinol process in that it uses a combination of a physical and chemical solvent for acid gas removal. It was developed by Lurgi GmbH and employs methanol as the physical solvent, as does the Rectisol process, which was co-developed by Lurgi (Bratzler and Doerges, 1974). The first plants practicing the Amisol process used alkanolamines (MEA and DEA) as the chemical solvents; however, the more recent plants, where selective H_2S removal was an objective, have used alphatic alkylamines (Kriebel, 1985, 1989).

The Amisol process can be used for either selective desulfurization or complete removal of CO_2, H_2S, COS, and other organic sulfur compounds. Reportedly sulfur can be removed to less than 0.1 ppm and CO_2 to less than 5 ppm (Lurgi GmbH, 1988B). Through 1993, there were six plants employing the Amisol process, five of which removed H_2S and other impurities from gases derived from the gasification of coal, peat, or heavy oil, while the sixth removed CO_2 from reformer effluent and recycle gases (Lurgi GmbH, 1993).

Basic Data

The specific alkylamines—diisopropylamine (DIPAM) and diethylamine (DETA)—differ from MEA and DEA in that they have (a) greater chemical stability, (b) higher acid gas loading, (c) high H_2S selectivity, (d) easier regeneration (including a lower reboiler temperature), and (e) higher volatility. Like the alkanolamines, they are soluble in water. Properties of the alkylamines are shown in **Table 14-27.** Properties of DEA are included for comparison.

Table 14-27
Properties of Amines Used in the Amisol Process

	DIPAM	DETA	DEA
Chemical Formula	$[(CH_3)_2CH]_2$ NH	$(C_2H_5)_2$ NH	$(HOC_2H_4)_2$ NH
Molecular Weight	101.2	73.14	105.14
Boiling Point, °C	84	56	269
Vapor Pressure, mmbar at 20°C	100	253	0.1
Specific gravity, at 20°C	0.716	0.704	1.092

Source: Kriebel (1985)

Kriebel (1985, 1989) presents solubility data for Amisol systems using DIPAM and DETA showing that the carrying capacities of the Amisol mixed solvents for H_2S are significantly greater than both DEA and MDEA at H_2S partial pressures above about one bar.

Process Operation

Amisol plants are in use in Europe and China to purify various synthesis gases derived from coal, peat, and heavy oil and fuel gas derived from coal. Feed gas compositions and conditions for three different coal gasification cases described by Kriebel (1985) are presented in **Table 14-28.**

The flow diagram for one of the cases (selective desulfurization of gas from an air-blown VEW entrained bed gasifier) is shown in **Figure 14-23.** This plant uses the newer version of the Amisol process that employs DETA as the chemical solvent.

A prewash to remove impurities such as HCN and NH_3 is contained in the bottom of the absorber. For other gas streams, such as that obtained from the British Gas/Lurgi slagging gasifier, a more elaborate prewash is required. Because of the high volatility of the solvent components, both the absorber, which operates at ambient temperature, and the regenerator, which operates at about 80°C, require water wash stages at the top of the columns. The water absorbs vaporized solvent and the resulting aqueous solution is fed to a distillation column. Methanol and amine vapors from the top of the still are condensed to provide heat for the regenerator and the condensate is added to the main circulating solvent stream. Solvent-free water from the bottom of the still is reused as wash water.

The absorber/regenerator system shown on the left of the diagram is conventional, but the additional reabsorber, shown on the right, is not commonly used in amine plants. It serves to selectively remove H_2S from the CO_2-rich vapor stream extracted from the regenerator, concentrating the H_2S offgas to a level that can be sent to a Claus plant. Enrichment schemes such as this have usually been limited to pure physical solvent systems.

Selefining Process

This process was developed by Snamprogetti SpA of Milan, Italy, for selectively removing H_2S from natural and synthesis gases also containing CO_2. The Selefining solvent consists of a tertiary amine mixed with an undisclosed physical solvent. The physical solvent

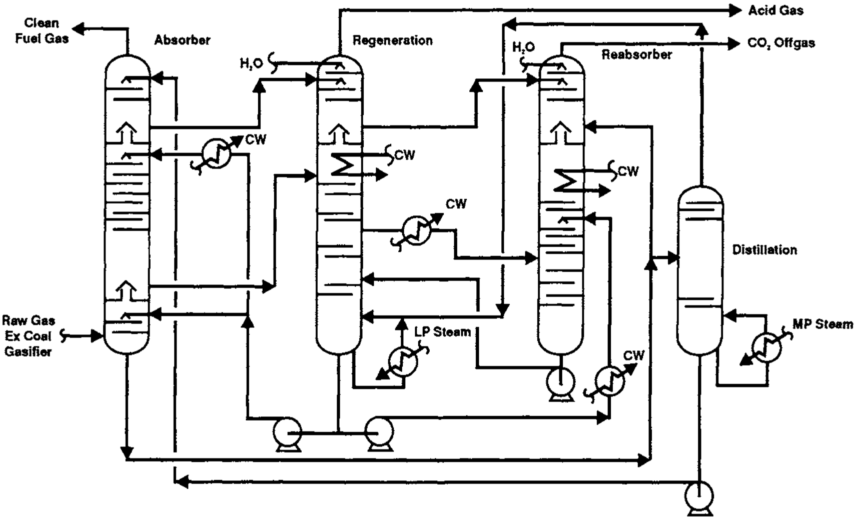


Figure 14-23. Simplified flow diagram of Amisol process for selective desulfurization of gas from an air-blown entrained-bed coal gasifier. (*Kriebel, 1985*)

Table 14-28
Composition of Amisol Plant Feed Gas Streams from Coal Gasifiers

	RBW Hydro Gasifier	VEW Entrained Bed Gasifier	BGL Slagging Gasifier
Major Components, Vol %			
CO_2	1.8	4.17	3.96
CO	7.2	22.36	60.65
H_2	53.1	11.46	25.15
N_2	0.8	61.48	0.87
CH_4	36.3	0.2	8.11
C_2H_6	0.6		0.33
C_2H_4	—	—	0.14
C_3 hydrocarbons	—	—	0.16
C_4 hydrocarbons	—	—	0.04
C_5 hydrocarbons	—	—	0.01
C_6H_6	0.05	—	—
H_2S	0.1	0.21	0.49
Trace Components, ppmv			
COS	5	244	200
RSH	134	—	—
CS_2	—	14	200
HCN	9	66	600
NH_3	9	34	100
Thiophene	—	—	10
Naphthalene	—	—	7
Pressure, Bar	51	19	55
Temperature, °C	40	60	40

RBW = Rheinische Braunkohlenwerke, A. G. Kohn
VEW = Vereinigte Electrizitatswerke Westfalen, Dortmun
BGL = British Gas Corporation, London
Source: Kriebel (1985)

water content is maintained at a low level. Although a physical solvent is used in much the same manner as Shell's Sulfinol and Lurgi's Amisol Process, the developer considers Selefining to be an amine process. The tertiary amine can react with CO_2 in the presence of water to produce carbonate, but cannot produce carbamates. By mixing the tertiary amine with a physical solvent rather than with water, the hydration of CO_2 in the solution is retarded still further, promoting selective H_2S removal. The extent of CO_2 removal can be controlled by adjusting the water content of the solution. H_2S can react directly with tertiary amines without the requirement for water.

In 1988, it was reported that three plants had been licensed, including an existing system that was retrofitted from MEA-DEG to Selefining (Snamprogetti SpA, 1988). The retrofitted plant, which is described by Gazzi and Rescalli (1988), treats 12 MMscfd of natural gas at Ferrandina in southern Italy. The feed gas contains 1.5% H_2S and 4.45% CO_2 at 580 psia. Treated gas is produced containing less than 1 ppmv of H_2S and 1.5% CO_2. The process is capable of higher CO_2 slippage; however, for this application 1.5% CO_2 represents the maximum acceptable for pipeline use.

REFERENCES

BASF, 1992, private communication, Dr. Hefner, May 14.

Beavon, D. K., and Roszkowski, T. R., 1969, "Purisol removes carbon dioxide from hydrogen, ammonia syngas," *Oil & Gas J.,* Vol. 67, April 14, pp. 138–142.

Boston, F. C., and Schneider, M. L., 1971, *Proceedings Gas Conditioning Conference,* University of Oklahoma, Norman, OK.

Bratzler, K., and Doerges, A., 1974, "Amisol Process Purifies Gas," *Hydro. Process.,* April, pp. 78–80.

Buckingham, P. A., 1961, "Fluor Solvent Process Demonstrated in EPNG Plant," paper presented at NGAA Regional Meeting, Odessa, TX, May.

Buckingham, P. A., 1964, "Fluor Solvent Process Plants: How They Are Working," *Hydro. Process.,* Vol. 43, April, pp. 113–116.

Bucklin, R. W., and Schendel, R. L., 1985, "Comparison of Physical Solvents Used for Gas Processing," in *Acid and Sour Gas Treating Processes,* S. A. Newman, editor, Gulf Publishing Co., Houston, TX, pp. 42–79.

Christensen, R. E., 1979, "Shell solves sour-gas plant problems," *Oil & Gas J.,* Jan. 15, pp. 126–129.

Clare, R. T., and Valentine, J. P., 1975, "Acid Gas Removal Using the Selexol Process," paper presented at Second Quarterly Meeting of the Canadian Gas Processors Association, Edmonton, Alberta, Canada, June 5.

Cook, T. P., and Tennyson, R. N., 1969, "Improved Economics in Synthesis Gas Plants," *Chem. Eng. Progr.,* Vol. 65, No. 11, pp. 61–64.

Dow Chemical of Canada, Ltd., 1962, *Gas Conditioning Fact Book.*

Dreisbach, R. R., 1952, *Pressure-Volume-Temperature Relationships of Organic Compounds, 3rd ed.,* Chart 20, New York: McGraw-Hill Book Company, Inc.

Dunn, C. L., Freitas, E. R., Goodenbour, J. W., Henderson, H. T., and Papadopoulos, M. N., 1964, "New Pilot Plant Data on Sulfinol Process," *Hydro. Process.,* Vol. 43, March, pp. 150–154.

Dunn, C. L., Freitas, E. R., Hill, E. S., and Sheeler, J. E. R., 1965, "First Plant Data From Sulfinol Process," *Hydro. Process.*, Vol. 44, April, pp. 137–140.

England, C., 1986, *Chem. Eng.*, No. 8, April 28, p. 63.

Epps, R., 1994, "Use of SELEXOL Solvent for Hydrocarbon Dewpoint Control and Dehydration of Natural Gas," *Laurence Reid Gas Conditioning Conference Proceedings,* University of Oklahoma, Norman, OK, Feb. 27–March 2.

Epps, R., 1992A, Union Carbide Chemicals and Plastics Company, Inc., personal communication, May 6.

Epps, R., 1992B, "Processing of Landfill Gas for Commercial Applications," paper presented at ECO WORLD '92, Washington, D.C., June 15.

Fluor Daniel unpublished data, 1993, personal communication, P. Buckingham, May 20.

Franckowiak, S., and Nitschke, E., 1970, "Estasolvan: New Gas Treating Process," *Hydro. Process.,* Vol. 49, May, pp. 145–148.

Frazier, J., 1970, "How's the Sulfinol Process Working?" *Hydro. Process., Vol.* 49, April, pp. 101–102.

Freireich, E., and Tennyson, R. N., 1977, "Increased Natural Gas Recovery from Physical Solvent Gas Treating Systems," *Proceedings Gas Conditioning Conference,* University of Oklahoma, Norman, OK, March 7–9.

Gazzi, L., and Rescalli, C., 1988, "An MEA-DEG Plant Successfully Retrofitted to Selenfining," *Energy Prog.*, Vol. 8, No. 2, June, pp. 113–117.

Grünewald, G., 1989, "Selective Physical Absorption Using the Purisol Process," paper presented at 6th Continental Meeting of the European Chapter of the GPA, Bremen, Germany, May 19.

Hegwer, A. M., and Harris, R. A., 1970, "Selexol Solves High H_2S/CO_2 Problem," *Hydro. Process.*, Vol. 49, April, pp. 103–104.

Herbert, W., 1956, *Erdol u. Kohle,* Vol. 9, No. 2, pp. 77–81.

Hernandez, R. J., and Huurdeman, T. L., 1989, "Solvent Unit Cleans Synthesis Gas," *Chem. Eng.,* February, pp. 154, 156.

Hernandez, R. J. and Huurdeman, T. L., 1991, "SELEXOL Solvent Process in Ammonia Synthesis Gas Treating, Use and Experience," paper SC-1683A, Union Carbide Chemicals and Plastics, Inc. May 3.

Hochgesand, G., 1968, *Chemie-Ing.-Techn.*, Vol. 40, No. 9/10, pp. 432–440.

Hochgesand, G., 1970, "Rectisol and Purisol," *Ind. Eng. Chem.*, Vol. 62, No. 7, pp. 37–43.

Hoogendoorn, J. C., and Solomon, J. M., 1957, *Brit. Chem. Eng.*, Vol. 2, May, pp. 238–244.

Institut Français du Pétrole, 1992, "Ifpexol," *Hydro. Process., Gas Process Handbook '92,* April, p. 112.

Institut Français du Pétrole, 1996, "Ifpexol," *Hydro. Process., Gas Process '96,* April, p. 124.

Judd, D. K., 1978, "Selexol unit saves energy," *Hydro. Process.*, Vol. 57, No. 4, April, pp. 122–124.

Kapp, E., 1970, *Erdöl and Kohle-Erdgas-Petrochemie Vereinigt mit Brennstoff Chemie,* Vol. 23, No. 9, pp. 566–571.

Knapp, H., 1968, "Low Temperature Absorption—the Rectisol Process," *Proceedings of the 1968 Gas Conditioning Conference,* University of Oklahoma, Norman, OK.

Kohl, A. L., and Miller, F. E., 1960, U.S. Patent 2,926,751, March 1.

Kohl, A. L., and Buckingham, P. A., 1960, "Fluor Solvent CO_2 Removal Process," *Petr. Refiner,* Vol. 39, May, pp. 193–196.

Kriebel, M., 1985, "Improved Amisol Process for Gas Purification," in *Acid and Sour Gas Treating Processes,* S. A. Newman, editor, Gulf Publishing Co., Houston, TX, pp. 112–130. (See also *Energy Prog.,* Vol. 4, No. 3, September, pp. 143–146).

Kriebel, M., 1989, *Ullmann's Encyclopedia of Industrial Chemistry, Gas Production,* VCH Verlagsgesellschaft mbH. Weinheim, pp. 253–258.

Linde AG, and Lurgi GmbH, 1992, *Hydro. Process., Gas Process Handbook '92,* April, p. 125.

Lurgi GmbH, 1978, "Purisol for Gas Treating," Brochure 1163/6.78.

Lurgi GmbH, 1988A, "Purisol," *Hydro. Process., 1988 Gas Process Handbook,* April, p. 69.

Lurgi GmbH, 1988B, "Amisol," *Hydro. Process., 1988 Gas Process Handbook,* April, p. 53.

Lurgi GmbH, 1993, "References: Gas and Synthesis Technology," Brochure 1569e/9.93/4.10.

Lurgi Öl-Gas-Chemie GmbH, 1996, "Purisol," *Hydro. Process, Gas Processes '96,* April, p. 133.

Lurgi Öl-Gas-Chemie GmbH, and Linde AG, 1996, "Rectisol," *Hydro. Process, Gas Processes '96,* p. 134.

Makranczy, J., Szeness, M. M., and Rusz, L., 1965, *Veszpremi Vegyipari Egyetem Kozlemenyei,* Vol. 9, pp. 95–105 (University of Chemical Industries, Institute of General and Inorganic Chemistry, Veszprem, Hungary).

Miller, W. R., and Lang, R. A., 1985, *Great Plains Coal Gasification Plant Public Design, Volume I,* DOE/CH/10088-1874, Technical Information Center, U.S. DOE.

Minkkinen, A., and Levier, J. F., 1992, "Ifpexol: Complete Gas Treatment with a Basic Single Solvent," *Laurance Reid Gas Conditioning Conference Proceedings,* University of Oklahoma, Norman, OK.

Nasir, P., 1990, "A Mixed Solvent for a Low Total Sulfur Specification," paper presented at the AIChE National Meeting, San Diego, CA, Aug. 19.

Raney, D. R., 1976, "Remove carbon dioxide with Selexol," *Hydro. Process.,* Vol. 55, No. 4, pp. 73–75.

Ranke, G., 1973, *Linde Reports on Science and Technology,* Vol. 18.

Ranke, G., and Mohr, V. H., 1985, "The Rectisol Wash—New Developments in Acid Gas Removal from Synthesis Gas," in *Acid and Sour Gas Treating Processes,* S. A. Newman, editor, Gulf Publishing Company, Houston, TX, pp. 80–111.

Schmack, P., and Bittrich, H. J., 1966, *Wissenschaftl. Zeitschrift,* Vol. 8, No. 2/3, pp. 182–186.

Schmeal, W. R., MacNab, A. J., and Rhodes, P. R., 1978, "Corrosion in Amine/Sour Gas Treating Contactors," *Chem. Eng. Progr.,* Vol. 74, No. 3, pp. 37–42.

Shah, V. A., and McFarland, J., 1988, "Low cost ammonia and CO_2 recovery," *Hydro. Process.,* March, pp. 43–46.

Shell Oil Company, 1992, private communication, D. Lancaster, April 21.

Shell Oil Company, and Shell International Research Mij. B.V., 1996, "Sulfinol," *Hydro. Process, Gas Processes '96,* April, p. 142.

Snamprogetti SpA, 1988, *Hydro. Process., 1988 Gas Process Handbook,* April, p. 71.

Stein, W. H., 1969, *Erdöl-Erdgas-Zeitschrift,* Vol. 85, pp. 467–470.

Swanson, C. G., 1978, "Carbon Dioxide Removal in Ammonia Synthesis Gas by Selexol," paper presented at 71st AIChE Meeting, Miami Beach, FL, Nov. 12–16.

Sweeney, C. W., Ritter, T. J., and McGinley, E. B., 1988, "A Strategy for Screening Physical Solvents," *Chem. Eng.,* Vol 95, No. 9, June 20, pp. 119–125.

Sweny, J. W., 1973, "Synthetic Fuel Gas Purification by the SELEXOL Process," paper presented at 165th National Meeting of the American Chemical Society, Division of Fuel Chemistry, Dallas, TX, April 8–12.

Sweny, J. W., 1976, "The SELEXOL Process in Fuel Gas Treating," paper presented at 81st National Meeting of the American Institute of Chemical Engineers, Kansas City, MO April 11–14.

Sweny, J. W., 1980, "High CO_2-High H_2S Removal with Selexol Solvent," paper presented at 59th Annual GPA Convention, Houston, TX, March 17–19.

Sweny, J. W., and Valentine, J. P., 1970, "Physical Solvent Stars in Gas Treatment/Purification," *Chem. Eng.,* Vol. 77, No. 19, Sept. 7, pp. 54–56.

Sweny, J. W., 1985, "Gas Treating with a Physical Solvent" in *Acid and Sour Gas Treating Processes,* S. A. Newman, editor, Gulf Publishing Company, Houston, TX, pp. 1–41.

Taylor, N. A., and Hugill, J. A., 1991, "Sulfinol-M Provides the Solution to a Tough Treating Challenge," *Laurance Reid Gas Conditioning Conference Proceedings,* Univ. of Oklahoma, Norman, OK, March.

Uhde GmbH, 1992, private communication, Dr. Mundo, April 23.

Valentine, J. P., 1974, "New solvent process purifies crude, coal acid gases," *Oil & Gas J.,* Vol. 72, No. 46, pp. 60–62.

Valentine, J. P., 1975, "Economics of the SELEXOL Solvent Gas Purification Process," paper presented at the 79th National Meeting of the American Institute of Chemical Engineers, Houston, TX, March 19.

Van Deraerschot, R., and Valentine, J. P., 1976, "The SELEXOL Solvent Process for Selective Removal of Sulfur Compounds," paper presented at 2nd International Conference on the Control of Gaseous Sulphur and Nitrogen Emission, Salford University, England, April 6–8.

Woertz, B. B., 1971, *J. of Pet. Tech.,* April, pp. 483–490.

Woertz, B. B., 1975, *Soc. Pet. Eng. J.,* Feb. 7–12.

Wölfer, W., Schwartz, E., Vodrazka, K., and Volkamer, K., 1980, "Solvent shows greater efficiency in sweetening of gas," *Oil & Gas J.,* Jan. 21, pp. 66–70.

Wölfer, W., 1982, "Helpful hints for physical solvent absorption," *Hydro. Process.,* Vol. 61, No. 11, November, pp. 193–197.

Zawacki, T. S., Duncan, D. A., and Macriss, R. A., 1981, "Process optimized for high pressure gas cleanup," *Hydro. Process.,* Vol. 59, No. 4, April, pp. 143–149.