CO_2/EOR GAS PROCESSING

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ABSTRACT

With the advent of numerous CO_2 injection projects, the need has arisen for processing variable composition gases containing over 90% CO_2. Traditional gas sweetening plants were geared for removal of small amounts of CO_2 (and H_2S) from natural gas streams. Enhanced oil recovery projects require gas processing plants to remove methane, H_2S and NGL's from CO_2 laden gas to produce purified CO_2 for reinjection.

Of paramount importance is the efficient recovery of the ethane and heavier NGL's, as they represent a key revenue stream for project viability. Enhancement of the NGL content of the produced gas by crude stripping is recognized in pilot and actual projects. Design of process facilities to economically recover the NGL's and purify the CO_2 represents an interesting challenge for the gas processing industry.

INTRODUCTION

In the mid-1970's, many oil and gas companies began studying enhanced oil recovery (EOR) projects utilizing CO_2 injection. Numerous projects are now underway and many more in the planning stages. Reservoir model studies indicate that the associated gas production will change drastically over the life of these projects. The Willard EOR project using CO_2 injection (Figure 1) reflects the range of compositions and volumes which this gas processing facility must handle. The ethane and heavier hydrocarbon content (on a CO_2 free basis) increases with time due to stripping of mid-range components from the crude in the reservoir and separation facilities. Not only will the total gas volume increase ten-fold, but also the CO_2 composition would increase to the 90% range in virtually all cases. This dramatic change in the produced gas affects all segments of a production system, particularly the gas processing facility required to handle such gases.

Since CO_2 purchase is the largest single cost component of a CO_2 flood project, CO_2 produced after breakthrough must be used to limit outside purchased quantities. Purchased CO_2 in West Texas costs about $1.00 to $1.35/MCF, but produced CO_2 can be recycled for 50 to 60¢/MCF! Therefore, a primary objective of the gas treating facilities is the conservation and purification of the CO_2 for reinjection.

Traditionally, gas processing plants have always treated CO_2 as a contaminant to be removed and discarded. These gas sweetening processes were designed to handle small amounts of acid gas (CO_2 and H_2S). Traditional solvent systems (amines, carbonates, and physical solvents) were simply not designed to handle the large volume of CO_2 in EOR-type gases. The capital, operating, and energy costs of these solvent systems increase in proportion to acid gas content.

Many people still approach EOR gas processing as a CO_2 removal problem. In reality, it is just the opposite. The problem is the efficient removal of NGL's, H_2S, and methane from the CO_2. Once this concept is accepted, appropriate gas processing alternatives can be identified.

Gas processing for CO_2 projects is generally more complicated and more expensive per MCF than traditional gas processing facilities. The processing can take on many forms, but generally will include compression, dehydrations, NGL recovery, and H_2S removal (if present). Additionally, methane removal for fuel or sales is often included.

COMPRESSION

Probably the largest single cost item in a CO_2 flood processing plant is the gas compression equipment. In many cases, compression may represent two-thirds of the capital cost. The compression is in two blocks (Figure 2): inlet and injection compression. The inlet compression takes the separator gas from 25 to 100 psig up to processing pressures. Typical processing pressures range from 300 to 450 psig. After processing, the CO_2 is compressed further to injection. Injection pressures range from 1600 to 2000 psig in West Texas. Injection pressure in other locations may range up to 3500 psig. One processing scheme produces CO_2 as a liquid phase at 500 psig, and it is pumped to injection pressure.[1]

Inlet compression involves handling water-saturated CO_2. Condensed water from this stream has a pH of 4 to 5, which is severely corrosive. Stainless steel metallurgy is required any place where water may be condensed. This includes interstage coolers, suction scrubbers, and associated piping and valves. We have used 304 or 316L stainless steel in these applications, depending on expected chloride concentrations. Special metallurgy is not used for discharge lines and compression cylinders.

After dehydration, stainless steel is not required in the process system except as dictated by low process temperatures. Thus, injection compression is all carbon steel construction.

Horsepower requirements for CO_2 compression will tend to be higher than for natural gas. Recent experience has shown efficiencies for higher speed electric motor driven reciprocating units to be below 75%. Three hundred RPM units have higher efficiencies but are still below those expected for sweet natural gas. These reduced efficiencies appear to be a result of increased valve losses from the higher molecular weight of CO_2.

DEHYDRATION

All CO_2 process facilities will include dehydration for hydrate prevention and corrosion control. CO_2 has a characteristically higher water content than natural gas (Figure 3). Recent data by Kobayashi[2,3] has extended the CO_2 data of Weibe[4] to include many more temperature and pressure regions. The water content of the CO_2 is not only higher than that of sweet natural gas but reaches a minimum in the 800 to 1000 psig area at normal temperatures.

Typical computer simulation of CO_2 compression trains will tend to underestimate the water content to the dehydration unit. Until such actual data can be incorporated, simulations should be adjusted prior to beginning the design of the dehydration system.

Triethylene glycol (TEG) dehydration units are typically used for CO_2 dehydration. Dehydration of CO_2 is similar to natural gas dehydration except that several additional aspects must be considered.

Several years ago ARCO Oil and Gas Company and others funded a study by Dr. Kobayashi at Rice University to determine CO_2 equilibrium solubility data with various TEG concentrations. These data[5] demonstrate much higher solubilities than previous data. This solubility must be allowed for in dehydration design. Early CO_2 dehydration design resulted in undersized regeneration equipment due to the extra heat required for CO_2 dissolution.

Several authors[6,7] have proposed using a gas stripper column between the absorber and regenerator to strip CO_2 from the glycol. While this may be attractive for some designs, we have used a hot flash to drive off the CO_2 at an intermediate pressure (Figure 4). The resulting flash gas is then recycled to a low pressure point in the plant. In either case, the residual CO_2 must be included in the regenerator sizing.

Water vapor from the regeneration system which contains CO_2 may be recycled to conserve the CO_2 depending on the particular application. If a low pressure system, such as a vapor recovery unit, is available, the water can be condensed and the CO_2 recycled. If the gas stream contains H_2S, then the water vapor will contain H_2S and must be recycled to compression.

Many CO_2 dehydration systems are being constructed totally of stainless steel. This is an extreme requirement that may be relaxed with the selected use of stainless steel in parts of the system where CO_2 and water are in a phase separate from the TEG. Figure 4 shows areas where stainless steel is required. Additionally, stainless or stainless-clad contactors are used frequently. This requirement may also be relaxed with a diligent glycol pH program. If this control is questionable, a stainless clad contactor is the conservative approach to minimize corrosion problems.

NGL RECOVERY

Probably the most neglected item in the early years of EOR gas processing planning was the recovery of NGL's. All facility planning was geared toward the minimum investment for CO_2 reinjection for oil recovery. The NGL's were simply to be reinjected with the CO_2. With price decontrol of NGL's, maximum NGL recovery can significantly impact EOR project economics.

An area which is still overlooked in many projects is the NGL enhancement as a result of crude stripping by the CO_2. Crude stripping is a complicated item to predict as it is a function of reservoir performance, gas-oil ratio (GOR) and surface facilities.

West Texas fields with NGL-rich gas and low separator pressure will generally have percentages of crude stripped. Estimates for several fields are that 10 to 15% of the produced crude volume will be NGL's in the separator gas. Leaner, low GOR fields with higher separator pressures are estimated to see about 5 to 7% stripping. The net result of this stripping action is that the hydrocarbon component of the produced gas will increase continuously in ethane and heavier hydrocarbons as the CO_2 breakthrough increases.

Figure 5 is a composition profile for several wells in a current full-field CO_2 flood. Separator pressure is 100 psig with an initial GOR of 200. The gas is rather lean for associated gas, but the NGL content doubles by the time CO_2 reaches 90%. The majority of the enhancement is in the C_4+ component.

Figure 6 for a recent CO_2 pilot flood shows even more dramatic results. This case has a lower separator pressure which tends to increase the stripping. The NGL content in this flood increased 4 to 5 times the initial value. This particular pilot showed a marked increase in all NGL components, including ethane. This incremental volume must surely include reservoir stripping action.

Peak NGL volumes for various projects may reach over 30% of the crude volume. Thus the efficient recovery of these components is critical to project economics.

NGL recovery levels from CO_2 flood produced streams are traditionally limited by thermodynamic considerations. The CO_2 and ethane form an azeotrope of approximately 2/3 CO_2 and 1/3 ethane regardless of pressure. This azeotrope prevents ethane recovery from high CO_2 streams and limits NGL recovery to high propane recovery.

Recovery of the propane and heavier NGL's can be accomplished by straight refrigeration and stabilization (Figure 7). The gas is chilled to a low temperature and run through a stabilizer column for removal of condensed CO_2. NGL product is ready for sale or in some cases may be blended with the crude.

Due to the low temperature operation, dehydration is required either upstream in a TEG unit, or glycol injection with Ethylene Glycol (EG) can be employed. In this setup, the EG is simply antifreeze for the condensed water.

The actual recovery level of the NGL's will depend on economics of a particular project. Higher recovery costs more and the operating costs will increase accordingly. Beyond about 80% C_3 recovery, the incremental cost for straight refrigeration will be difficult to pay out with product volume. Also, if 80% recovery is designed for the peak year, earlier year cases will have higher recovery levels approaching 100%. Higher propane and ethane recoveries are economically attractive only if the CO_2/ethane azeotrope can be broken.

H_2S REMOVAL

Surely the most controversial aspect of CO_2 flood gas processing is the removal of H_2S. The added cost of sulfur removal is seldom economically justified on sulfur sales. H_2S removal is normally required for safety considerations. The consequence of a high pressure gas leak with 90% CO_2 and up to several percent H_2S warrants the removal of H_2S. Typical allowance for residual H_2S levels in CO_2 floods is below 100 ppm. Most West Texas floods are designed for reinjection of CO_2 containing 50 ppm H_2S or below.

Traditional chemical or physical solvent acid gas removal processes are designed for simultaneous CO_2 and H_2S removal. For CO_2 flood processing, very high selectivities are required. For a typical gas with 90% CO_2 and 800 ppm H_2S, over 99% selectivity is required. Several companies have developed MDEA (methyl diethanol amine) processes which have high selectivity. However, to obtain extremely high selectivity, several stages are required. Physical solvents can be used, but they have a high affinity for NGL's and their use with NGL-rich EOR gases is a problem.

Direct conversion processes offer an interesting alternative. The most promising of these is probably the LO-CAT process[8] (Figure 8). This is an aqueous iron-based oxidation-reduction process which converts the H_2S to elemental sulfur with the solution regenerated with air. This process has the potential to have lower operating cost than competing processes.

H_2S can be fractionated from CO_2. However, the relative volatility is very low because CO_2 and H_2S approach an azeotropic state near the CO_2 end of the binary phase diagram. This separation can be accomplished by adding a third component to achieve separation by extractive distillation.

METHANE REMOVAL

Methane removal may be required to meet miscibility criteria. The presence of methane (and nitrogen) has a dramatic effect on reservoir miscibility pressure. Each reservoir will react differently to these light gases, but one example of this effect is shown in Figure 9 for one West Texas reservoir. The reservoir pressure for this field must not exceed 1800 psig. Therefore, methane must be removed to below 10%. Even if methane removal is not required to maintain miscibility, removal for fuel or sales may be desired based on the economics of a given CO_2 flood.

A wide variety of processes can be used for this separation step. Conventional chemical solvents such as amines and potassium carbonates are energy intensive and costly for high-CO_2 streams. Physical solvents have the problem of solubility of NGL's in the solvent. Bulk removal by tertiary amines has been proposed[10] and should be considered for "peaking" operations. Membranes have been used successfully at SACROC[11] for front-end unloading of existing plants. All of these processes have a common problem: the CO_2 is returned at low pressure and in some cases water saturated. Thus, the compression which is already the largest cost component of the project, must be increased by as much as 60%. The presence of H_2S can also be a complicating item as H_2S may distribute between the CO_2 and methane streams, requiring its removal from both streams.

CO_2 and methane have very high relative volatilities, and from this standpoint the fractionation of these two components is quite easy. The problem lies in the very real potential of CO_2 solid formation at low temperatures required for this separation. Figure 10 shows a temperature profile for CO_2/methane separation. In order to obtain high purity methane, the fractionation operating line crosses into the solid phase region.

As with H_2S/CO_2 separation, this separation can be made feasible by introducing a third component into the fractionation. By moving the operating line away from the solid-phase region, the separation can be accomplished. One process, the Ryan/Holmes process, utilizes an NGL additive to perform the separation of CO_2/CO_1, CO_2/C_2, and CO_2/H_2S.[12]

RYAN/HOLMES PROCESS

The Ryan/Holmes process was developed specifically for CO_2/EOR gas processing. The process is patented and licensed by Koch Process Systems (KPS).

The process, as originally conceived,[12] is a three column fractionation process (Figure 11). The first column separates a high quality methane product from the main feed gas. The second column produces a CO_2 stream overhead for injection. The bottom product from this column contains ethane, H_2S and essentially all heavier components. The third column produces NGL's and an NGL additive stream for recycle to columns 1 and 2. It is this additive recycle which makes the process work. In the first column, the additive prevents CO_2 solid formation. In the second column, it permits breaking of the CO_2/C_2 azeotrope such that high ethane recovery is achieved. Additionally, the H_2S is removed from the CO_2 and produced with the ethane and propane out of the additive column. The ethane recovery can be controlled over a broad range while maintaining H_2S content of the CO_2 at ppm levels.

If methane removal is not desired, a two-column configuration is used (Figure 12). In this case, the methane is produced with the CO_2. Ethane and H_2S removal efficiency is affected very little. If a high percentage of methane is present, an additional demethanization step would likely be required.

Since the early development work on the Ryan/Holmes process, specific applications have pointed to new configurations for the process which significantly reduce the horsepower and energy requirements.[13,14] For an application where methane removal is needed, a four-column arrangement is used (Figure 13). This configuration includes a bulk CO_2 removal column and a demethanizer which produces specification fuel gas. Both columns operate in the 500-600 psig range. The CO_2 is produced as a liquid and is pumped to injection. This pumping represents a significant savings over compression and is the arrangement currently being designed for several CO_2 floods.

Another interesting development is the use of this process in a propane recovery scheme. This is accomplished by adjusting the operating parameters on the ethane recovery column to reject ethane and obtain high propane recoveries. Such recovery can be achieved with less refrigeration horsepower than with straight refrigeration. Any H_2S in the gas stream will be concentrated in the CO_2 stream. Thus, H_2S must be taken out upstream or tolerated in the CO_2 product.

INVESTMENT AND OPERATING COSTS

The investment and operating costs for an EOR facility vary from project to project and are affected by many variables:

- Inlet pressure
- Injection pressure
- H_2S content
- NGL content and recovery efficiency
- Methane content (if removal is required)
- Capacity

The inlet pressure is a key item. Lower separator pressure will increase compression horsepower and result in increased crude stripping. The injection pressure is a rather minor variable which will typically be in the 2000 psig range. For many of the West Texas floods, the actual cost for H_2S removal and sulfur conversion is less than 5% of the project cost. However, for higher H_2S concentrations sulfur recovery and tail-gas clean-up can become a major cost component. Increasing NGL content requires more equipment for removal. This is a very desirable circumstance due to increased product volumes, but does increase the facility cost. Methane separation, if required, will add about 10 to 15% to the project cost.

Generally, the larger the plant the higher the cost. However, larger facilities benefit from an economy of scale, up to a practical train size. Thus the cost per MCF actually drops as plant capacity increases until multiple trains are required.

Total plant costs range from $.8 to $1.25 MM per MMSCF capacity. A general planning figure of $1MM/MMSCF capacity is a reasonable value subject to adjustment for the variables mentioned above.

Operating costs run in the 50 to 60¢/MCF range. For electric motor driven compression plants, the costs will tend to be near the higher end of this range. Gas-fired facilities will have lower operating costs (assuming internally generated methane is valued at injectant value).

CONCLUSIONS

Enhanced Oil Recovery projects utilizing CO_2 injection have required the development of process designs to handle a new generation of process problems associated with high EOR gas streams. The alternative designs have undergone a series of change from processes focusing on CO_2 removal to processes which conserve CO_2 for reuse. NGL removal has become a significant factor in all EOR planning.

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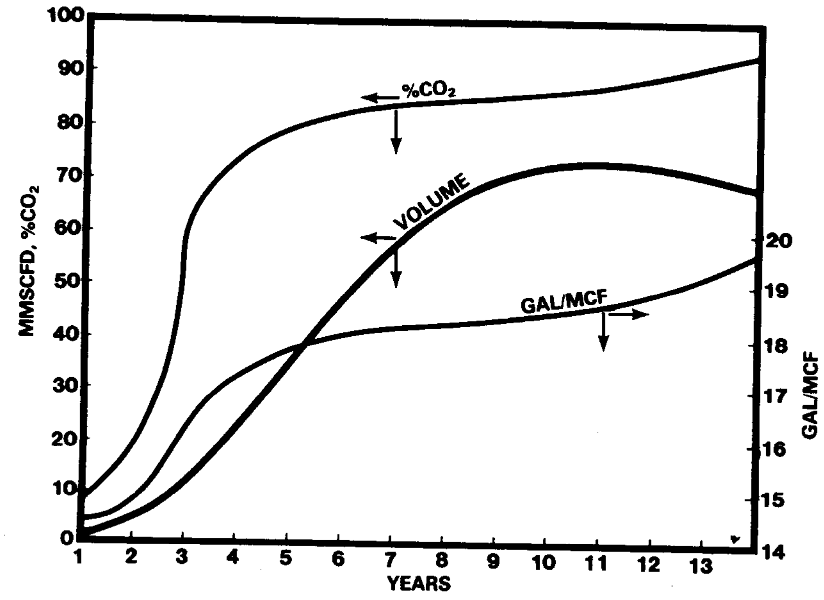

Figure 1 - Willard production forecast

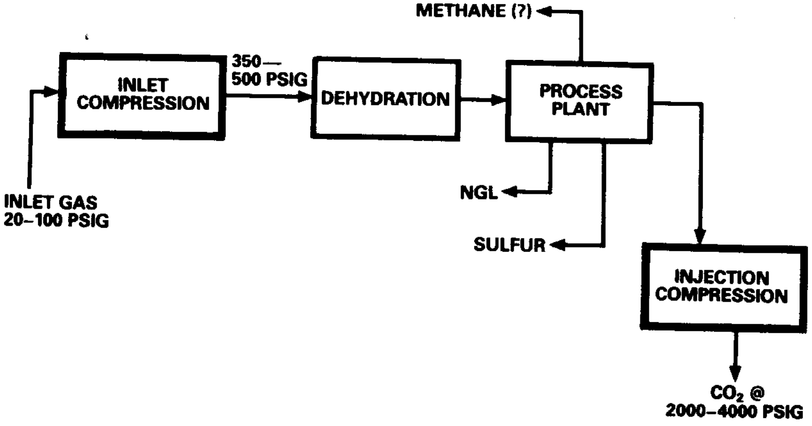

Figure 2 - Compression requirements

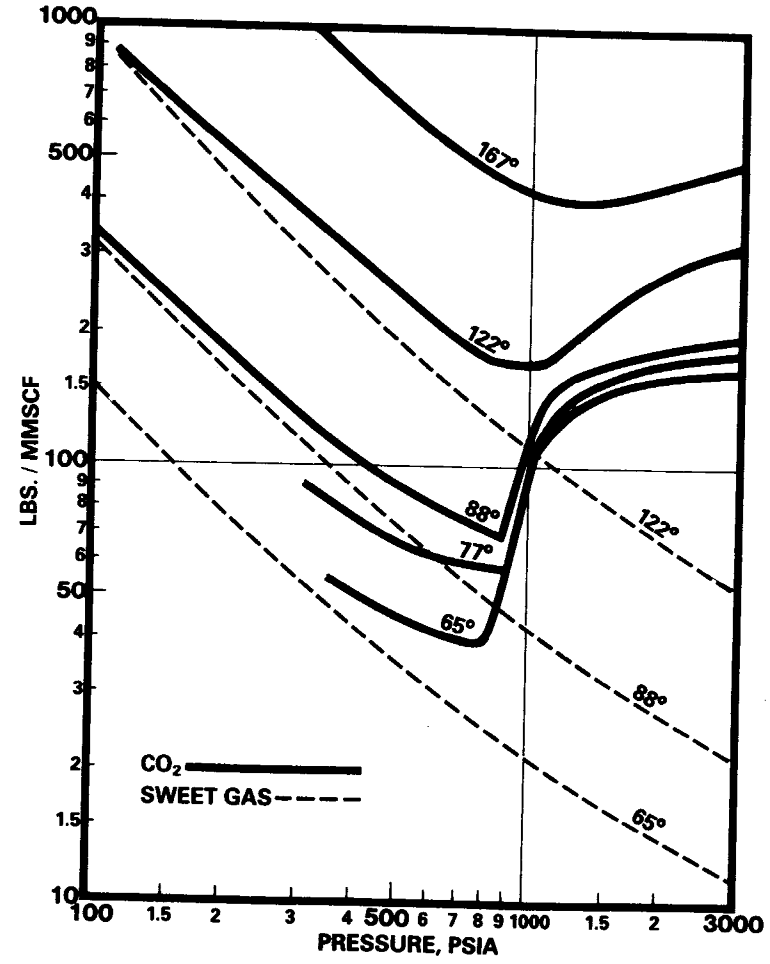

Figure 3 - Water content of CO$_2$

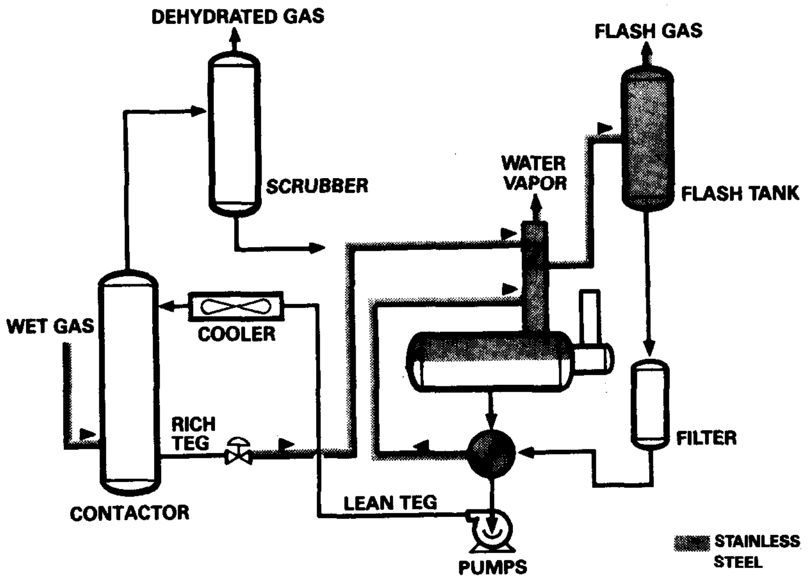

Figure 4 - Typical TEG system

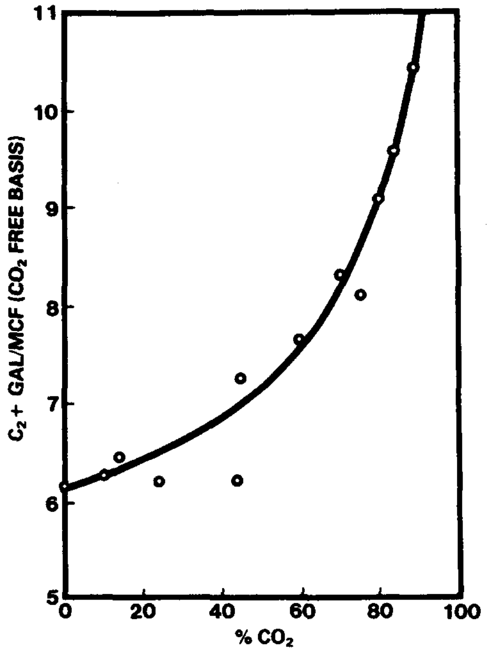

Figure 5 - NGL content - full field flood

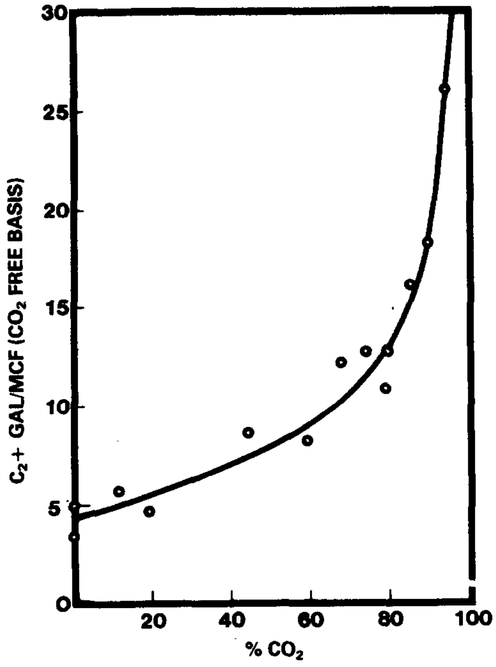

Figure 6 - NGL content - pilot flood

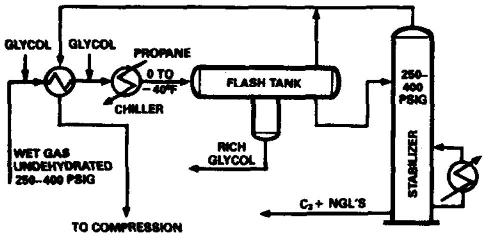

Figure 7 - NGL recovery - straight refrigeration

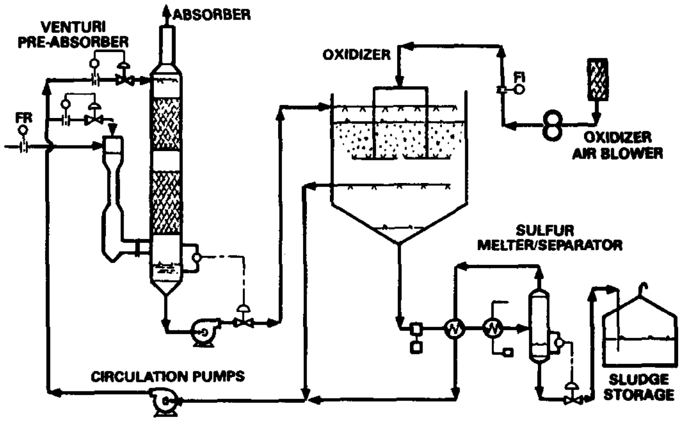

Figure 8 - LO-CAT process

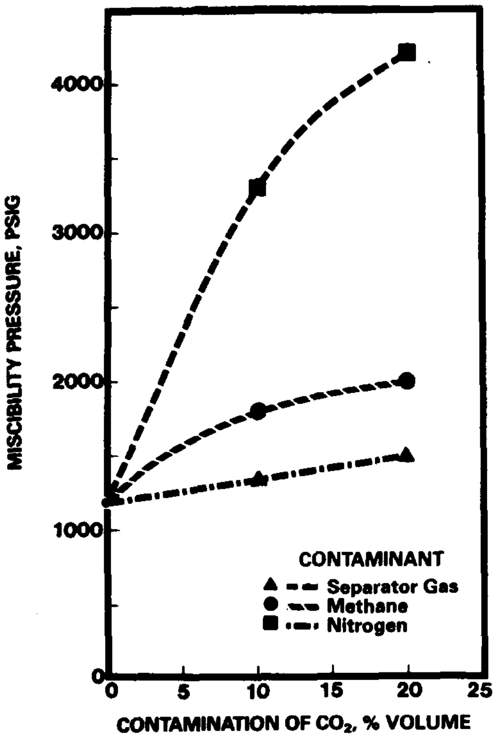

Figure 9 - Miscibility pressure vs. CO_2 contamination

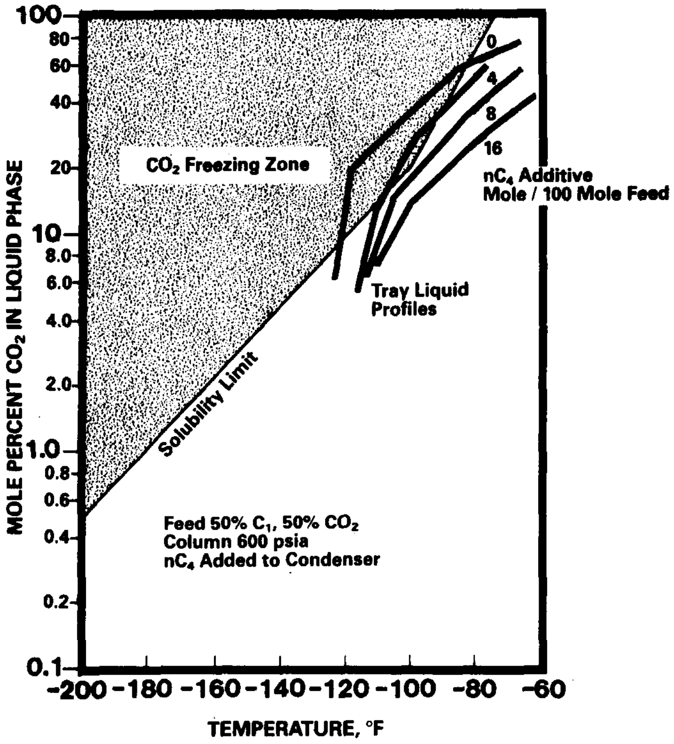

Figure 10 - Distillation profile - binary feed with nC_4 additive

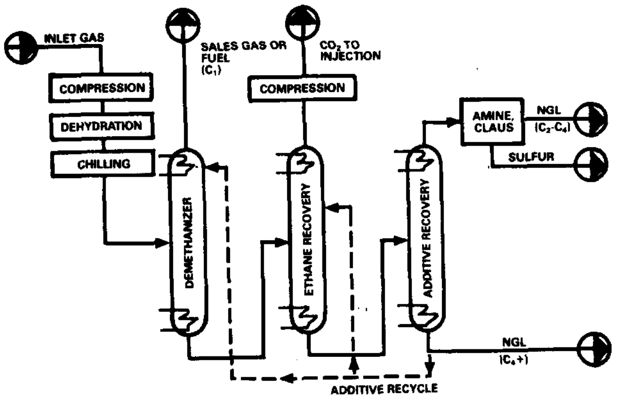

Figure 11 - Three column Ryan/Holmes process

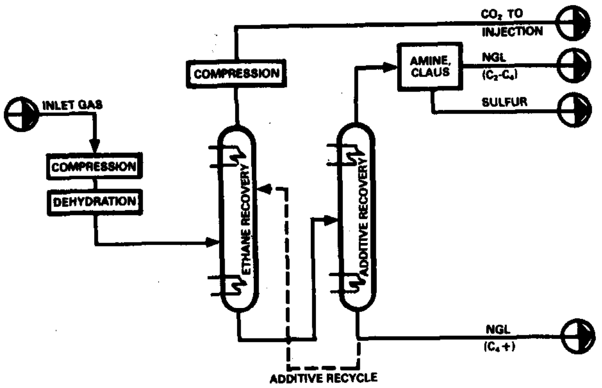

Figure 12 - Two column Ryan/Holmes process

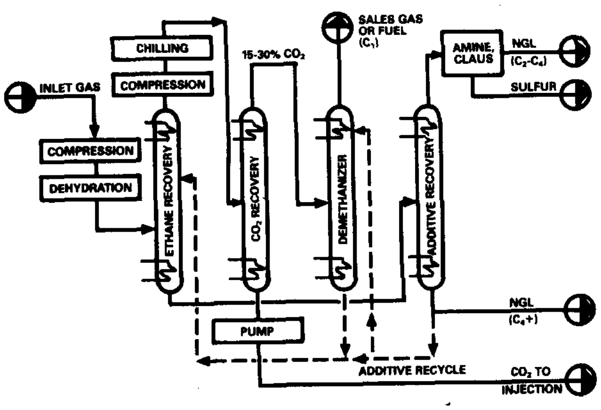

Figure 13 - Four column Ryan/Holmes process