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Low-Quality Natural Gas Sulfur Removal/Recovery

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DISCLAIMER

Low Quality Natural Gas Sulfur Removal/Recovery

CONTRACT INFORMATION

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Period of Performance	October 1, 1992 - December 31, 1995

Schedule/Milestones

FY95 Program Schedule

	O	N	D	J	F	M	A	M	J	J	A	S
3. Bench-Scale Testing	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
3.1 Triple Point Crystallizer	✓	✓	✓	✓		✓	✓	✓	✓	✓	✓	✓
3.2 Sulfur Recovery Unit Testing	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
3.3 Final Report												✓

OBJECTIVES

1. Develop the CFZ and CNG-Claus process for treatment of low quality natural gas having a high carbon dioxide content (>10%) and hydrogen sulfide.
2. Test the carbon dioxide triple point crystallizer and the modified high pressure thermal Claus sulfur reactor at a bench scale.

BACKGROUND

Low Quality Natural Gas (LQNG)

Natural gas is generally categorized as low quality if its acid gas content or inert content is above the minimum specifications of a natural gas transmission company. Pipeline specifications for acid gas content are usually a maximum of ¼ grain H_2S per 100 SCF (4 ppm H_2S) and less than 2%

CO_2. Hugman's [1] definition of low quality gas appears as suitable as any other: " . . . *any volume of gas containing levels of carbon dioxide above 2 percent or of nitrogen above 4 percent or gas with carbon dioxide plus nitrogen above 4 percent, or significant (more than trace) quantities of H_2S.*"

Motivation to Tap LQNG Reserves

Increased use of natural gas (methane) in the domestic energy market will force the development of large domestic non-producing gas reserves now considered low quality.

New Federal regulations embodied in the Clean Air Act of 1990, Title III and Title V, are creating strong new market opportunities for natural gas. These include natural gas co-firing and reburn in coal-fired power plants to help reduce SO_2 and NOx emissions; natural gas fired turbines for peak-shaving and on-site generation of electrical power and steam; and natural gas as an alternative clean transportation fuel. The American Gas Association forecasts these new markets will increase the annual demand for natural gas by 2 TCF, more than 13% of current production. To meet these anticipated gas supply demands, domestic production of natural gas must begin to exploit the large reserves of low quality gas available but not now produced for technical, economic, or environmental reasons.

Target LQNG

The target high acid gas LQNG for processing with the CFZ-CNG-Claus Process contains more than 10% CO_2, is contaminated with H_2S, possibly COS and other sulfur compounds, and may contain nitrogen and other inerts such as helium. Conventional gas treatment in the form of amine based chemical solvents, physical solvents, and newer membrane based processes, is accustomed to processing LQNG contaminated with only modest levels of acid gas, e.g., up to several percent of H_2S and CO_2. With the possible exception of physical absorption processes such as Selexol, existing technologies do not now process high acid gas LQNG in an economic, environmentally acceptable manner.

The major proven non-producing reserve of high acid gas LQNG is located in the LaBarge reservoir of southwestern Wyoming; the amount of gas is large, dwarfing all other proven reserves combined. Estimates place the LaBarge reservoir recoverable gas at 167 TCF (trillion cubic feet), of which at least 33 TCF is methane. The LaBarge reservoir is high in CO_2 and prone to other contaminants such as H_2S, COS, N_2 and He [1,2].

The CFZ/CNG-Claus process is designed to treat the relatively large quantity of LQNG containing >10% CO_2 which may also contain either or both of H_2S and COS and which cannot be economically treated on a large scale by other known technologies.

LQNG Production Barriers

There are many technical and economic barriers which now prevent the up-grade of LQNG to pipeline standards [3] These include but are not limited to:

- removal of H_2S to pipeline specification of 4 ppm H_2S;
- removal of N_2 to increase heating value, decrease transportation cost;
- regeneration of separating agents [4];
- degradation of polymeric membrane materials;
- poor selectivity for CH_4 in presence of acid gases, or for H_2S in presence of CO_2;
- separation of isolated acid gases into pure CO_2 and concentrated H_2S;
- recovery of sulfur from separated H_2S;
- dissipation of high CO_2 partial pressure available in high-CO_2 LQNG;
- recompression of CO_2 for commodity use or sales.

The above list mentions explicitly only the three major contaminants (aside from water) of LQNG: nitrogen, hydrogen sulfide, and carbon dioxide. The presence of additional contaminants,

especially sulfur species such as carbonyl sulfide (COS) and mercaptans (RSH), increases the difficulty of treating LQNG.

CFZ-CNG LQNG Process

The technology comprises four process technologies integrated to produce pipeline methane from LQNG by efficient separation of relatively large amounts of hydrogen sulfide and carbon dioxide. These process technologies are:

- Exxon's Controlled Freeze Zone (CFZ) Process
- CNG's Liquid CO_2 Absorption of Sulfur Contaminants
- CNG's Triple-Point Crystallization (TPC) Process, and
- CNG's High Pressure Sulfur Recovery Process (HPSRU).

Exxon developed the CFZ process to separate methane from acid gases in a single cryogenic distillation operation. CNG Research Company developed the TPC process to purify carbon dioxide and concentrate hydrogen sulfide by alternately freezing and melting CO_2 at or near its triple point conditions (-69.9°F, 75.1 psia). The CNG HPSRU combines the high initial conversion obtained in a Claus thermal reactor with recycle of unconverted H_2S to effectively remove all sulfur components in the HPSRU feed gas. Liquid CO_2 is used to absorb sulfur compounds from HPSRU tail gas, and can be used to absorb sulfur containing contaminants from LQNG in a process variant which does not use CFZ to separate methane from acid gases.

The conceptual designs developed in the Base Program separate hydrogen sulfide and large amounts of carbon dioxide (>20%) from methane, convert hydrogen sulfide to elemental sulfur, produce a substantial portion of the carbon dioxide as EOR or food grade CO_2, and vent residual CO_2 virtually free of contaminating sulfur containing compounds.

CFZ-CNG Process Features

Controlled Freeze Zone

- Acid gas removal in single distillation step,
- No solvents or additives necessary,
- Contaminant insensitivity,
- High pressure acid gas,
- Synergy with cryogenic NRU, LNG product,
- Non-corrosive process streams.

Liquid Carbon Dioxide Contaminant Absorption

- Attractive physical properties (density/viscosity/mol weight),
- Favorable contaminant equilibrium,
- High stage efficiency,
- No solvents or additives necessary, available from raw gas,
- Not combustible

Triple-Point Crystallization

- Concentrated hydrogen sulfide,
- Commercially pure LCO_2 for market or absorption of H_2S
- Sharp separation of trace contaminants
- No solvents or additives necessary,
- Direct contact heat exchange,
- Small pressure changes cause phase changes.

CNG High Pressure Claus Sulfur Recovery

- Claus thermal stage at elevated pressure,
- Eliminates catalytic stages, tail gas unit, and incinerator,
- Oxygen or enriched air,
- No solvents or additives necessary,
- High sulfur recovery, low sulfur emissions.

PROJECT DESCRIPTION

The project comprises a Base Program and an Optional Program. The Base Program, which included NEPA reporting, process design and an experimental research plan for the optional program, was completed August 31, 1993 with submission of the Task 2 Final Report. The Optional Program, Task 3, began in July 1994. The project goal is to further develop and demonstrate two of the component technologies of the CFZ-CNG Process: 1) pilot-scale triple-point crystallization of carbon dioxide, producing commercially pure carbon dioxide from contaminated carbon dioxide at the rate of 25 ton/day, and 2) bench-scale modified high pressure Claus technology, recovering elemental sulfur from hydrogen sulfide at the rate of 200 lb/day.

RESULTS AND DISCUSSION

A complete discussion of Base Program results is contained in Task 2 Final Report [5] and Research Plan [6], Contract DE-AC21-92MC29470. Optional program work is ongoing.

Base Program Results

CFZ Process

The Controlled Freeze Zone (CFZ) Process is a cryogenic technology for the separation of carbon dioxide from natural gas by distillation. CFZ is a proprietary process developed and wholly owned by Exxon Production Research Company [7]. The CFZ concept has been successfully demonstrated in a 600 MSCFD pilot plant at Clear Lake, near Houston, Texas [8,9]. CFZ is the most fully developed of the component technologies comprising the CFZ-CNG LCNG Process. As such, further development of Exxon's CFZ process is not a contract objective, and no DOE funds are allocated for that purpose.

Natural gas processing involves the separation and recovery of valuable hydrocarbon components, and the removal of undesirable components such as H_2S, CO_2 and water. Low temperature physical separations, based on turbo-expander and Joule-Thomson (J-T) operations, and direct fractionation are the preferred methods for processing natural gas whenever possible. However, cryogenic fractionation of a gas containing more than about 5% CO_2 can lead to solidification of CO_2 at an intermediate point in a cryogenic demethanizer rendering such tower inoperative [10]. Thus alternative technologies, using solvents or freeze-prevention additives, have been utilized in the past. The CFZ process, in contrast, achieves a direct cryogenic separation of methane and CO_2. In an otherwise conventional distillation tower, solid CO_2 is confined to a special section of the tower, *the CFZ section*, specifically designed to control the formation and melting of solid CO_2.

TPC Process

Acid gas removal from gases with a high CO_2 to H_2S ratio requires the separation of CO_2 and H_2S to produce a CO_2 byproduct or vent stream free of sulfur compounds and a concentrated H_2S Claus feed. Distillation of CO_2 and H_2S to produce a pure CO_2 product is not practical due to the low relative volatility of CO_2 to H_2S and high CO_2 purity requirements at the pure CO_2 end (top) of the distillation column.

The continuous triple point crystallizer separates pure carbon dioxide from a variety of contaminants such as H_2S, COS, CH_3SH and hydrocarbons. The process has been developed and patented by Consolidated Natural Gas Company (CNG Research Company) [11,12,13,14,15,16]. The crystallizer operates at or near the triple point of CO_2. Solid CO_2 crystals are formed by adiabatic flashing at pressures slightly *below* the CO_2 triple point, and melted by adiabatic contact with CO_2 vapor at pressures slightly *above* the CO_2 triple point. No solid CO_2 is formed on heat exchange surfaces by indirect heat exchange; all solid CO_2 is formed and melted by direct contact heat exchange.

Experimental operation of a laboratory crystallizer has demonstrated that a very high

degree of separation can be achieved in a single stage of crystallization. Experimentally measured separation factors, the ratios of contaminant concentrations in the flash zone (solid forming) to the melt zone, are 1000 to 1500 for H_2S and over 3000 for COS [16]. Pure CO_2 containing less than 1 ppm by volume H_2S has been produced by triple point crystallization from contaminated CO_2 mixtures. In this particular low quality natural gas processing application, two stages of triple point crystallization produce pure CO_2 and a concentrated H_2S product.

The triple point crystallizer has been tested extensively in the laboratory at bench-scale (up to 6-inch vessel diameters) [16]. With the laboratory bench-scale equipment continuous runs of up to 72 hours duration were achieved and terminated routinely. A large scale flash vessel (18-inch diameter) built to test rates of solid carbon dioxide production and slurry pumping characteristics was operated in continuous runs of up to 40 hours duration at production rates of 25 tons of solid CO_2 per day [17]. No unusual wear or abrasion on the slurry pump was observed after many tests totaling hundreds of hours. Slurries of 25 wt% solid CO_2 were routinely pumped.

HPSRU Process

A new sulfur recovery process [18] based on the Claus thermal reaction, with no catalytic stages or conventional tailgas cleanup, is made possible by TPC's ability to separate hydrogen sulfide and other contaminants from carbon dioxide. The high pressure sulfur recovery unit (HPSRU) comprises four operations: 1) Claus thermal reaction to convert hydrogen sulfide to sulfur, 2) waste heat exchange and sulfur condensation, 3) hydrogenation of sulfur and SO_2 in the Claus reactor effluent to hydrogen sulfide, and 4) quench and dehydration. All hydrogen sulfide is recycled to the TPC which concentrates acid gases by rejecting carbon dioxide and other inert species such as nitrogen

To recover 99+% sulfur, the conventional Claus plant normally comprises a thermal reactor, several catalytic reactors in series, and a tail gas cleanup unit . As noted by Hyne [19], "more than 50% of the conversion of hydrogen sulfide to elemental sulfur takes place in the front end reaction furnace; (while the) downstream components do no more than convert that part of the sour gas feed stream that is not converted to product sulfur in the front end reaction furnace." The high conversion of hydrogen sulfide to sulfur achieved in the front end reaction furnace is achieved at relatively modest cost -- about 20% of the total Claus plant capital cost. The downstream components, which accomplish roughly 40% of hydrogen sulfide conversion to sulfur, account for about 80% of the capital cost.

The new HPSRU process retains the high recovery/low cost of the Claus thermal reactor, but eliminates the low recovery/high cost catalytic stages and tailgas cleanup unit. Unreacted hydrogen sulfide is recycled to the thermal reactor inlet via the TPC section; this tail gas recycle approach enables essentially 100% sulfur recovery, free of thermodynamic and kinetic limitations imposed by the Claus reaction.

Aside from the Claus thermal reactor, the remaining equipment is more conventional. Concern for corrosion should be limited to the quench tower where liquid water and hydrogen sulfide are present. However, quench towers performing comparable service are presently used in the SCOT and Beavon tail gas cleanup processes. Also, sulfur dioxide, which is much more acidic in aqueous solution than hydrogen sulfide, is not present in the quench tower because of upstream hydrogenation.

Contaminant Absorption with Liquid CO_2

Sulfur contaminants in the HPSRU tail gas, H_2S and COS, are absorbed with pure liquid CO_2 from the TPC. These sulfur contaminants are recycled to the TPC. Liquid CO_2's low molecular weight (44) and high density (1.18 g/cm^3 at -70°F)

provide high absorption capacity per unit volume of solvent. Liquid CO_2's low viscosity (0.25 cp at -70°F) promotes high stage efficiency. Liquid CO_2 absorption of H_2S and COS has been measured experimentally in a pilot absorption unit processing 20 MCFD of gas [16].

Liquid CO_2 is an effective absorbent for removal of contaminants from raw gas streams which contain CO_2. Favorable contaminant equilibrium data has been measured for many compounds which contain sulfur, chlorine, or an aromatic ring structure. Liquid CO_2 absorption efficiently cleans landfill gas because of its high CO_2 content and the many, often unknown, contaminants which are present [20].

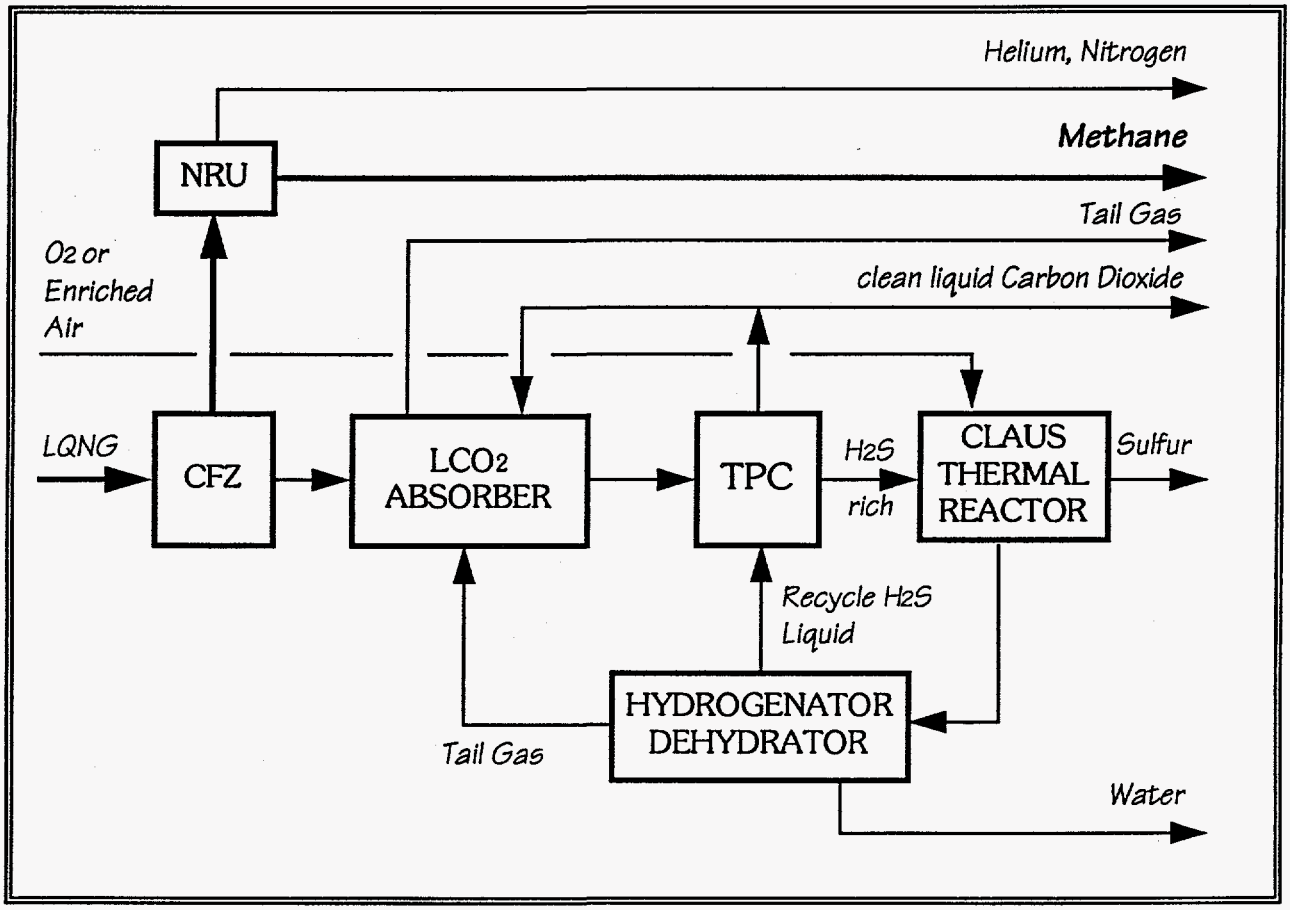

Figure 1. Conceptual CFZ/CNG Claus LQNG Treatment Process

Conceptual CFZ-CNG LQNG Process

The integrated process is shown in Figure 1. After dehydration and cooling the feed gas is sent to the CFZ tower which separates the CH_4 and other light components such as He and N_2 from CO_2, H_2S and other trace heavy components such as COS and C_2H_6. If the CH_4 overhead product contains significant amounts of N_2 it is sent to a cryogenic nitrogen rejection unit (NRU). The CO_2 rich bottoms product is sent to the TPC section of

the process.

The TPC section contains an absorber-stripper which strips out small amounts of CH_4 (approximately 1%) and C_2H_6 carried over in the CFZ bottoms. H_2S in the vent stripping gas is re-absorbed with clean liquid CO_2 from the crystallizer. The vent gas also contains the inert components N_2, argon, and hydrogen brought to the TPC with the HPSRU recycle stream. The stripped CO_2 is sent to the TPC which produces pure CO_2 and a CO_2 stream concentrated in H_2S. Pure CO_2 product can be used for EOR or commodity CO_2 applications. H_2S rich TPC product is further enriched by stripping out CO_2 and is sent to the Claus plant. Tail gas from the HPSRU is returned to the TPC for reconcentration of the unreacted H_2S.

Two feed gas mixtures, each 200 million SCF/day, were studied having CO_2 contents covering a wide range of process applicability. One case is a high CO_2 gas now processed at Exxon's Shute Creek facility near LaBarge, Wyoming. The feed gas for the second case is a lower CO_2 content generic subquality gas. These crude gas streams are more fully described below.

The LaBarge case examines treatment of LQNG produced from the LaBarge field in southwestern Wyoming. The formation is estimated to contain 167 TCF of low Btu raw gas [1]. This crude gas is characterized below in Table 1. The product slate includes methane (pipeline gas), elemental sulfur, helium, and EOR grade carbon dioxide. The CFZ methane product has 50 ppm CO_2 and less than 4 ppm H_2S (¼ grain/SCF). The low CO_2 content of the methane prevents formation of solid CO_2 in the cryogenic NRU. The final methane product specification after nitrogen and helium rejection and recompression is 97% CH_4 at 1000 psia. The EOR-grade liquid CO_2 product, at 2000 psia, contains less than 16 ppm H_2S.

The generic case examines treatment of LQNG with composition shown in Table 1. Product specifications for the generic case include a methane product with 4 ppm H_2S (¼ grain/SCF) and less than 2% CO_2 (0.25% CO_2 is achieved as dictated by the controlling spec on H_2S). In the design of this case, no market was assumed to exist for CO_2. Pipeline methane and a small stream of elemental sulfur are the only salable products produced from this generic subquality gas.

Process economics, evaluated for high and low product price scenarios, were developed on the basis of a breakeven allowance per MSCF of raw gas, i.e., the raw gas cost per MSCF at which plant net revenues become zero. Plant net revenue is positive for raw gas cost below the breakeven allowance, negative above. Breakeven allowances range from 20¢ to $2.14/MSCF of raw gas for low and high product price scenarios, assuming a simple five year capital payout. Capital and operating costs estimated for the conceptual process compare favorably with costs derived for the Selexol process treating low quality LaBarge gas [21]. Comparable breakeven allowances derived for the Selexol process are 8¢ and 73¢.

Optional Program Unit Operation Testing and Demonstration

The Optional Program goal is to further test and demonstrate two of the most technologically advanced component technologies of the CFZ-CNG Process, the pilot-scale carbon dioxide triple-point crystallizer, and the bench-scale modified high pressure Claus reactor.

The triple point crystallizer pilot unit has been constructed by Acrion in Cleveland OH. The unit occupies a space 15' wide by 60' long by 10' high in Acrion's laboratory. The feed to the unit is a contaminated liquid carbon dioxide stream. The unit operates in a total recycle mode with the products, purified liquid CO_2 and contaminant enriched liquid CO_2 being returned as feed. The unit has three stainless steel vessels with diameters of 12 to 18 inches. They are the solid forming vessel or flasher, the solid melting vessel (melter) and a storage vessel for purified liquid CO_2 or boiler. The solid is transported by a slurry pump

from the flasher to the bottom of the melter. Cooling for solid formation is provided by vaporizing a portion of the flasher liquid. This vapor is compressed in a reciprocating compressor, condensed in an aluminum plate fin heat exchanger and recycled to the flasher. On the opposite side of the heat exchanger, liquid from the boiler is vaporized to provide melting gas to the top of the melter. The pilot unit also includes a 3 ton refrigeration system for startup and to compensate for heat leaks in the system.

During a crystallizer test run the pressures, temperatures, levels, mass flows and slurry density are recorded. Contaminant concentrations are measured with a gas chromatograph. Up to now, the crystallizer pilot unit has been operated with contaminants less toxic than H_2S, e.g. propane, acetone and toluene, at contaminant concentrations of from 1 % to 4%(mole%). Carbon dioxide purities 100 to 1000 times greater than the feed liquid have been measured. Most recent efforts have looked at ways of modifying the melter and flasher internals to improve the production rate and operability of the unit.

The modified high pressure Claus reactor consists of a ceramic lined reactor furnace capable of operating at up to 2500F and 100 psig, a waste heat exchanger and a sulfur condenser. Also included are a feed metering system to adjust the acid gas composition (H_2S to CO_2 ratio), acid gas flow, oxygen flow and startup fuel gas flow from the gas cylinders to the reactor and the sampling system to measure the concentrations in the reactor, and the feed and product streams. The reactor will be tested over a range of residence times, acid gas compositions(50% to 90% H_2S), and percentage of stoiciometric oxygen (40% to 90%). Since the reactor is adiabatic, the acid gas composition and percent stoiciometric oxygen determine the reactor temperature (1500 to 2500F). Test data to be measured includes the amount of sulfur produced, the gas composition, pressures and reactor temperature. This will allow determination of the sulfur conversion and the amount of reducing gas (H_2 and CO) available for the hydrogenation of SO_2.

The Claus reactor system is being designed and constructed by Bovar in Houston TX. After initial testing the system will be transported to CNG's Southwest Davis Gas Plant in Davis OK. The reactor system will be connected to the flare at the site for disposal of H_2S. All test runs will be conducted on site.

FUTURE WORK

Operation of the one-stage triple point crystallizer will continue. Test runs will determine the maximum production rate and purity of the CO_2 product. The goal of the TPC demonstration is production at a scale of 25 ton/day.

The HPSRU design is based on an equilibrium model of the thermal reactor. The model has been shown valid for many systems with a similar array of reacting components. Reaction kinetics may have an effect on conversion efficiency, reaction temperature and the extent of side reactions such as hydrogen or carbon monoxide formation. These effects will be quantified by operation of the bench scale high pressure Claus reactor. The HPSRU scale will be 200 lb sulfur/day.

REFERENCES

1. Hugman, R.H., E.H. Vidas, and P.S. Springer, "Chemical Composition of Discovered and Undiscovered Natural Gas in the Lower 48 United States," GRI Contract 5088-222-1745, GRI 90/0248, November, 1990.
2. Meyer, Howard S., Presentation, Chemical Process Research Department, Gas Research Institute, October 3, 1990.
3. Kohl, Arthur, and Fred Riesenfeld, *Gas Purification,* Gulf Publishing Company, Houston, 1974.
4. Rosseau, R.W., et al, "Regeneration of Physical Solvents in Conditioning Gases from Coal," in *Acid and Sour Gas Treating,* Stephen A. Newman, Ed., Gulf Publishing Company, Houston, 1985, p 131.

5. Cook, W. Jeffrey, Marina Neyman, Wm R. Brown, Bruce W. Klint, Larry Kuehn, John O'Connell, Harold Paskall, and Peter Dale "TASK 2 REPORT, Low Quality Natural Gas Sulfur Removal/Recovery," US Department of Energy, Morgantown Energy Technology Center, Contract DE-AC21-92MC29470, August 16, 1993.

6. Siwajek, Lawrence A., Clark C. Turner, Sheldon Asnien, Bruce W. Klint, Larry Kuehn, John O'Connell, Harold Paskall, and Peter Dale, "RESEARCH PLAN, Low Quality Natural Gas Sulfur Removal/Recovery," US Department of Energy, Morgantown Energy Technology Center, Contract DE-AC21-92MC29470, August 16, 1993.

7. Valencia, J. A. and Denton, R. D., "Method and Apparatus for Separating Carbon Dioxide and Other Acid Gases from Methane by the Use of Distillation and a Controlled Freeze Zone", U.S. Patent 4,533,372, August 6, 1985.

8. Victory D. J., and J. A. Valencia, "The CFZ Process: Direct Methane-Carbon Dioxide Factionation," *Hydrocarbon Processing,* 66 (5) 1987.

9. Haut, R. C., et. al., "Development and Application of the Controlled Freeze Zone Process," SPE Production Engineering, p 265, August 1989.

10. Donnelly, H. G. and Katz, D. L., "Phase Equilibria in the Carbon Dioxide - Methane System", *Ind & Eng Chem,* Vol. 46, No. 3, p. 511, March 1954.

11. Brown, W.R., et al, "Gas Separation Process," U.S. Patent 4,270,937, June 2, 1981.

12. Brown, W.R., et al, "Gas Separation Process," U.S. Patent 4,581,052, April 8, 1986.

13. Brown, W.R., et al, "Gas Separation Process," U.S. Patent 4,609,388, September 2, 1986.

14. Brown, W.R., Cook, W.J., et al, "Crystallization Process," U.S. Patent 4,623,372, November 18, 1986.

15. Brown, W.R., et al, "Triple-Point Crystallization Separates and Concentrates Acid Gases," presented at AIChE Spring National Meeting, March 27-31, 1983, Houston, Texas.

16. Siwajek, L.A., et al, "CNG Acid Gas Removal Process," Final Technical Report, US Department of Energy, Morgantown Energy Technology Center, Contract DE-AC21-83MC20230, July, 1986.

17. Siwajek, L.A., Brown, W.R., et. al., "CNG Gas Separation Process," Final Technical Report, Gas Research Institute Contract 5086-222-1429, September 1988.

18. Hise, Ralph E., and Jeffrey Cook, "Sulfur Recovery Process," US Patent 5,021,232, June 4, 1991.

19. Hyne, J.B., "Design and Chemistry of Front End Reaction Furnaces," *Canadian Gas Journal,* March-April 1972, pp 12-16.

20. Siwajek, Lawrence. A., Clark C. Turner, W. Jeffrey Cook, and William R. Brown, "Landfill Gas Recovery for Compressed Natural Gas Vehicles and Food Grade Carbon Dioxide," SBIR Phase I Final Report, Contract No DE-FG02-91ER81223, May 4, 1992.

21. Johnson, John E., and Arthur C. Homme, Jr., "Selexol Solvent Process Reduces Lean, High-CO2 Natural Gas Treating Costs," Paper 65c, AIChE 1983 Summer National Meeting, Denver, August 29, 1983.

Table 1. Gas Compositions and Process Conditions

	Case 1: LaBarge		Case 2: Generic	
Specie:	mol%	lb mol/hr	mol%	lb mol/hr
CH_4	20.50	4,494	80.50	17,679
CO_2	66.50	14,578	19.00	4,172
H_2S	5.00	1,096	0.50	110
N_2	7.35	1,644		
COS	0.05	10		
C_2H_6	0.01	2		
He	0.60	132		
TOTAL	100.00	21,956	100.00	21,961
Pressure	1,060 psia		715 psia	
Temperature	60°F		90°F	
Gas Flow	200 MMSCF/day		200 MMSCF/day	
Water	10 lb/MMSCF		75 lb/MMSCF	
Claus Plant	High Pressure Oxygen		High Pressure Oxygen	
Oxygen	90% O_2 210 Ton/day		90% O_2 21 Ton/day	
EOR CO_2	16 ppm H_2S 2,000 psia		None	
Methane	50 ppm CO_2 undetectable H_2S 40 MMSCFD		0.25% CO_2 4 ppm H_2S 160 MMSCFD	
Sulfur	375 LT/day 99.9% recovery		38 LT/day 99.9% recovery	
CO_2 Vent	16 ppm H_2S 13 Ton H_2S/yr		16 ppm H_2S 8.5 Ton H_2S/yr	

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