

H₂S REMOVAL FROM CO₂ BY DISTILLATION

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Abstract

This paper introduces a new process configuration developed by Air Products and Chemicals, Inc. to efficiently separate carbon dioxide (CO₂) and hydrogen sulfide (H₂S) using traditional distillation methods without needing an additive to increase the relative volatility of CO₂ and H₂S. The removal of H₂S from CO₂ is of high importance in industries such as Enhanced Oil Recovery where purified CO₂ is often preferred; however the separation of H₂S from CO₂ by distillation is technically challenging and energy-intensive due to the low relative volatility at low H₂S concentrations. Traditionally, distillation has been considered technically feasible but deemed to have high capital and energy requirements. This paper describes the application of advances in distillation technology, heat exchanger design, and process optimization to lower the cost of this challenging separation even in cases where nitrogen, methane, natural gas liquids (NGL) or other components are present. Many of these advances are currently applied at large scale in other challenging distillation separations, such as O₂/Ar in the air separation industry. The advantages of this new distillation process for H₂S and CO₂ will be demonstrated through comparison with conventional solvent-based processes that have been applied to the separation of H₂S from CO₂.

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I. Introduction

A growing fraction of today's oil is produced via Enhanced Oil Recovery (EOR) using carbon dioxide (CO₂) [1]. CO₂ EOR requires large quantities of CO₂, and sources capable of supplying these requirements can be grouped into a few categories:

- Natural sources that are mostly CO₂
- Recycle from EOR
- Byproduct from natural gas processes
- Byproduct from industrial processes
- Byproduct from power generation

Some of these CO₂ sources can contain hydrogen sulfide (H₂S) in amounts that can be considered higher than desired, e.g., greater than 0.5 mol%. Hydrogen sulfide is not particularly detrimental to the efficiency of CO₂ in EOR service, however it is often removed prior to CO₂ transmission pipelines due to various reasons, such as its toxicity [2]. The need for the H₂S removal process is situational, depending upon location, regulations, public perception, safety, concerns for H₂S buildup in the reservoir, the quality of oil to be extracted or pipeline requirements.

One of the most significant issues that may force the need for removing H₂S from EOR CO₂ is pipeline requirements. Many (but not all) CO₂ supply pipelines that serve EOR areas have a specification for H₂S; a range of 10 – 100 ppmv is common. Therefore, in situations where CO₂ that contains significant amounts of H₂S needs to be transported via pipeline for a significant distance, H₂S removal is often required.

A. Overview of the Conventional H₂S Removal Technologies

The choice of process technology for removal of H₂S from CO₂ streams in EOR applications depends on several factors and varies greatly with CO₂ to H₂S ratio, size of the plant, presence of other components in the gas, feed pressure and constraints on the disposition of the H₂S. In turn, these factors determine the capital and operating costs [3]. Similar to a common rule-of-thumb for the removal of H₂S from natural gas, the total amount of elemental sulfur that needs to be removed is a good indicator for screening the suitability of alternative technologies.

Typically, for natural gas streams with low H₂S levels, e.g., where the total amount of H₂S to be removed is significantly less than 1 LTPD of elemental sulfur, H₂S scavengers are usually found

to be a good techno-economic fit. As the amount of H₂S to be removed from the gas increases to a medium scale of roughly 1 to 20 LTPD, liquid redox type processes and some other technologies have been applied. For the larger scale of more than about 20 LTPD, amine units with Claus units are frequently selected for removal and disposal of H₂S [3].

For the removal of H₂S from gas streams that are primarily CO₂, the application of conventional selective amine technologies tend to be more difficult due to the fact that amines cannot achieve perfect selectivity for H₂S removal in the presence of CO₂. Therefore treatment of streams that are primarily CO₂ tends to be more difficult and the processes applied more complex compared to the treatment of natural gas, particularly at large scale. The concentration of H₂S in the CO₂ feed stream, and the concentration to which it must be removed to in the treated gas are also very important in the selection of process technology.

For larger scale applications requiring the removal of more than about 20 LTPD of H₂S from a gas stream that is primarily CO₂, amines, physical solvents (e.g., DEPG), conventional distillation, extractive distillation (e.g., Ryan-Holmes), or combinations of these technologies may be preferred. All of these technologies effect the separation of H₂S from the CO₂, resulting in the production of a hydrogen sulfide-rich acid gas byproduct stream. The hydrogen sulfide-rich byproduct stream may then be converted to sulfur via the Claus process, or may be injected. Acid gas injection may be practiced preferentially in conjunction with CO₂ treatment for EOR.

For large CO₂ sources that contain relatively high concentrations of H₂S (greater than 0.5 mol%) the equivalent amount of elemental sulfur that needs to be removed can be an order of magnitude larger than 20 LTPD, which is already considered large scale. For example, for a CO₂ source at a flow rate 100 MMSCFD that contains 1% H₂S, the amount of elemental sulfur that needs to be removed is approximately 226 LTPD. As the H₂S concentration in the CO₂ source increases above 5 mol%, the process technologies that can economically remove H₂S to meet the CO₂ pipeline requirements are limited. For high H₂S concentration CO₂ sources, solvent-based Acid Gas Removal (AGR) processes like amines [3] and physical solvents have typically been used to remove H₂S from gas streams [4][5]. When amines are applied for the absorption of H₂S from CO₂, an Acid Gas Enrichment (AGE) unit may also be required because the H₂S concentration of the AGR regeneration gas may not be sufficient (due to selectivity limitations) to allow for the economical operation of a Claus unit or acid gas injection.

Purification of EOR-grade carbon dioxide, where the hydrogen sulfide-rich byproduct stream is prepared for acid gas injection with greater than 50 mol% hydrogen sulfide content, has been accomplished commercially by solvent-based Acid Gas Removal and extractive distillation processes such as Ryan-Holmes [6].

Solvent-based AGR systems, such as Dimethyl Ethers of Polyethylene Glycol (DEPG) have been commercially proven in removal of acid gases such as carbon dioxide and hydrogen sulfide from natural gas sources or syngas. While most of the physical solvents have an order of magnitude higher affinity for H₂S than for CO₂[7], they still co-absorb significant quantities of CO₂. The CO₂ that is co-absorbed during H₂S removal requires a series of lower pressure flashes and/or a hydrogen sulfide enrichment column in order to produce a hydrogen sulfide stream from the solvent regenerator that does not contain excessive amounts of CO₂. The flashed CO₂ then has to be compressed and recycled back into the feed of the absorber in order to achieve high

carbon dioxide recovery and/or for environmental and safety considerations. This leads to higher energy consumption and capital requirement compared to an equivalent system without the low pressure flashes.

B. Overview of CO₂/H₂S Distillation Processes

The vapor liquid equilibrium of the CO₂ and H₂S binary system has been studied extensively. Bierlein et al. [8] concluded that while no azeotrope existed for CO₂ and H₂S, evidence of strong intermolecular forces existed at high CO₂ concentrations. While the traditional distillation of CO₂ and H₂S is technically feasible, it has been regarded as a difficult separation due to the low relative volatility of CO₂ and H₂S at high CO₂ concentrations. Traditionally, this would dictate large columns with high energy requirements to meet the purity requirements typically dictated by EOR use [9].

Ryan-Holmes processes employ distillation to effect the CO₂-H₂S separation, however they differ from traditional distillation in that a hydrocarbon-based additive like n-butane or a mixture containing n-butane is used to increase the relative volatility of CO₂ with respect to H₂S. Figure 1 shows the CO₂/H₂S relative volatility at 600 psia for a CO₂ and H₂S binary system and CO₂/H₂S/n-butane ternary system.

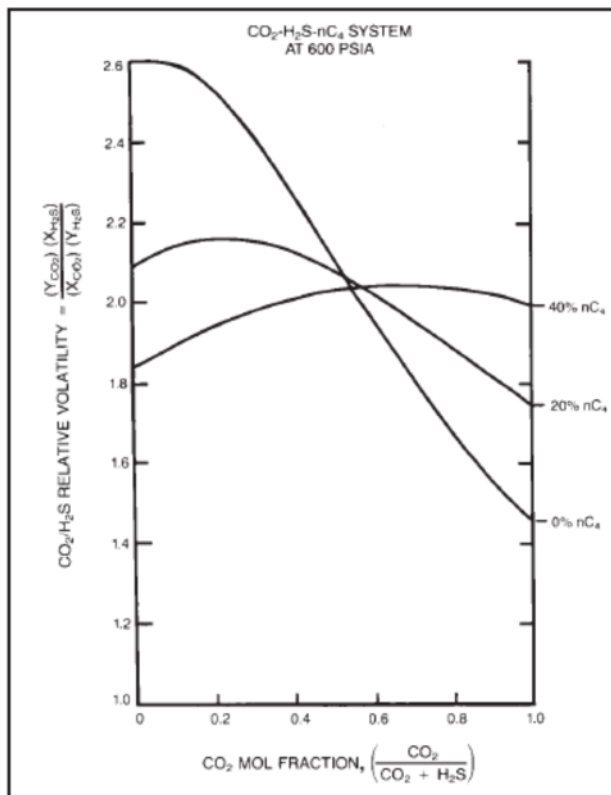


Figure 1 - CO₂ - H₂S - nC₄ System at 600 psia[6]

For the CO₂ and H₂S binary system, previously reported CO₂/H₂S relative volatilities at CO₂ rich concentrations are approximately 1.42-1.45 at 600 psia [8]. With the addition of n-butane, the relative volatility of CO₂ and H₂S can be increased to 1.8-2.0 thus reducing the number of stages required, reflux requirements and energy intensity of the H₂S/CO₂ separation. The Ryan-Holmes process is more suited to applications where the additives used for improving CO₂/H₂S relative volatility are already present within the feed gas. These additives are typically an n-C₄₊ cut of Natural Gas Liquids (NGL). In the Ryan-Holmes process, the increase in relative volatility can be controlled by recycling more or less of the additive. The Ryan-Holmes process is employed commercially in high CO₂ gas fields or EOR facilities that recover NGL from produced gas and recycle carbon dioxide [9]. While the Ryan-Holmes process reduces the energy requirements for the separation of CO₂ and H₂S by distillation, it requires additional fractionation steps to recover the additives from the H₂S stream. This additive recovery requirement and the plant infrastructure needed to store and recycle these additives increases the capital and energy intensity of the Ryan-Holmes process. In applications where the feed gas does not contain enough heavy hydrocarbons to balance the process additive losses, the Ryan-Holmes process requires purchase of these additives, thus increasing the operating cost.

While processes for the removal of H₂S from CO₂ by distillation have been developed and studied, no known commercial plants have been built. Pryor [10] describes a process for removal of CO₂ and H₂S from a hydrogen-rich gas by condensation, where the stream of condensed CO₂ and H₂S then feeds into a distillation column and is separated into a CO₂ rich overhead and a bottoms stream containing at least 10 vol% H₂S. Overhead vapor from the column is condensed using an external closed-loop propane refrigerant and bottoms liquid is reboiled using process cooling water. The distillation column has 100 trays and operates at about 590 psia.

C. Distillation of Mixtures with Low Relative Volatility

While a relative volatility of approximately 1.4 for CO₂ at rich CO₂ concentrations indicates a difficult separation requiring a large number of theoretical stages and high reflux ratios, more difficult separations have been performed commercially when the economics support them, e.g., in cryogenic air separation units to separate oxygen and argon. The argon/oxygen system has a relative volatility ranging from 1.05 to 1.1 at dilute oxygen concentration. A typical commercial argon product specification is less than 1 ppmv oxygen content. 180 to 220 theoretical stages are required to achieve the separation. The oxygen/argon separation energy intensity and capital requirements have been reduced significantly since the 1990s with advances in distillation technology using advanced heat integration techniques and structured packing distillation column internals[11][12].

Although the high energy intensity of the CO₂ and H₂S separation by distillation cannot be eliminated, the efficiency of the separation process can be maximized with advanced process configurations tailored for systems containing CO₂. Similar configurations have been studied for the purification of CO₂ following capture from power plants. The quantities of CO₂ used in EOR operations are similar to CO₂ flow rates planned in the Carbon dioxide Purification Units (CPU) of oxyfuel power plants in the 200-300 MW power plant size range.

The technical advances in auto-refrigerated CO₂ purification processes are the foundation for a first-of-a-kind commercial helium recovery plant where CO₂ makes up more than 95% of the

feed gas. It is in the final stages of construction at the time of writing this paper [13]. The plant will be treating 170 MMSCFD of CO₂, the scale associated with EOR operations.

II. The New Process for H₂S Removal from CO₂ by Distillation

Building on these advances, Air Products has developed a novel process that separates CO₂ and H₂S efficiently using traditional distillation methods without needing to use an additive to increase the relative volatility of CO₂ and H₂S.

The process flow diagram of this new configuration is shown in Figure 1 [14]. The feed in this example is primarily a CO₂/H₂S mixture in the liquid phase at approximately 650 psia. These feed conditions could be obtained as a result of processes that rely on the condensation or freezing of CO₂ and/or H₂S [15] [16] [4] from low quality natural gas resources. Liquid feed is not a requirement; alternatively the feed can be gaseous CO₂ and H₂S as typically seen in recycled CO₂ from sour EOR fields.

The process includes a multi-stream Brazed Aluminum Heat Exchanger (BAHX), a CO₂ recycle compressor and aftercooler, a CO₂/H₂S distillation column and product pressurization pumps.

The liquid feed is first subcooled in the BAHX then reduced in pressure via a feed Joule Thompson (JT) valve. The resulting two-phase feed stream is fed to the BAHX to be warmed up and vaporized and fed to the distillation column. The subcooling of the feed before let down in pressure increases the utilizable refrigeration that is provided when the feed stream evaporated, improving the efficiency of the process. The distillation column operates at approximately 300 psia. The main light component in this distillation process is CO₂ and the purified CO₂ product is obtained from the top of the distillation column. The top section of the column rectifies CO₂ and is designed to meet the specification of H₂S in the CO₂ for EOR applications, typically less than 100 ppmv of H₂S. The heavier component in this separation is H₂S and this is obtained at the bottom of the column. The bottom of the column strips CO₂ from the H₂S to produce a H₂S stream that contains greater than 80% H₂S at the column pressure of 300 psia; this H₂S by-product would usually be sent to a Claus unit or to acid gas injection. In contrast to solvent-based acid gas separation processes, both the CO₂ and the H₂S are kept at elevated pressure throughout the process and this significantly reduces the product pumping or compression requirements.

The overhead of the column is warmed up in the BAHX, compressed in the recycle compressor to approximately 450 psia and then sent to the aftercooler. The higher pressure gaseous recycle CO₂ stream is then condensed and subcooled in the BAHX against the side and bottom reboilers of the distillation column. The now subcooled CO₂ recycle stream is reduced in pressure to approximately 350 psia in the condenser separator. The condenser separator contains a liquid CO₂ stream that contains less than 100 ppmv of H₂S which is then split into two streams; a portion of it is sent to the distillation column as reflux and the remaining portion is pumped above critical pressure via a CO₂ booster pump. By keeping the condenser separator sufficiently above the column pressure, reflux can be sent to the top of the column without the need for reflux pumps.

The CO₂ after the CO₂ booster pump is warmed up in the BAHX and pumped to the final carbon dioxide pipeline pressure of 1,500 - 2,500 psia via the CO₂ product pump.

This type of process is typically referred to as an auto-refrigerated configuration since it does not require any additional external refrigeration. The condenser and reboilers of the CO₂/H₂S distillation column are configured as a heat pump circuit; vaporizing CO₂ in the reboilers provides the refrigeration for the recycle CO₂ condensing at higher pressure.

In this configuration, high CO₂ recoveries in excess of 99% can be achieved with a 5 mol% H₂S feed and 85 mol% H₂S in the waste H₂S stream. The CO₂ losses will be primarily due to CO₂ leaving with the waste H₂S stream and, to a lesser extent, losses that typically occur in compressor and pump seals.

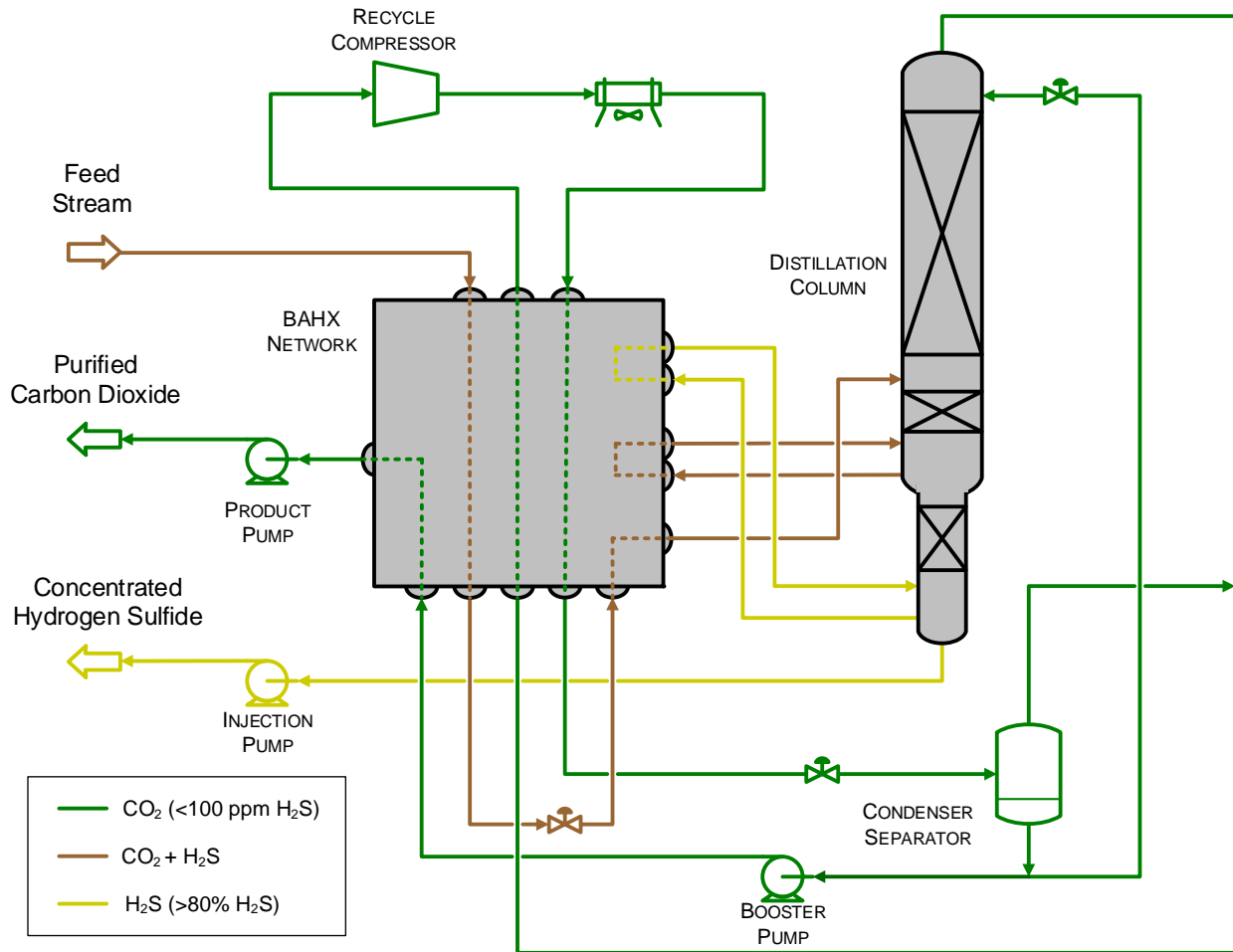


Figure 2 - Process Flow Diagram

III. Case Study

The following case study has been developed to demonstrate the performance of this process. In this example, a feed stream needs to be purified in order to meet the typical pipeline requirements of carbon dioxide for EOR. The feed in this example could be from another process that condenses CO₂ and H₂S from a gas reservoir [15][4].

Table 1 - Feed and Product Requirements

	Feed	CO₂ Product	Waste H₂S
Pressure, psia	650	2,500	3,500
Temperature, F	45	< 120	< 120
Flow Rate, MMSCFD*	100		
Molar Composition			
CO ₂	92.725%	> 95%	< 15%
H ₂ S	6.0%	< 25 ppmv	> 85%
COS	250 ppmv		
CH ₄	1.0%	< 5%	
N ₂	0.25%	< 5%	
Notes: * MMSCF is 1,000,000 Standard Cubic Feet (SCF) at 14.696 psia and 60°F.			

The separation of the liquid phase feed stream into a CO₂ product and waste H₂S was characterized using two different distillation process configurations: external refrigeration and auto-refrigerated processes. The power requirements and energy intensity of these two process configurations are compared in this section.

Both processes were simulated with Aspen Technology Inc.'s Aspen Plus® simulation software using a customized equation of state model. The CO₂ and H₂S parameters for the equation of state model were obtained through Vapor Liquid Equilibrium (VLE) laboratory measurements performed for the pressure, temperature and composition ranges of interest.

The CO₂ and H₂S distillation column in each process was simulated with 80 theoretical stages plus a condenser and a bottom reboiler. Air coolers were used for the process cooling with a design ambient air temperature of 90 °F and a minimum temperature approach of 20 °F. In both cases, a polytropic efficiency of 80% was used for the compressors.

A. External Refrigeration Distillation Process Configuration

Figure 3. The heat exchangers used in this process configuration are shown as a single heat exchanger network for the example case. This heat exchanger network can be split into multiple heat exchangers depending on the physical equipment requirements and economic consideration. The feed is subcooled in the heat exchanger network and then let down to approximately 300 psia, evaporated against subcooling refrigerant, and fed to the CO₂/H₂S distillation column towards the bottom.

The distillation column features a total condenser and bottom reboiler that are integrated into the heat exchanger network. The condenser separator contains a liquid CO₂ stream that contains less than 25 ppmv of H₂S, which is then split into two streams; a portion of it is sent to the distillation column as reflux, and the remaining portion is pumped above critical pressure via a CO₂ booster pump. The CO₂ after the CO₂ booster pump is warmed up in the heat exchanger network and pumped to the final CO₂ pipeline pressure of 2,500 psia via the CO₂ product pump. The

refrigeration for the process is provided with a single stage propane refrigeration system with subcooling. The propane compressor is a two stage compressor with air cooled intercooler and aftercooler. The compressed and cooled propane is then condensed against the column reboiler and subcooled against evaporating feed in the heat exchanger network.

The waste H₂S product stream with greater than 85% H₂S is obtained from the bottom of the column as liquid and pumped to a final pressure of 3,500 psia using the acid gas injection pump.

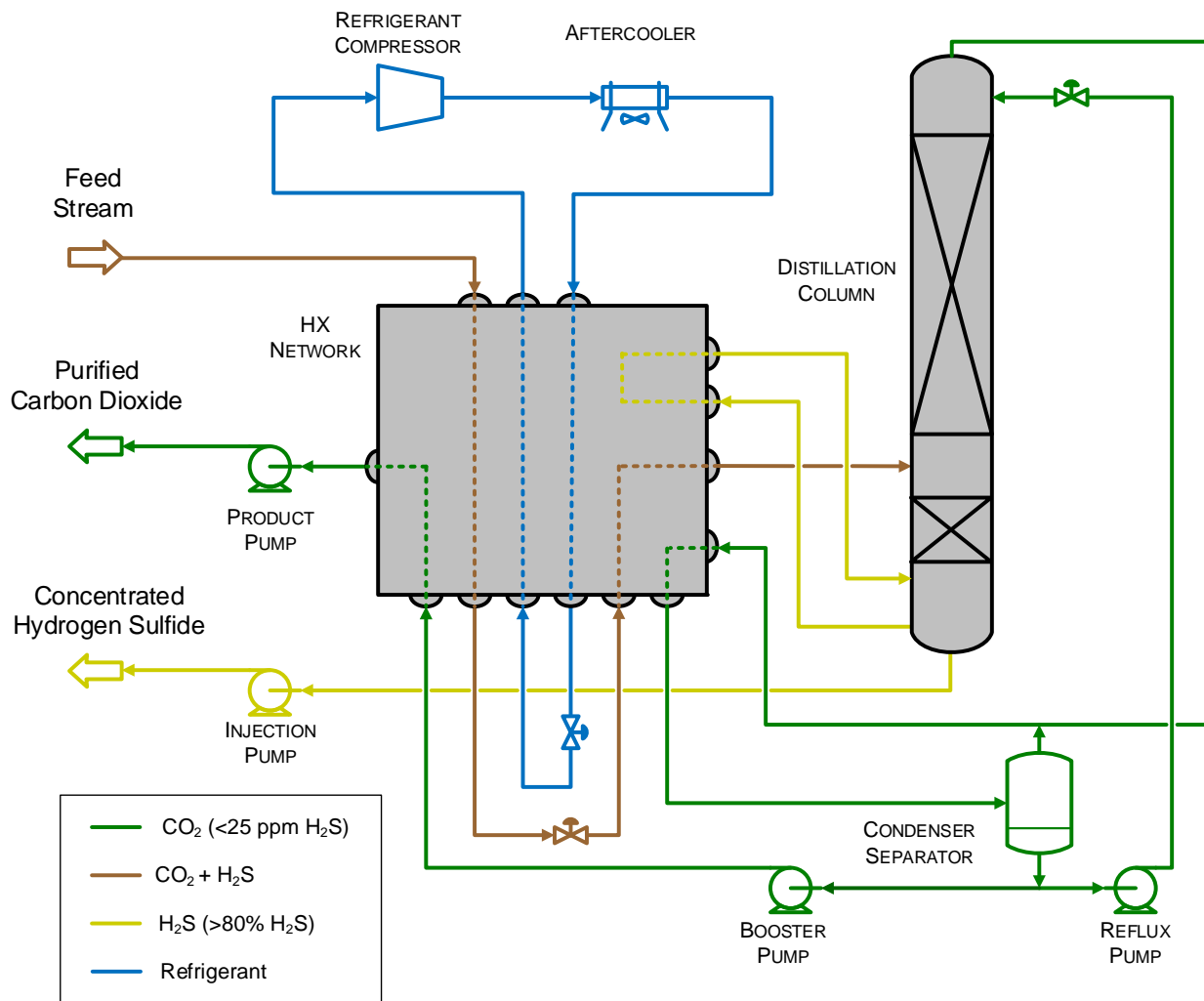


Figure 3 – External Refrigeration Distillation Process Configuration

A summary of process power consumption is shown in Table 2.

Table 2 - Externally Refrigerated Process Power Summary	
	Power Consumption, hp
Refrigeration Compressors	27,000
Waste H ₂ S Injection Pump	190
CO ₂ Booster Pump	560
CO ₂ Pipeline Pump	1,520
Total Power	29,270

The propane condenser integrated with the reboiler of the column in the heat exchanger network reduces the condensing pressure of the propane to approximately 90 psia compared to condensing against air which would have required 220 psia, thereby reducing the propane compressor power.

B. Auto Refrigerated Distillation Process Configuration

In this example, a similar configuration to the auto-refrigerated distillation process that was introduced in Figure 2 is used. The new process configuration is shown in Figure 4. The change to the process in Figure 2 is the addition of a high pressure CO₂ recycle compressor. Approximately 10% of the recycle flow goes through the high pressure recycle compressor and this further improves the efficiency of the process.

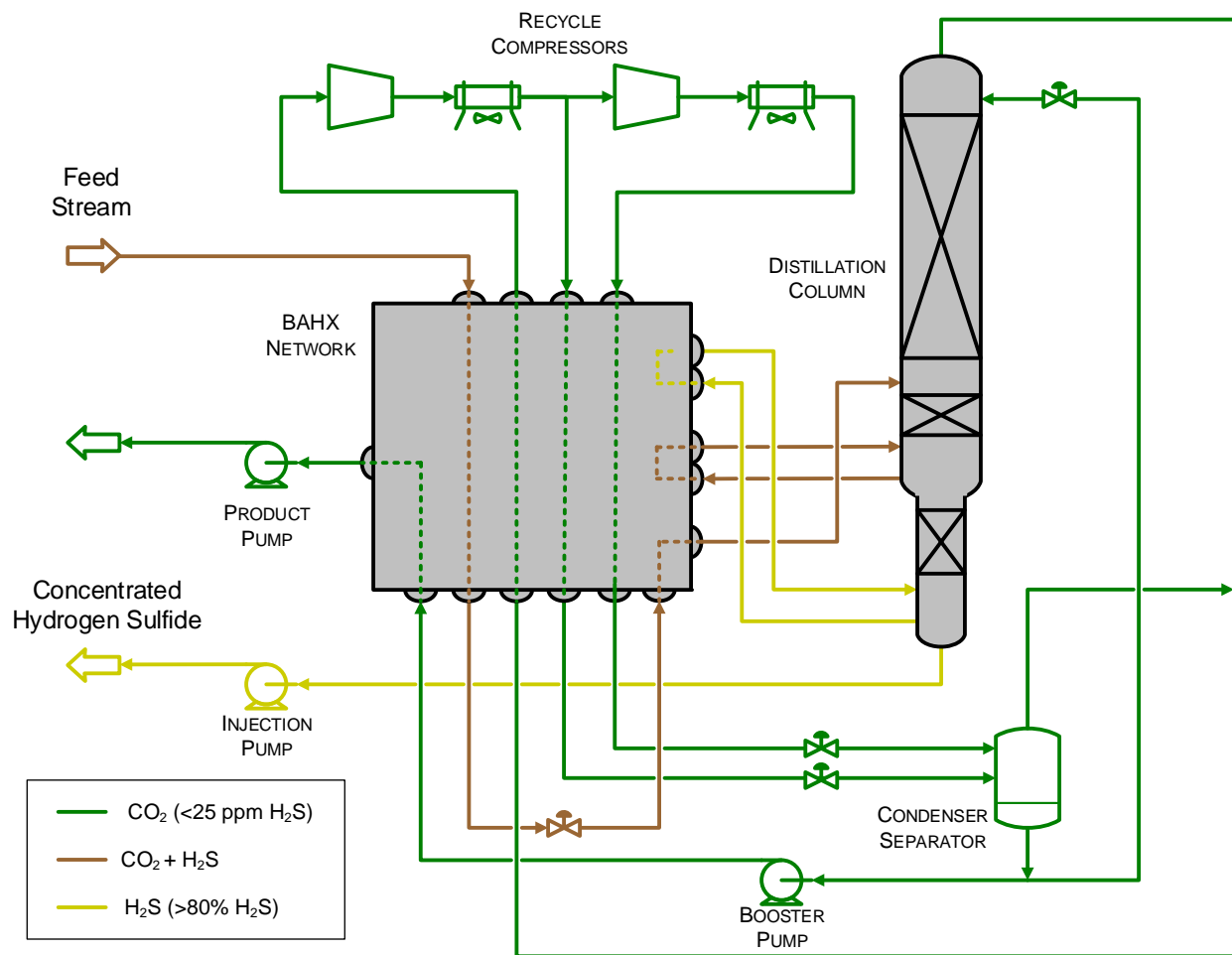


Figure 4 - Auto-Refrigerated Distillation Process Flow Diagram

In this two-stage auto-refrigerated distillation process, the reboiler duty required is split into side and bottom reboilers and provided by the condensing carbon dioxide at two pressures in a heat pump arrangement.

The auto-refrigerated process power consumptions are given in Table 3.

Table 3 - Auto Refrigerated Distillation Process Power Summary

	Power Consumption, hp
Recycle Compressor	8,600
HP Recycle Compressor	590
Waste H ₂ S Injection Pump	190
CO ₂ Booster Pump	610
CO ₂ Pipeline Pump	1360
Total Power	11,350

As can be seen from the comparison of the results presented in Table 2 and Table 3, the auto-refrigerated process offers significantly lower power consumption than the externally refrigerated process. These benefits are primarily due to the higher thermodynamic efficiency of the process. In addition, it offers potential capital cost savings due to the substitution of the large external refrigeration system with a much smaller recycle compressor.

IV. Process Sensitivities

In this section, additional considerations that affect the power consumption and capital requirements of the new auto-refrigerated distillation process are summarized.

A. Feed Conditions; Temperature and Pressure

If obtained from another process upstream, the feed to the distillation process can be a liquid CO₂/H₂S mixture at an elevated pressure as shown in the example case. Alternatively the feed can be at a lower pressure and the CO₂/H₂S mixture can be gaseous as typically seen in the CO₂ recycle streams of EOR operations. The feed to the distillation column is vapor phase at approximately 300 psia, so for lower pressure feed sources, compression of the feed will be required.

In the case of a liquid feed, some of the refrigeration required for the condensation of the recycle CO₂ is obtained by vaporization of the subcooled feed. If the feed is in the vapor phase, the recycle compressor power requirements increase to replace the refrigeration that is otherwise obtained from vaporization of the liquid feed stream. At the same temperature and pressure, a vapor feed requires less than 10% additional power to substitute the refrigeration obtained from the feed stream.

B. Effect of CO₂ Product H₂S specification

The impact of changing the H₂S content of the CO₂ product on the power consumed by the process is shown in Figure 5. As the CO₂ product H₂S specification is tightened, the reflux requirement for the carbon dioxide/hydrogen sulfide distillation increases for a fixed total number of distillation column stages. For this example, the reduction of H₂S content of the CO₂ product leads to a nearly exponential increase in the power consumption. To mitigate this effect,

the total number of stages of the distillation column can be optimized based on power and capital requirement considerations on a case by case basis.

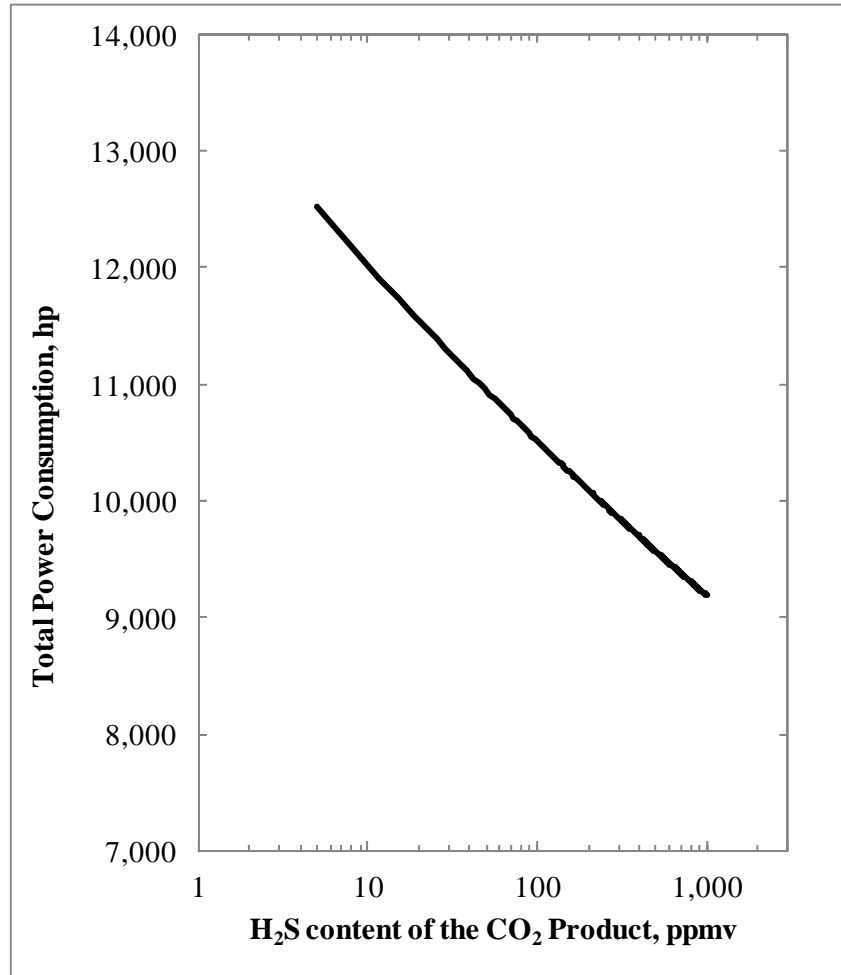


Figure 5 - CO₂ Product H₂S Specification Sensitivity for a fixed total number of distillation column stages

C. Effect of H₂S concentration in the Feed

The relative volatility of CO₂ in a CO₂/H₂S mixture increases to reach about 2.6 at high H₂S concentrations at 600 psia as shown in Figure 1. This indicates that stripping of CO₂ from H₂S is relatively easier at high H₂S concentrations. As a result, the total power consumption of the process tends to increase linearly with increasing H₂S concentration in the feed gas, as shown in Figure 6.

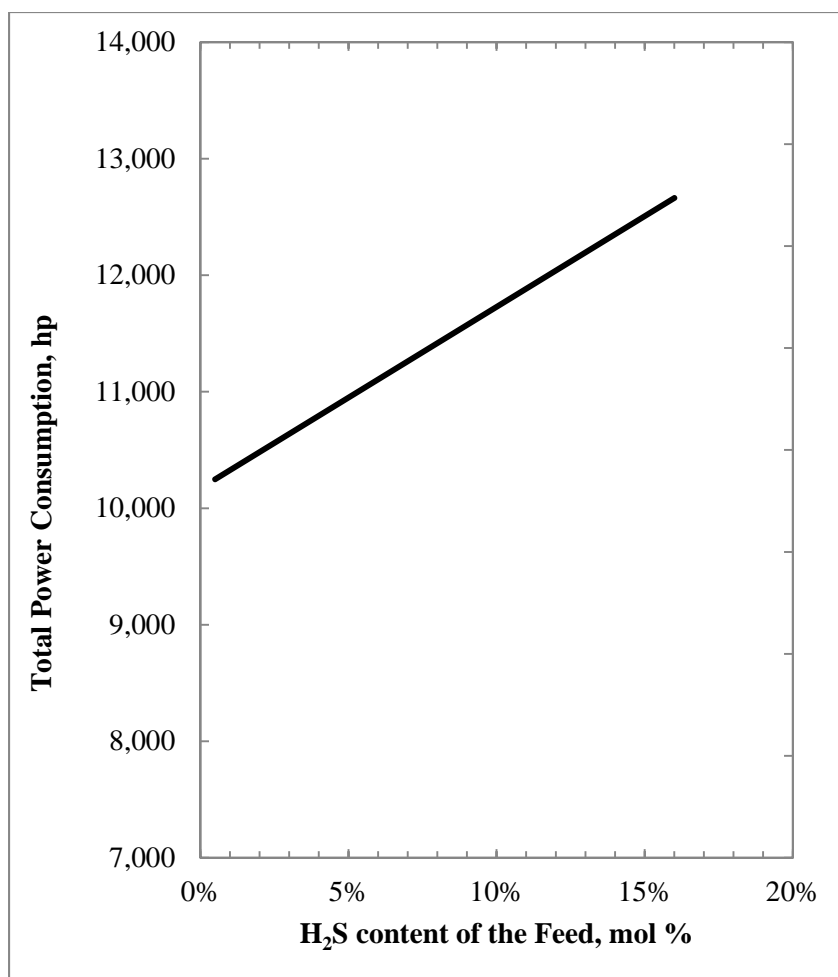


Figure 6 - Feed H₂S Content Impact for a fixed total number of distillation column stages

D. Effect of Light Components in the Feed

The process configuration in Figure 2 can be used for feed streams that have less than about 2 mol% lights (like methane and nitrogen) without any modification. As the lights concentration increases above 2%, some of the lights are preferably rejected from the heat pump circuit in order to prevent build-up of lights causing an increase in total power consumption as the condensing pressure increases. As the subcooled recycled CO₂ stream is let down in pressure to the condenser separator, the light components dissolved in the CO₂ flash off and can be purged from the overhead of condenser separator. Purging light components also results in a small amount of CO₂ loss from the process. Depending on the value of the CO₂, the amount of CO₂ lost can be minimized or it can be recovered with alternative process configurations. The best approach can be evaluated on a case by case basis.

E. Effect of NGLs in the Feed

Depending on the source of the feed to the plant, the feed can contain NGLs (C₃+). Typically CO₂ that is recycled at EOR fields contains NGLs, or the gas source could contain NGLs. The NGLs do not have to be removed upstream of the process and most of the NGLs condense with

H₂S. In this case, an additional small column can be used to separate the NGLs from the condensed H₂S where H₂S can be stripped out of the NGLs to low ppm levels. With this type of configuration approximately 90% recovery of C₃+ and near 100% recovery of C₄+ can be achieved. The energy and capital requirements of recovering NGLs are comparatively small. The C₃ recovery is limited to approximately 90% as some C₃ is lost with the H₂S at the C₃/H₂S azeotropic concentration.

F. Feed Carbonyl Sulfide (COS) Impact

Sour gas fields with high H₂S concentrations can also have a few hundred parts per million of Carbonyl Sulfide (COS). While there are no commonly accepted COS specifications for EOR pipelines, there may be total sulfur specifications that need to be met.

The removal of COS from gas streams is challenging for conventional solvent-based AGR systems, as COS removal efficiencies are typically limited because the COS affinity is close to CO₂ [7]. In cases where COS is a concern for the pipeline, additional COS removal processes can be required.

In the distillation process, based on phase equilibrium considerations, nearly all of the COS is expected to be removed from the CO₂ along with the H₂S. Thus the COS may be conveniently disposed of using acid gas injection.

V. Conventional Solvent-Based AGR Process

Acid gas removal processes have been demonstrated commercially for high H₂S content natural gas fields at Exxon Mobil's Shute Creek Facility [4] and the Lost Cabin Gas Processing Plant [5] where the H₂S concentrations are greater than 4% mole. Both of these plants use DEPG as a solvent to remove H₂S and CO₂ from the gas.

A typical AGR process flow diagram that uses DEPG as solvent is shown in Figure 7. The liquid CO₂/H₂S feed is vaporized against the condensing treated CO₂ in the economizer heat exchanger. The feed is then contacted with the cold lean solvent in the absorber column for removal of H₂S to meet the CO₂ product requirements. The treated gas leaving the absorber column is dehydrated and compressed to approximately 800 psia which enables condensing against the incoming liquid feed that is at 45 °F. The condensed product CO₂ is then pumped to the final pipeline pressure of 2,500 psia.

While H₂S is removed in the absorber, some CO₂ is also co-absorbed with the lean cold DEPG solvent. This co-absorbed CO₂ is recovered from the rich solvent with High Pressure (HP), Medium Pressure (MP) and Low Pressure (LP) flashes: 290 psia, 90 psia and 19 psia respectively. These flash stages concentrate H₂S in the semi-lean solvent that is sent to the stripping column.

The flashed CO₂ and H₂S are compressed in a three stage recycle compressor to the absorber feed pressure and recycled to the absorber column. The semi-lean solvent after LP flash is warmed up in the lean-rich heat exchanger against the hot lean solvent leaving the stripper column bottom. The warmed-up semi-lean solvent then goes to the stripping column where the solvent is regenerated using heat supplied from an external source such as steam or hot oil. Lean

solvent leaving the stripper column is pumped and cooled, first in the lean-rich heat exchanger, then in the trim air cooler and in the lean solvent cooler that uses external refrigeration. The overhead of the stripper column has greater than 85 mol% H₂S and the remainder is CO₂. The low pressure gaseous concentrated H₂S is then compressed in a four stage acid gas compressor that uses air cooled intercoolers and an aftercooler. The acid gas is compressed above 700 psia to enable condensing against air in the aftercooler. The condensed acid gas is then pumped to final injection pressure of 3,500 psia with the injection pump.

The liquid knock-outs after the intercoolers (which are not shown Figure 7) are recycled with make-up water to the stripping column.

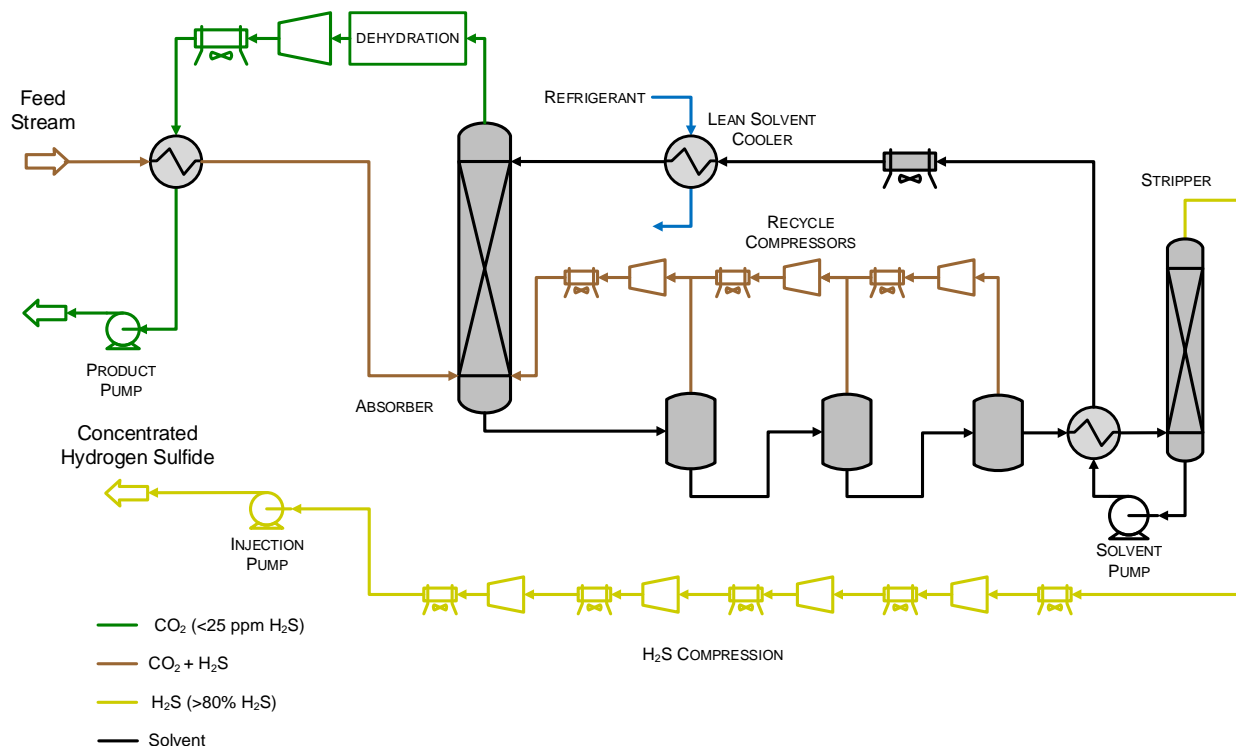


Figure 7 - Solvent Based AGR Process Flow Diagram

Alternative configurations of the solvent based AGR system to that shown in Figure 7 can be used to optimize the capital and operating cost trade-offs. The process in Figure 7 is modeled using the Aspen Plus® simulation software package with customized DEPG properties for the example case feed and product composition summarized in Table 1.

Table 4 - Solvent-Based AGR and Auto Refrigerated Process Comparison

Economic Parameters		Value	
Power	\$/kWh	0.06	
Fuel	\$/MMBtu	3.5	
On Stream	day/yr	356	
Process Configuration		DEPG	Auto-Refrigerated Distillation
Total Power	hp	14,800	11,350
Fuel	MMBtu/hr	48	-
Power Cost	\$/yr	5,650,000	4,340,000
Fuel Cost	\$/yr	1,435,000	-
Total Utility	\$/yr	7,085,000	4,340,000

In Table 4, the DEPG solvent-based AGR system utility costs are compared against the auto-refrigerated distillation process. The auto-refrigerated distillation process shows yearly utility cost savings of nearly 40% over the DEPG solvent based AGR system. In addition, the DEPG AGR system may require dehydration of the treated gas that will also require additional fuel. The DEPG solvent removes approximately 20% of the COS in the feed thus leaving approximately 220ppmv of COS in the treated gas. The COS in the CO₂ product might not be desirable for the EOR operators and so might require additional COS removal either upstream or downstream of the DEPG process.

VI. Summary and Conclusions

The novel technical features of the auto-refrigerated distillation process configuration have been described and a significant energy intensity advantage over using external refrigeration is demonstrated for the separation of CO₂ and H₂S using conventional distillation. The energy intensity is reduced primarily due to the efficiency of the heat pump arrangement; a significant reduction in the heat exchanger duty by using the same fluid in a reboiler/condenser arrangement rather than a separate reboiler and condenser, in addition the improved distillation efficiency due to having the side reboiler. In addition, it offers potential capital cost savings due to the substitution of the large external refrigeration system with a much smaller recycle compressor. Since the refrigeration is provided by recycled CO₂, which is non-flammable, this type of process offers additional safety benefits for the facility. Additional refrigerant storage and routine make-up may be reduced or eliminated. The auto-refrigerated process configuration is also compared against the conventional DEPG solvent based AGR process, and yearly utility cost savings nearly 40% are shown in the example case.

For the example case, the power cost of the CO₂ purification process is \$0.13 per MSCF of CO₂ assuming a unit cost for power of \$0.06/kWh. However, this includes product compression and, if the next best alternative is acid gas injection of the feed stream, the power required to increase the pressure of the feed to 3,500 psia would be approximately 2,600 hp. Therefore the additional power cost of removing H₂S from the CO₂ is \$0.10 per MSCF compared to pumping of the feed mixture for acid gas injection.

Detailed operating and capital cost evaluation of this process configuration leads to a total processing cost in the range of \$0.70-1.20 per MSCF of CO₂ in 2014 for a 100 MMSCFD plant

located in the continental US. While the estimate of CO₂ processing cost is provided in this paper for the benefit of the reader, it should be used with caution as the actual cost of any plant will depend greatly on the size, location and other critical project considerations and will require detailed engineering and cost estimation to determine accurately.

Given that historically the price of CO₂ for EOR is \$0.50 per MSCF plus 1.5% of the oil price, approximately \$2/MSCF of CO₂ for \$100 per barrel of oil [17], the cost of CO₂ cleanup using this technology in the range of \$0.70 to \$1.20 could bring additional CO₂ to the market for beneficial EOR use.

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