Acid and Sour Gas Treating Processes
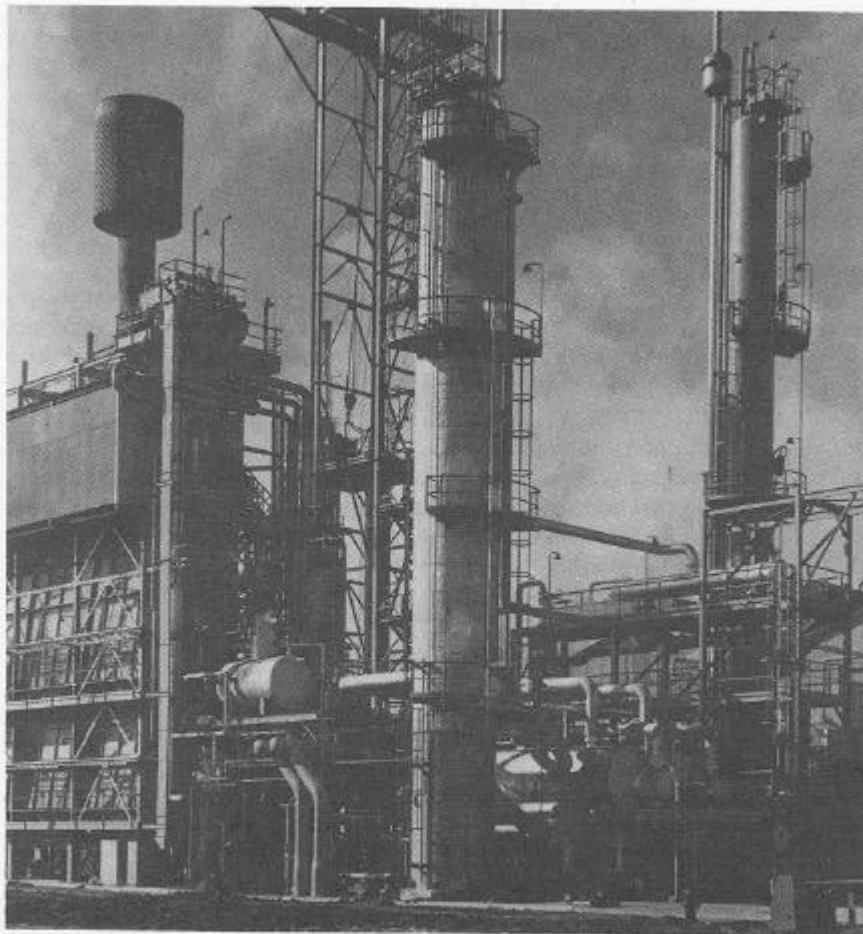
Latest data and methods for designing and operating today's gas treating facilities

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Contents

In the late 1950's, the Fluor Solvent process using propylene carbonate was commercialized by the cooperative efforts of El Paso Natural Gas Company and Fluor.[1,2] El Paso's Terrell County Treating Plant was a first of a kind using a physical solvent at mild sub-ambient temperatures for carbon dioxide removal. The process objectives of lowest possible capital and operating costs were achieved. Neither external heat nor alloy steel equipment were required to satisfy the process conditions. The process was unique in that the only significant energy consumers were the solvent circulation pumps and the recycle gas compressor. The process design was very simple, involving only a high pressure contactor where the CO_2 was removed from the methane, followed by a series of flash tanks at successively lower pressures to achieve solvent regeneration. A compressor was used to recycle the flash gases from an intermediate pressure flash tank to minimize methane losses. Hydraulic turbines were used to recover about half of the required pumping energy. The same type of mechanical arrangement and flow scheme have since been used in several gas treating plants with competitive physical solvents developed since that time.

The chief criterion for selection of propylene carbonate for Fluor Solvent was its high CO_2 solubility concurrent with a relatively low methane solubility. Even today, propylene carbonate ranks somewhat better than other physical solvents for bulk CO_2 removal with minimum hydrocarbon loss as the only contingent requirement.

As developments in physical solvent processing matured, other solvents, better suited to meet specific process requirements, have been developed.

COMPARISON OF COMMERCIAL PHYSICAL SOLVENTS

Today the commercially proven physical solvent processes and their solvents are:

        Estasolvan   - tributyl phosphate or TBP
        Fluor Solvent   - propylene carbonate or PC
        Purisol   - normal methyl pyrrolidone or NMP
        Rectisol   - methanol
        Selexol   - dimethyl ether of polyethylene glycol or Selexol
        Sepasolv-MPE   - mixture of polyethylene glycol dialkyl ethers or
                          Sepasolv

Of these solvents, methanol is relatively high in vapor pressure at normal process conditions and therefore requires deep refrigeration or special recovery methods to prevent high solvent losses. This paper will omit methanol from comparisons of solvents since the processing conditions and equipment are so unlike the others.

Most of the equilibrium data are proprietary to the process licensors. Therefore, definitive comparative information about solvent performance cannot be published without violating existing secrecy agreements. It is possible, however, to use public information to indicate relative circulation rates, relative recycle stream volumes, and stream compositions for identical process configurations and conditions in order to illustrate how some solvents differ in basic character and performance. Selexol and propylene carbonate are compared in this manner in the case study later in this paper.

Table 1 [3,4,5,6,7] is a comparison of miscellaneous solvent data. All of the solvents are noncorrosive, nontoxic and require only carbon steel construction for a simple cycle process scheme.

The relatively poor CO_2 solubility of TBP may explain why no commercial plants using the Estasolvan process have been built.

Table 2[4,7,8,9,10] compares each solvent's affinity for various gases relative to carbon dioxide.

There is a wide variation in molecular weights and significant differences in densities of the various solvents. Therefore, the comparison of mol fraction or weight portion of solute in the solvent at saturation would not be good indicators of the solvent's relative effectiveness in removing the solute. The volume of solute expressed as vapor at the reference condition per unit volume of solvent at the reference condition is a useful comparative value for solvents to be used in similar processing schemes. This is true because the size of process equipment and piping as well as power requirements for the process are largely determined by the required volume of solvent circulation.

All of the physical solvent processes being compared are concerned primarily with acid gas removal from either hydrocarbon gases (natural and landfill gas) or synthesis gases (hydrogen and carbon monoxide). In cases wherein either bulk or essentially complete CO_2 removal is desired the most significant comparative solvent data is solubility data on volume of carbon dioxide per volume of solvent at a suitable reference condition. Operating Process temperature ranges from 30°C to -20°C cover most of the commercial applications, so 25°C is a suitable reference temperature for this comparison. Solubility data at 25°C and one atmosphere partial pressure of solute is in the public domain for all of the commercial solvents we are comparing except Sepasolv. The value for Sepasolv was extrapolated from published data7 at 0°C using the same slope of a similar ether on a log log plot of Henry's constant vs 1/T.

In all cases, the solution is relatively dilute with respect to the solute. The polar compounds CO_2 and H_2S tend to deviate significantly from ideal, so that Henry's Law is applicable only in dilute solutions. Even though there can be sizeable interaction effects between the solutes

in multicomponent mixtures, it is assumed for this comparison that the relative selectivities will not vary significantly in relation to each other in the majority of actual process conditions.

PROCESS SELECTION

The selection of a physical solvent process depends on process objectives and characteristics of the solvents, such as selectivity for H_2S, COS, HCN, etc., ease of handling water content in feed gas, ease of controlling water content of circulating solvent, concurrent hydrocarbon loss or removal with acid gas removal, solvent cost, solvent supply, chemical inertness, royalty cost, thermal stability and proven plant performance for various processing techniques.

Solvent Loss

All of the solvents have low vapor pressures. Although propylene carbonate has a vapor pressure much higher than the high molecular weight solvents, solvent losses have generally been very low. NMP has a vapor pressure about five times higher than PC. The licensor recommends water washing of both the treated gas and the rejected acid gases for solvent recovery.[11]

Selective H_2S Removal

The data indicate that Selexol, NMP and Sepasolv are superior to PC if selective H_2S removal from gas containing carbon dioxide is required. Actual experience confirms this prediction. The authors know of no cases where propylene carbonate would be recommended for selective H_2S removal. In fact, it is difficult to find situations where PC would be recommended if H_2S is present in more than trace concentrations. This is so because the low concentration of H_2S usually permitted in the treated gas (1/4 grain per 100 SCF for natural gas) means H_2S removal is controlling.

Effect of Water in Feed gas

Differences in water handling flexibility can also be important. As shown in Table 1, NMP, Selexol and Sepasolv have infinite water solubility and are thermally stable at temperatures required to reject water at atmospheric pressure. Slipstreams of these solvents can be processed to control the water content of the circulating solvent stream.

PC and TBP have limited water solubility and therefore require a different solvent for hydrate control during feed gas chilldown. TBP is thermally stable for water removal by atmospheric distillation. PC

slowly reacts irreversibly with water and carbon dioxide at temperatures around 90°C and is therefore unsuitable for water control by atmospheric distillation.[12]

The reported design water content of the various solvents has a range from one to six percent by weight. At these levels, solvent capacity for CO_2 and H_2S is not greatly impaired for any of the solvents. The most significant penalty of water content is the cost of pumping the extra water.

Physical solvents may be used to simultaneously dehydrate the gas and meet very low treated gas specifications for CO_2 and H_2S. This is accomplished by use of a solvent regenerator using inert gas and/or heat to strip the lean solvent as required. NMP cannot be used for simultaneous gas dehydration if a water wash is used to limit solvent loss.

Both PC and Selexol tend to get slushy with water at temperatures below –18°C (0°F) so process conditions must be held warmer than the slush temperature.

Effect of Heavy Hydrocarbons

In natural gas treating, loss of heavy hydrocarbons is a concern. NMP, Selexol and Sepasolv are miscible with water, and water may be used to reject these hydrocarbons. As shown in Figure 1, a slipstream of the circulating solvent from the lean solvent pump may be mixed with the feed gas and fed through the feed gas cooldown using water absorbed from the feed gas to separate a hydrocarbon liquid phase and then distilling off the water. Water can actually be added to this stream to reduce hydrocarbon solubility further. In this case the size of the slipstream might be set by the desired maximum hydrocarbon content of the lean solvent rather than by the maximum water buildup in the lean solvent. The water content of the return solvent slipstream can be controlled by the slipstream regenerator bottoms temperature and pressure conditions.

Effect of Recycle Compressor

A major energy user in physical solvent processes is compression for the recycle of flash gas to limit methane losses. The relative compression horsepower required to recycle these intermediate flash tank gases to the high pressure contactor can be predicted from the solubility of methane in the various solvents as shown in Table 3. The higher the solubility of the methane, the higher the recycle compressor horsepower for the same amount of methane product in the treated gas.

<u>Solvent Reactivity</u>

Propylene carbonate reacts with amines and ammonia at all conditions and with water and carbon dioxide at elevated temperatures. PC has been used for bulk CO_2 removal followed by a downstream MEA treater in two successful installations. Careful design of the Fluor Solvent Treated Gas scrubber is required to avoid the possibility of destroying both the amine and the propylene carbonate upon mixing. None of the other solvents being compared are chemically reactive with the components normally found in either natural gas or synthesis gas.

<u>Process Configuration</u>

Good thermal stability, chemical inertness, and thermal conductivity are also necessary to permit flexibility in process schemes. For example, selective H_2S removal can be benefitted by the use of heat. This can be particularly important in designs to produce a high concentration H_2S feedstock to a downstream Claus plant. Reboiling a solvent in a regenerator may be necessary to) meet treated gas purity requirements for CO_2 H_2S or COS.

Reboiled absorbers, refrigerated solvent presaturators, absorber side chillers and absorber bottoms to feed gas pumparound chillers are examples of absorption process techniques used to minimize circulation rates which are applicable to physical solvent processes.

<u>SYNTHESIS GAS TREATING COMPARISONS</u>

Table 4 is a comparison of relative solubilities for some of the gases formed in steam reforming processes, by partial oxidation of heavy hydrocarbons or by coal gasification.

The differences between the solvents are not as significant as the ratios would indicate since the quantity of hydrogen and carbon monoxide absorbed concurrent With the CO_2 is relatively small. There might be a moderately significant difference in compression power requirements for intermediate pressure gases recycled to minimize product loss.

Product purity requirements might be more important in process selection. If the desired purity can be obtained with solvent regeneration by atmospheric regeneration Of the solvent using inert gas stripping or by vacuum flashing, the processes are essentially equal for CO_2 removal. If H_2S is present in more than trace amounts, NMP, Selexol and Sepasolv would be favored. If control of water concentration by solvent distillation were required, PC would require an alternative independent water removal step on the feed gas. The optimum choice in most of the synthesis gas applications may be a result of designer ingenuity or client preference rather than basic solvent capabilities.

CASE STUDY

As mentioned earlier, piopylene carbonate has temperature limitations
which prevent use of heat for solvent regeneration. This limits options
for process configurations and may be a significant detriment when
processing gases with hydrogen sulfide.

In applications where CO_2 removal only is required, the process selection
is less clear. Hydrocarbons are more soluble when compared to CO_2 in
Selexol than Fluor Solvent (see Table 3). Therefore, applications where
CO_2 removal only is required and where hydrocarbons are to remain in the
methane stream for downstream recovery or increased heat value, Fluor
Solvent should show an advantage.

D. K. Judd has described the successful conversion of Northern Natural
Gas Company's Mitchell plant from high load DEA to Selexol.[13] Since this
is a simple flash regeneration scheme (see Figure 2), it is an
appropriate example to examine.

Feed gas enters the Selexol plant inlet scrubber at about 120OF and 895
psig. The gas is cooled by exchange against the residue gas. The residue
gas contains about 3.5% CO_2 and enters the pipeline at about 90°F. The
cool inlet gas next flows through the feed gas scrubber where condensed
water is removed. The gas then enters the absorption towers where the gas
contacts Selexol solvent in countercurrent flow.

The rich solvent goes to a sump tank where entrained gas (methane) is
allowed to separate and returned to the contactor. The solvent next is
chilled with a packaged mechanical refrigeration unit to overcome heat of
pumping and heat leaks. The solvent next passes through a hydraulic
turbine to recover power and then to a high-pressure flash tank operating
at 252 PSIG. The high-pressure vapors are compressed and recycled to the
absorber feed. The solvent next passes through a second hydraulic turbine
to the intermediate pressure (25 psia) flash tank. Vapors from the flash
tank are routed to compressors for pipeline transmission and injection
for enhanced oil recovery. The solvent is further regenerated by flashing
to 5 psia vacuum before returning to the contractor. The vapors from the
5 psia flash are compressed and join the 25 psia flash tank vapors for
further compression.

A Fluor Solvent plant was designed for the same application. Table 6
presents the composition of the feed gas to the Mitchell plant and the
material balance, as presented in the 1978 paper with the addition of
Fluor Solvent data for Comparison. The Fluor Solvent design produces an
additional 148.8 MMBTU/hour in residue gas. This reflects the low
solubility of hydrocarbons in Fluor Solvent, as shown in Table 5. The
Fluor solvent design does require water removal at the front-end.

Table 7 shows a comparison of horsepower requirements based on
information available from the Judd paper and the Fluor Solvent design.
As indicated, there is a net savings in horsepower as well as improved

47

hydrocarbon recovery. We suspect that the 2,000 BHP motor used in the Mitchell plant retrofit is considerably larger than required. The recycle compressor in the Fluor Solvent design is 1,000 BHP. We expect the comparable Selexol requirement is about 1,500 BHP.

It should be noted, where separate recovery of natural gas liquids or heavier hydrocarbons are desirable, process configurations may be employed which deviate significantly from this simple pressure let-down scheme. The value of the hydrocarbons to be recovered may dictate the process configuration and solvent choice.

SUMMARY AND CONCLUSIONS

A preliminary screening of physical solvent characteristics can eliminate those solvents that are clearly unsuitable or noncompetitive for a particular application.

Considerable weight should be given to proven performance with the type of process configuration proposed. Innovative designs into unproven territory might lead to undesirable results. The high cost of testing and commercializing a new solvent in any process configuration is a good incentive to stick with proven processes if they can do a satisfactory job.

The demands on physical solvent processes are increasing, losses of valuable components must, be minimized, removal of acid gas and trace components to lower levels must be achieved and processes must be capable of selective H_2S removal with simultaneous production of suitable Claus sulfur plant feed. This is causing a revival of performance improving processing techniques common to absorption processes such as the refrigerated oil absorption plants for natural gas liquids recovery built two or three decades ago. The process designer's ingenuity and innovations might easily outdistance small inherent advantages of one solvent over another.

Selexol has a clear experience advantage over all other solvents in all applications involving H_2S and CO_2 removal in hydrocarbon systems.

Fluor Solvent and Selexol both enjoy a clear experience advantage over the other processes in applications for CO_2 removal only.

TABLE 1 [3,4,5,6,7]

MISCELLANEOUS COMPARATIVE DATA
OF SOLVENTS

Process Name	Selexol	Fluor Solvent	Purisol	Sepasolv MPE	Estasolvan
Solvent Name	Selexol	PC	NMP	Sepasolv	TBP
Solvent Cost $/lb FOB Fact.	1.32	.74	1.34		
Licensor	Norton	Fluor	Lurgi	B.A.S.F.	Uhde & IFP
Viscosity @ 25°C, cp.	5.8	3.0	1.65	–	2.9
Specific Gravity @ 25°C, KG/M3	1030	1195	1027	–	973
Mol Weight	280	102	99	320	266
Vapor Pressure @ 25°C, MM Hg	7.3×10^{-4}	8.5×10^{-2}	4.0×10^{-1}	3.7×10^{-4}	$<1.0 \times 10^{-2}$
Freezing Point, °c	–28	–48	–24		–80
Boiling Point, °c @ 760 MM Hg		240	202	320	(180o @ 30 MM Hg)
Thermal Conductivity Btu/Hr/Ft2/(oF/Ft)	0.11	0.12	0.095		
Maximum Operating Temp., °c	175	65	–	175	–
Specific Heat @ 250F	0.49	0.339	0.40		
Water Solubility @ 250C	oo	94 gm/l	oo	oo	65 gm/l
Solvent Solubility in Water @ 25°C	oo	236 gm/l	oo	oo	0.42 gm/l
Ft3 CO_2 Solubility/ U.S. Gal @ 25°C	0.485	0.455	0.477	0.455	0.329
Number of Commercial Plants	32	13	5	4	0
Bulk CO_2 Removal					
Synthesis Gas	6	3	2	0	
Natural Gas	6	10	1	0	
Landfill Gas	3	0	0	0	
Selective H_2S Removal					
Synthesis Gas	9	0	1	0	
Natural Gas	8	0	1	4	

TABLE 2 [4,7,8,9,10]

SOLUBILITIES OF VARIOUS GASES IN SOLVENTS RELATIVE TO CARBON DIOXIDE AT 25°C

Comp.	Selexol	PC	NMP	Sepasolv	TBP
H_2	1.3×10^{-2}	7.8×10^{-3}	6.4×10^{-3}	5.0×10^{-3}	
N_2	–	8.4×10^{-3}	–		
O_2	–	2.6×10^{-2}	3.5×10^{-2}		
CO	2.8×10^{-2}	2.1×10^{-2}	2.1×10^{-2}		
C_1	6.7×10^{-2}	3.8×10^{-2}	7.2×10^{-2}	6.6×10^{-2}	4.0×10^{-2}
C_2	4.2×10^{-1}	1.7×10^{-1}	3.8×10^{-1}		
C_2H_4	4.9×10^{-1}	3.5×10^{-1}	5.5×10^{-1}		
CO_2	1.0	1.0	1.0	1.0	1.0
C_3	1.02	0.51	1.07		
iC_4	1.87	1.13	2.21		
nC_4	2.33	1.75	3.48		
COS	2.33	1.88	2.72	2.54	
iC_5	4.47	3.50	–		
C_2H_2	4.53	2.87	7.37		
NH_3	4.87	–	–		
nC_5	5.53	5.0	–		
H_2S	8.93	3.29	10.2	6.86	5.6
NO_2	–	17.1			
nC6	11.0	13.5	42.7		
2,4 DMP	–	17.5	–		
CH_3SH	22.7	27.2	34.0	23.1	
nC_7	24.0	29.2	50.0		
CS_2	24.0	30.9	–		
CYCLO-C6	–	46.7	–		
nC_8		65.6	–		
C_2H_5SH	–	–	78.8		
SO_2	93.3	68.6	–		
$(CH3)_2S$	–	–	91.9		
C_6H_6	253	200	–		
nC_{10}	–	284	–		
C_4H_4S	540	–	–		
H_2O	733	300	4,000		
HCN	1200	–	–		

TABLE 3

COMPARATIVE HYDROCARBON LOSSES*
RELATIVE TO PROPYLENE CARBONATE

Ratio of Table 2 Data

Comp.	PC	Selexol	NMP	Sepasolv	TBP
C_1	1.0	1.76	1.89	1.74	1.05
C_2	1.0	2.47	2.24	–	–
C_3	1.0	2.00	2.10	–	–
iC_4	1.0	1.65	1.96	–	–
nC_4	1.0	1.33	1.99	–	–
iC_5	1.0	–	–	–	–
nC_5	1.0	1.11	–	–	–
nC_6	1.0	0.81	3.16	–	–
nC_7	1.0	0.82	–	–	–

*Losses could be termed as recovery if it is desirable to either remove hydrocarbons with the carbon dioxide in order to reduce treated gas heating value or to recover the propane and heavier hydrocarbons from the CO_2 in downstream processing.

TABLE 4

COMPARATIVE PERFORMANCE FOR SYNTHESIS GASES

Relative to Propylene Carbonate
Ratio of Table 2 Data

Component	PC	Selexol	Sepasolv	NMP
H_2	1.0	1.67	0.64	0.82
CO	1.0	1.33		1.0
C_1	1.0	1.76	1.74	1.89
CO_2	1.0	1.0	1.0	1.0

TABLE 5

MITCHELL PLANT DESIGN

	Percent of Hydrocarbon Loss		Ratio of Hydrocarbon Loss
	Selexol	PC	Selexol/PC
C_1	3.50	2.17	1.61
C_2	14.34	5.72	2.51
C_3	98.57	35.54	2.72
iC_4	97.47	40.51	2.41
nC_4	96-85	71.65	1.35
iC_5	93.75	79.17	1.18
nC_5	91.67	79-17	1.16
nC_6	87.43	73.15	1.12

TABLE 6

COMPARATIVE DESIGN MATERIAL BALANCE
MOLS/HR FOR SELEXOL AND FLUOR SOLVENT

Stream No.	1	2		3		4	
Stream Name	Feed Gas	Residue Gas		Atmospheric Flash Gas		Vacuum Flash	
Solvent	Selexol and Fluor Solvent	Selexol	Fluor Solvent	Selexol	Fluor Solvent	Selexol	Fluor Solvent
Comp.							
N_2	71.1	71.0	71.0	0.1	0.1	--	-
CO_2	4,398.3	395.7	407.1	3,490.5	3,325.3	513.0	665.9
H_2S	0.2	--	--	0.2	0.2	--	-
C_1	11,110.2	10,721.4	10,993.6	388.1	115.9	0.7	0.7
C_2	131.1	112.3	123.6	16.5	7.3	2.3	0.2
C_3	34.9	0.5	22.5	30.7	11.0	3.7	1.4
iC_4	7.9	0.2	4.7	6.4	2.7	1.3	0.5
nC_4	12.7	0.4	3.6	10.0	7.1	2.3	2.0
iC_5	4.8	0.3	1.0	3.2	2.7	1.3	1.1
nC_5	4.8	0.4	1.0	3.1	2.6	1.3	1.2
C_6*	17.5	2.2	4.7	10.5	8.5	4.8	4.3
H_2O	37.6	0.2	0.6	3.9	2.8	1.7	1.8
	15,831.1	11,304.6	11,633.4	3,963.2	3,486.2	532.4	679.1

TABLE 7

Comparative Requirements of Power Users

for

Selexol and Fluor Solvent after Retrofit

Item No.	Description	Selexol	Fluor Solvent
P-101 A&B	Lean Solvent Pumps, BHP	2,700*	2,700
	Power Recovery Turbines, BHP	1,350*	1,350
	Net Pump Motor, BHP	1,350*	1,350
R-12	Refrigeration, Tons	600	700
C-102	Recycle Compressor Motor	2,000 BHP Motor	1,000 BHP Motor
	Estimated Shaft BHP	1,500 Shaft BHP	850 Shaft BHP
C-103	Vacuum Compressor Motor	700 BHP Motor	900 HP Motor

*Developed from Judd's description of the refrigeration requirements and assumed pump efficiencies of 70%.

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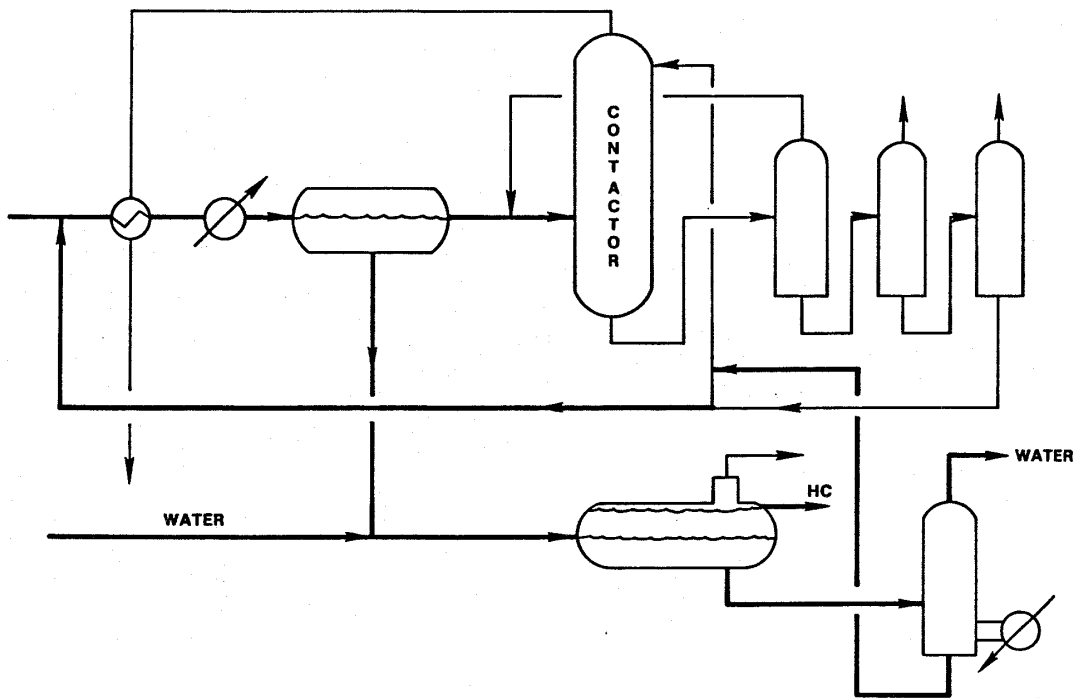13. Judd, D. K. "Northern Natural Gas Converts Mitchell Plant to Selexol", Paper presented at the Gas Conditioning Conference, Norman, Oklahoma. March 6-8, 1978.

FIGURE 1

FIGURE 2

MITCHELL PLANT SELEXOL UNIT