

ECONOMICAL OPTION FOR CO₂ / METHANE SEPARATION IN PRODUCED GAS CONTAINING A HIGH CO₂ FRACTION

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ABSTRACT

Produced natural gas often requires some sweetening and/or processing prior to being sent to a high-pressure gas transmission pipeline. Historically, however, it has not been economical to produce fields with extremely high CO₂ content due to the excessive capital and operating expenses and the relatively low value of the natural gas produced.

Sales gas pipeline operators generally require pipeline gas to contain less than 2-3 mole % CO₂ and/or less than 4 mole % total inert components. Removal of high volumes of CO₂ generally requires a large amount of compression power, high process heat input, or both. Increasingly strict environmental regulations limiting the amount of volatile organic compounds (VOC) emitted to the atmosphere within the United States frequently require that the CO₂ stream be thermally oxidized to destroy VOC prior to venting.

Increasing worldwide concern that CO₂ contributes to global warming may lead to limiting the volume of CO₂ that can be vented to the atmosphere. Within this political reality, CO₂ separated from the natural gas increasingly must either be utilized or sequestered. The primary means of sequestering large volumes of CO₂ is injection back into the earth. This typically requires that CO₂ be delivered to the injection well sites at pressures between 2,000 and 3,500 psig.

There are presently several methods used in the gas processing industry for removal of CO₂ from natural gas, including processes utilizing amines and physical solvents, membrane systems, and the Ryan-Holmes process. Those practiced in the art of gas treatment are aware of the details of those processes so they will not be reviewed in this paper.

This paper describes a new process that utilizes a dual refrigerant system for bulk CO₂ removal, followed by and integrated with a physical solvent process, such as UOP's SELEXOL[™] process (utilizing di-methyl ethers of polyethylene glycol - DEPG), for removing CO₂ to within pipeline specification. The maximum benefit of this process is achieved when CO₂ is sold into a CO₂ pipeline for use as an agent for enhanced oil recovery or when the CO₂ is injected back into the earth for sequestering. When treating produced gases with a CO₂ content in excess of 40%, the integrated process provides significant CAPEX and OPEX reduction over the use of physical solvents alone.

Increased demand for natural gas as an “environmentally friendly” source of energy has led to higher natural gas prices. The higher price for natural gas combined with the need for CO₂ in enhanced oil recovery projects has resulted in an economical project in the USA using the process described in this paper. The data presented is based upon information generated during the development of this project.

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Introduction

In some areas there are produced gas streams which contain very high concentrations of CO₂. These streams must be processed to remove CO₂ before they can be sold and transported in a commercial sales gas pipeline. CO₂ must be removed to levels of 2 to 3 mole % to meet typical gas pipeline specifications. There are many options for removing CO₂ in a natural gas stream down to acceptable levels. These options typically require large amounts of compression power and/or high levels of external process heat. As a result, processing these high CO₂ streams generally requires a very large capital investment (CAPEX) along with extremely high operating expenses (OPEX).

Beginning in the 1960's, significant gas deposits with relatively high CO₂ concentrations were discovered in several areas of the US. This paper describes a project within one of these producing fields that produces both low CO₂ content gas as well as gas with CO₂ levels between 40% and 70%. The high CO₂ containing deposits are relatively low in heavier (C₃-C₆+) hydrocarbon content.

In the subject area, production of the gas with low CO₂ content was begun shortly after discovery and continues today. Several gas processing plants were installed in the region in the 1970's to separate the CO₂ and hydrocarbons (primarily methane) so that the resulting hydrocarbons could be sold into the gas distribution system. The majority of the CO₂-natural gas separation facilities installed at this time were based on absorption of the CO₂ using the physical solvent SELEXOL[™]. Some of the CO₂ was compressed and sent to CO₂ pipelines, but a significant amount was vented to the atmosphere.

The first plants installed processed gas with up to 42% CO₂. Over a period of years, due to factors such as rising OPEX and exploration costs and low methane prices, the volume of gas processed by the existing facilities declined significantly. This trend continued until the early 2000's when further development of this field was initiated.

During the 1970-2000 time frame one of the major stumbling blocks for increasing gas production was the increased CO₂/hydrocarbon ratio of the produced gas and the limited market for the CO₂. As the CO₂ concentration increased, the cost per unit basis of the revenue producing stream (the hydrocarbon) increased. With the per unit OPEX costs increasing and with relatively low natural gas prices, there was little incentive for further development of these resources.

Another trend that inhibited the production of the high CO₂ content gas was the increasingly rigorous air quality standards being implemented by the state and federal governments. When the CO₂ is separated from the hydrocarbon, traces of C₃+ (VOC) remain in the CO₂

fraction. Since the majority of the CO₂ produced in these legacy physical solvent-based facilities is vented to the atmosphere, processing higher CO₂ content wellhead gas increases the volume of VOC-containing CO₂ emitted from the facility, creating issues with ever more restrictive air quality standards.

During the early to mid 2000's, three trends began to evolve which have had a major impact on the value of high CO₂ content gas reserves:

1. There has been an increased awareness that the use of natural gas to produce electricity has less impact on air quality than the production of electricity using either oil or coal as the fuel. This is a global phenomenon which has led to the increased installation of LNG liquefaction and vaporization facilities around the world, and an increase in natural gas usage domestically.
2. As the demand for natural gas for generation of electric power increased, the price of natural gas increased significantly (See Figure 1). This increase has enticed LNG producers and domestic natural gas producers to develop additional resources while still maintaining a price benefit over oil as an energy source.
3. The increase in oil prices has led to greater demand for enhanced oil recovery in oil fields that were approaching the end of their normal production lives. With CO₂ injection being one of the preferred methods to strip older fields of their remaining oil, CO₂ has value to oil producers with CO₂ flood projects.

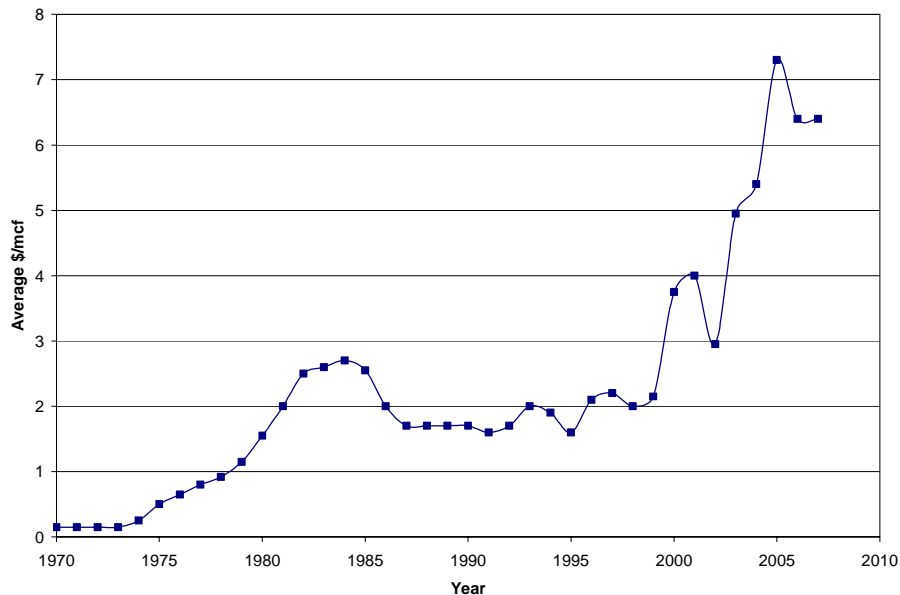


Figure 1. U.S. Wellhead Natural Gas Prices

In mid 2007 various methods to monetize the high CO₂ content reserves located in this field were evaluated. Several producing wells with approximately 65% CO₂ had been drilled over the previous several years and the existing processing facilities were operating at their current capacities. Two consulting firms were tasked with evaluating the various processes

available to separate gas production containing approximately 65% CO₂ and 35% hydrocarbon, predominately methane.

The two firms evaluated existing technologies and, independent from one another, determined that a simple SELEXOL[™] process would be the most economical proven technology. Other unproven technologies were expected to be much more efficient, but very risky in that no commercial facilities were in operation. At least one of the firms considered membranes or fractionation upstream of SELEXOL[™], but did not consider integrating the two processes. After evaluating the recommendations of the consulting firms, the owner began development based upon two parallel 200 mmscfd SELEXOL[™] trains for a total processing capacity of 400 mmscfd was initiated.

The balance of this paper will chronicle the evolution of this project from a 400 mmscfd SELEXOL[™] processing facility to the current 800 mmscfd integrated Dual CO₂ Refrigerant Fractionation / SELEXOL[™] facility now under construction (construction commenced 4Q2008).

Pre-FEED Evaluation

During the Pre-FEED phase of this project the benefits of an integrated process using CO₂ fractionation for bulk removal of CO₂ upstream of the SELEXOL[™] process was evaluated. Bulk CO₂ removal would reduce SELEXOL[™] circulation and reduce the volume of CO₂ to be compressed from relatively low pressures up to CO₂ pipeline pressures.

Ortloff developed process simulations to determine the optimal level of CO₂ removal using the Ortloff's proprietary Dual Refrigerant CO₂ Fractionation (DRCF) process. , This process uses an external refrigerant as well as using a portion of the liquid CO₂ as refrigerant. Once the optimal separation levels were determined, a comparison of the CAPEX and OPEX for this process and the SELEXOL[™] only was prepared for the customer's evaluation.

Description of the Two Processes Evaluated

Physical Solvent (SELEXOL[™])

Figure 2 shows a block diagram of a typical physical solvent system using the SELEXOL[™] process. The diagram represents the basic scheme selected for the plants installed in the early 1970's in West Texas. Physical solvents are an attractive option for treating produced gas streams with high acid gas partial pressures. The SELEXOL[™] process absorbs CO₂ from the produced gas at relatively high pressures (950-1,200 psig) and is regenerated in a series of flashes to lower pressure. The initial (high pressure) flash vapor contains significant hydrocarbon and is compressed back to the inlet of the SELEXOL[™] process unit. Successive flashes during the SELEXOL[™] regeneration process release primarily CO₂ vapor, with the final regeneration flash near atmospheric pressure. CO₂ vapor that is removed at the various flash pressures is compressed from relatively low pressures to the CO₂ pipeline delivery pressure through multiple stages of compression.

SELEXOL[™] has a higher affinity for water than for either H₂S or CO₂. Therefore, the SELEXOL[™] will absorb both water and acid gas. SELEXOL[™] also has a high

affinity for heavy hydrocarbons. The water absorbed by the SELEXOL™ is typically carried from the flash vessels by the CO₂ vapor. If the CO₂ is delivered to a pipeline, then additional dehydration may be required. Heavy hydrocarbons, if they are present in the feed gas, must be removed from the SELEXOL™ solution in a stripping column after the CO₂ is flashed off. If left untreated, hydrocarbon will continue to accumulate, inhibit acid gas absorption, and cause foaming in the absorber column.

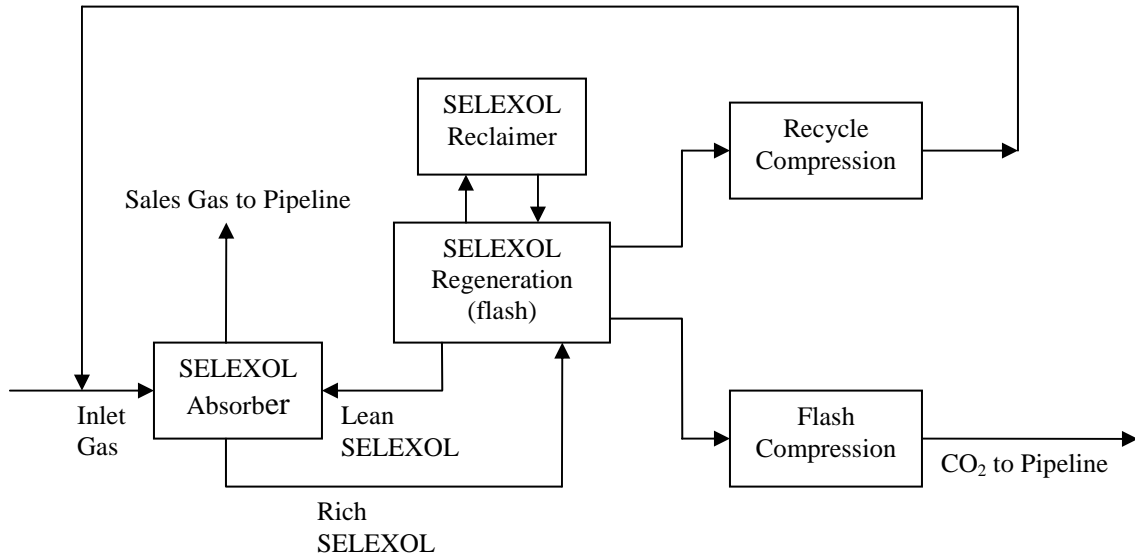


Figure 2. Typical Physical Solvent (SELEXOL™) Process

Integrated CO₂ Fractionation / SELEXOL™ Process

The CO₂ fractionation system performs the initial bulk CO₂ fractionation step and then the SELEXOL™ system performs the final CO₂ removal to meet the natural gas pipeline specification.

The Ortloff's Dual Refrigerant CO₂ Fractionation (DRCF) process which utilizes a commercial refrigerant for high-level refrigerant and a portion of the liquefied CO₂ as low-level refrigerant to reduces the CO₂ content to approximately 21 mole % before processing in the SELEXOL™ unit to meet final pipeline CO₂ specification of less than 2%.

A block diagram of this integrated bulk CO₂ fractionation/SELEXOL[™] scheme is shown in Figure 3. Volumes and compositions in Figure 3 are for the design using Ortloff's DRCF process.

CO₂ Fractionation Process Description

Inlet gas at a pressure of between 1125 psig and 1250 psig is dehydrated using molecular sieve upstream of the fractionation process. The dried gas is then chilled by heat integration with the fractionation column (furnishing reboiler duty for the column). The gas is then further chilled and partially condensed in the refrigerant chillers using an external refrigerant.

Next, the inlet stream is totally condensed and partially sub-cooled through further heat integration with streams leaving the cold section of the plant. Finally, it is flash expanded to the fractionation column at an optimum pressure designed for effective CO₂ / methane separation while avoiding CO₂ freezing issues. Vapor leaving the column overhead is further chilled and partially condensed in the overhead condenser with CO₂ refrigerant. The resultant CO₂-rich liquid is pumped back to the fractionation column following further heat integration within the process. Vapor not condensed in the reflux condenser is cross exchanged with the inlet gas and recompressed to 1,200 psig where it is fed to the SELEXOL[™] absorber.

In the Ortloff DRCF process, the refrigerant for the overhead condenser is a portion of the CO₂ product from the bottom of the fractionation column. This liquid CO₂ is then flashed to a relative low pressure where it chills and partially condenses the overhead vapor stream. The volume fraction of CO₂ in the gas leaving the reflux accumulator is approximately 21%. The CO₂ used as refrigerant in the overhead condenser is then compressed, cooled, and returned back to the fractionation column where it is recovered in liquid form.

The liquid CO₂ product leaving the bottom of the fractionation column is pumped to pipeline pressure. The majority of propane and heavier hydrocarbons exit the column with the liquefied CO₂.

Comparison of the Ortloff Dual Refrigerant CO₂ Fractionation Process with SELEXOL[™]-Only Process

Overall power requirements decrease as more of the CO₂ is removed by bulk fractionation since this CO₂ is pumped to pipeline delivery pressure rather than compressed. A comparison of the CO₂ removed by each process is evaluated in Table 1.

Table 1. CO₂ Removed by Process Unit
(per 400 MMSCFD train with inlet gas containing 65% CO₂)

Plant Process Option	CO ₂ Removed (MMSCFD) by Process Unit	
	SELEXOL	Dual Refrig. CO ₂ Frac.
Conventional SELEXOL [™]	260	--
Dual Refrigerant CO ₂ Frac. + SELEXOL [™]	38	222

Table 2 compares utility usage of these processes. As shown in Table 2, there is a significant reduction in the power requirements for an integrated refrigerated bulk fractionation / SELEXOL[™] system versus a conventional SELEXOL[™]-only scheme. This results in a significant savings in both capital and operating expense since the power requirement is the biggest component of both. As reflected in the table, the integrated system using the dual refrigerant saves approximately 36.4 MW over the SELEXOL[™]-only system (81.9-45.5=36.4).

Table 2. Rotating Equipment Power Required by Process Unit
(per 400 MMSCFD train with inlet gas containing 65% CO₂)

Plant Process Option	Rotating Equip. Power Required by Process Unit (MW)*				Total
	Compression		Pumping		
	CO ₂ Frac.	SELEXOL	CO ₂ Frac.	SELEXOL	
Conventional SELEXOL	--	71.3	--	10.6	81.9
Dual Refrig. CO ₂ Frac. + SELEXOL	11.5	26.1	5.0	2.9	45.5

* All compressors and pumps driven by electric motors. Power calculations include 10% excess capacity for all services and an electric motor service factor of 0.92.

In the hybrid design, overall plant power usage is minimized by maximizing recovery of CO₂ in the bulk fractionation system section of the plant at relatively high pressure. The power savings that is possible with bulk fractionation upstream of physical solvent absorption is due to the fractionated CO₂ stream leaving the system as a liquid at relatively high pressure. The liquid CO₂ product can then be pumped to the CO₂ pipeline or to injection wells rather than having to be compressed. In the conventional SELEXOL[™]-only scheme, all of the CO₂ must be compressed to the CO₂ pipeline from low pressure, a good portion of it from near atmospheric pressure.

During the development of the CO₂ Fractionation/SELEXOL[™] process it was discovered that the hydrocarbon losses are significantly reduced when the fractionation scheme is properly integrated with the SELEXOL[™] system. The integrated process reduces the calculated total hydrocarbon loss in the CO₂ product from approximately 4.0 mole% to 1.3 mole%. The bottom spec for the fraction column is 0.5 mole % C₁, not to exceed 1.0 mole %. The C₂+ component of the bottom CO₂ product is about 0.8 mole % for the particular feed stream used in the design.

For the straight SELEXOLtm facility, UOP was willing to guarantee that hydrocarbon (C₁+) content would not exceed 4 mole % in the CO₂ product. Data on the existing plants indicate that 3.5% methane in the CO₂ is a reasonable expectation. Note that, for a feed stream containing 33% methane, this equates to approximately 7% methane loss. The majority of the methane hydrocarbon absorbed in the SELEXOLtm is flashed off in the first two flash stages and recycled back to the absorber. With the straight SELEXOLtm process, hydrocarbon not recovered in these two “recycle” flashes is lost to the CO₂ product flashed from the last three flashes.

In the DRCFU/SELEXOLtm hybrid systems, the flash gases from the final three stages are compressed back to the inlet of the CO₂ Fractionation process unit, the CO₂ is recovered in the liquid phase (so that it is pumped to the pipeline delivery pressure), and the hydrocarbon fraction is recycled back to the absorber where it eventually leaves the absorber as pipeline-quality sales gas. The hydrocarbon fraction becomes even more significant as the SELEXOLtm feed CO₂ content decreases. While a 65 mole % CO₂ feed to the SELEXOLtm process will result in a ~3.5 mole % hydrocarbon content in the CO₂ product stream, a 21 mole % CO₂ feed stream will result in a ~8.5 mole % hydrocarbon content in the CO₂ product stream, under the same conditions.

The only hydrocarbons lost from the hybrid system leave the bottom of the fractionation column with the product CO₂. Based upon the inlet gas composition and simulation results, the calculated hydrocarbon content of the CO₂ product in the hybrid system is approximately 1.3%, with a process guarantee that the C₁ component will not exceed 1% of the produced CO₂. It should be noted that a portion of the C₂ component and most of the C₃+ fraction entering with the inlet gas will be retained in the CO₂ sales stream. Again, in this case, the C₂+ component is about 0.8 mole % of the CO₂ product stream.

Economic Comparison

An economic comparison of the two processes was prepared based upon two parameters. The first economic parameter was CAPEX. The CAPEX was developed by combining the estimated cost of compression for each processing unit with the estimated installed cost for the balance of the required equipment. A CAPEX summary is shown in Table 3. Since the fractionation process require more equipment than the SELEXOLtm process, the costs of pressure vessels, heat exchangers and air coolers, etc., were evaluated but had much less effect on the overall capital cost when compared to the compression.

Table 3. Estimated CAPEX Savings Compared to a Conventional SELEXOL™ System
(per 400 MMSCFD train with inlet gas containing 65% CO₂)

CAPEX Description (installed cost)	(\$MM) Dual Refrigerant CO₂ Fractionation + SELEXOL
Process Unit, excluding Compression	(50)
Compression (@ \$3000 / HP)	100
Total CAPEX Savings	50

The second parameter for the economic evaluation was OPEX. It was assumed that manpower costs were similar for the two processes and the SELEXOL™ losses into the sales gas had minimal impact on overall operations costs. The major component of the OPEX is energy costs to drive process equipment and hydrocarbon losses entrained in the CO₂ product. The power costs were evaluated at \$0.08 per KWH and hydrocarbon losses were valued at \$5.00/mmbtu. Table 4 tabulates the comparison of these costs.

Table 4. OPEX by Process Unit
(per 400 MMSCFD train with inlet gas containing 65% CO₂)

(MM\$/year)*						
Plant Process Option	Energy Cost		Methane Loss		Total OPEX	OPEX Savings Compared to Conventional SELEXOL
	CO₂ Frac.	SELEXOL	CO₂ Frac.	SELEXOL		
Conventional SELEXOL	0.0	56.6	0.0	16.4	73.0	0
Dual Refrigerant CO ₂ Fractionation + SELEXOL	11.4	20.0	2.3	0.0	33.7	39.3

* Based on plant operation of 360 days/year.

Conclusions

An integrated DRCF /SELEXOL™ process was chosen for this project. There are several advantages for using this scheme rather than a conventional SELEXOL™ system, including the following:

- Lower total power required for the operation resulting in significantly lower capital and operating expenses.

- Lower hydrocarbon losses to the CO₂ product, resulting in increased hydrocarbon gas sales.
- Although dehydration is required prior to the CO₂ fractionation system, neither the final hydrocarbon sales gas nor the CO₂ sales stream requires further dehydration. In addition, the SELEXOL[™] circulation system operates dry and a water removal system is not required.
- Since heavy hydrocarbons are removed in the fractionation system, potential hydrocarbon contamination of the SELEXOL[™] system is eliminated and a SELEXOL[™] reclaimer system is not required.
- Permitting of the facility was relatively simple since the only air emissions from the plant are generated by the molecular sieve regeneration gas heater and fugitive VOC from the equipment, valves, and piping. The commercial refrigerant R134A was used instead of propane as the refrigerant for this facility. This decision reduced the volume of liquid hydrocarbon contained within the facility; thus increasing safety and reducing potential environmental incidents.

Additional Comments

- It is estimated that the maximum capacity of a single CO₂ Fractionation/SELEXOL[™] train will be between 500-600 mmscfd limited by equipment sizes.
- The SELEXOL[™]-only process is simpler and there is probably some lower capacity where the additional complexity of the hybrid system is not economically justified. That limit has not yet been established.