Low Quality Natural Gas
Sulfur Removal and Recovery
CNG Claus Sulfur Recovery Process

Pilot Plant Test Program

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1.0 Introduction

Increased use of natural gas (methane) in the domestic energy market will force the development of large non-producing gas reserves now considered to be low quality. Large reserves of low quality natural gas (LQNG) contaminated with hydrogen sulfide (H_2S), carbon dioxide (CO_2) and nitrogen (N_2) are available but not suitable for treatment using current conventional gas treating methods due to economic and environmental constraints.

A group of three technologies have been integrated to allow for processing of these LQNG reserves; the Controlled Freeze Zone (CFZ) process for hydrocarbon / acid gas separation; the Triple Point Crystallizer (TPC) process for H_2S / CO_2 separation and the CNG Claus process for recovery of elemental sulfur from H_2S. The combined CFZ/TPC/CNG Claus group of processes is one program aimed at developing an alternative gas treating technology which is both economically and environmentally suitable for developing these low quality natural gas reserves.

The CFZ/TPC/CNG Claus process is capable of treating low quality natural gas containing >10% CO_2 and measurable levels of H_2S and N_2 to pipeline specifications. The integrated CFZ / CNG Claus Process or the stand-alone CNG Claus Process has a number of attractive features for treating LQNG. The processes are capable of treating raw gas with a variety of trace contaminant components. The processes can also accommodate large changes in raw gas composition and flow rates. The combined processes are capable of achieving virtually undetectable levels of H_2S and significantly less than 2% CO_2 in the product methane.

The separation processes operate at pressure and deliver a high pressure (ca. 100 psia) acid gas (H_2S) stream for processing in the CNG Claus unit. This allows for substantial reductions in plant vessel size as compared to conventional Claus / Tail gas treating technologies. A close integration of the components of the CNG Claus process also allow for use of the methane/H_2S separation unit as a Claus tail gas treating unit by recycling the CNG Claus tail gas stream. This allows for virtually 100 percent sulfur recovery efficiency (virtually zero SO_2 emissions) by recycling the sulfur laden tail gas to extinction. The use of the tail gas recycle scheme also de-emphasizes the conventional requirement in Claus units to have high unit conversion efficiency and thereby make the operation much less affected by process upsets and feed gas composition changes.

The development of these technologies has been ongoing for many years and both the CFZ and the TPC processes have been demonstrated at large pilot plant scales. On the other hand, prior to this project, the CNG Claus process had not been proven at any scale. Therefore, the primary objective of this portion of the program was to design, build and operate a pilot scale CNG Claus unit and demonstrate the required fundamental reaction chemistry and also demonstrate the viability of a reasonably sized working unit.

2.0 CNG Claus Program Objective

In the initial phases of this program, the technical viability of the CNG Claus process was evaluated with respect to two fundamental questions:

1. Would the required reaction chemistry (shown below) proceed to an acceptable level (in terms of unit sulfur conversion) under the unique operating conditions required by the process.

$$2\ H_2S + O_2 \leftrightarrows S_2 + 2\ H_2O$$
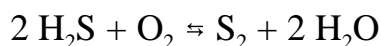
2. Can a pilot plant be successfully designed, built and operated under these unique conditions.

During this phase of the program it was determined through reaction modeling systems that the H_2S oxidation reaction should successfully proceed with an adequate yield to sulfur under the desired operating conditions. Also, through review of existing Claus recovery technology and equipment specification, it was determined that an operating unit could be designed and built successfully. It was determined that much of the commercially proven hardware components used in a conventional Claus plant would have equal applicability to the unique CNG Claus operating conditions.

Therefore, the primary objective of this portion of the program was to design, build and operate a pilot scale CNG Claus unit and demonstrate the required fundamental reaction chemistry and also demonstrate the operational viability of a reasonably sized working unit.

Specific Program Objectives

The pilot plant phase of the program was designed to realize the following specific objectives:

1. Design and construct a viable pilot scale unit.

2. Demonstrate the operation of the unit under the unique CNG Claus conditions in order to verify the applicability of the physical pilot plant unit.

3. Demonstrate the operation of the unit under the unique CNG Claus conditions in order to verify the desired reaction chemistry.

4. Identify technical barriers to the design and operation of a commercial CNG Claus sulfur recovery unit.

3.0 CNG Claus Process and Pilot Plant Overview

The pilot plant was designed to demonstrate the successful operation of the most critical portion of the CNG Claus unit; the Free Flame Reaction Furnace (RF). It is in this unit that the H_2S and O_2 react vigorously to produce the desired product, elemental sulfur and other reaction by-products. The subsequent treating of the reaction by-products would be completed using conventional tail gas treating technology. Since all components of the tail gas treating technology have been in wide commercial use for many years, these components were not included in the CNG Claus pilot plant unit.

3.1 CNG Claus Process Description

The CNG Claus process is based on a single stage, free flame reactor system. In this unit the acid gas feed is combusted with an oxygen bearing stream (ambient air or high concentration O_2 stream as required) in a reaction furnace unit. This will result in the direct oxidation and conversion of H_2S to elemental sulfur. The elemental sulfur is then recovered via condensation in a conventional shell and tube heat exchange condenser unit. The CNG Claus tail gas is processed in a conventional catalytic hydrogenation reactor in order to react all remaining sulfur compounds back to H_2S. This stream is then further treated to cool the process gas and remove most of the residual water in a direct contact water contactor and a conventional dehydration unit.

The cooled, dehydrated tail gas is then re-compressed to be recycled to the TPC system. The full process flow diagram is given in Figure 3.1. The primary operating units, their functions and the most important unit details are as follows:

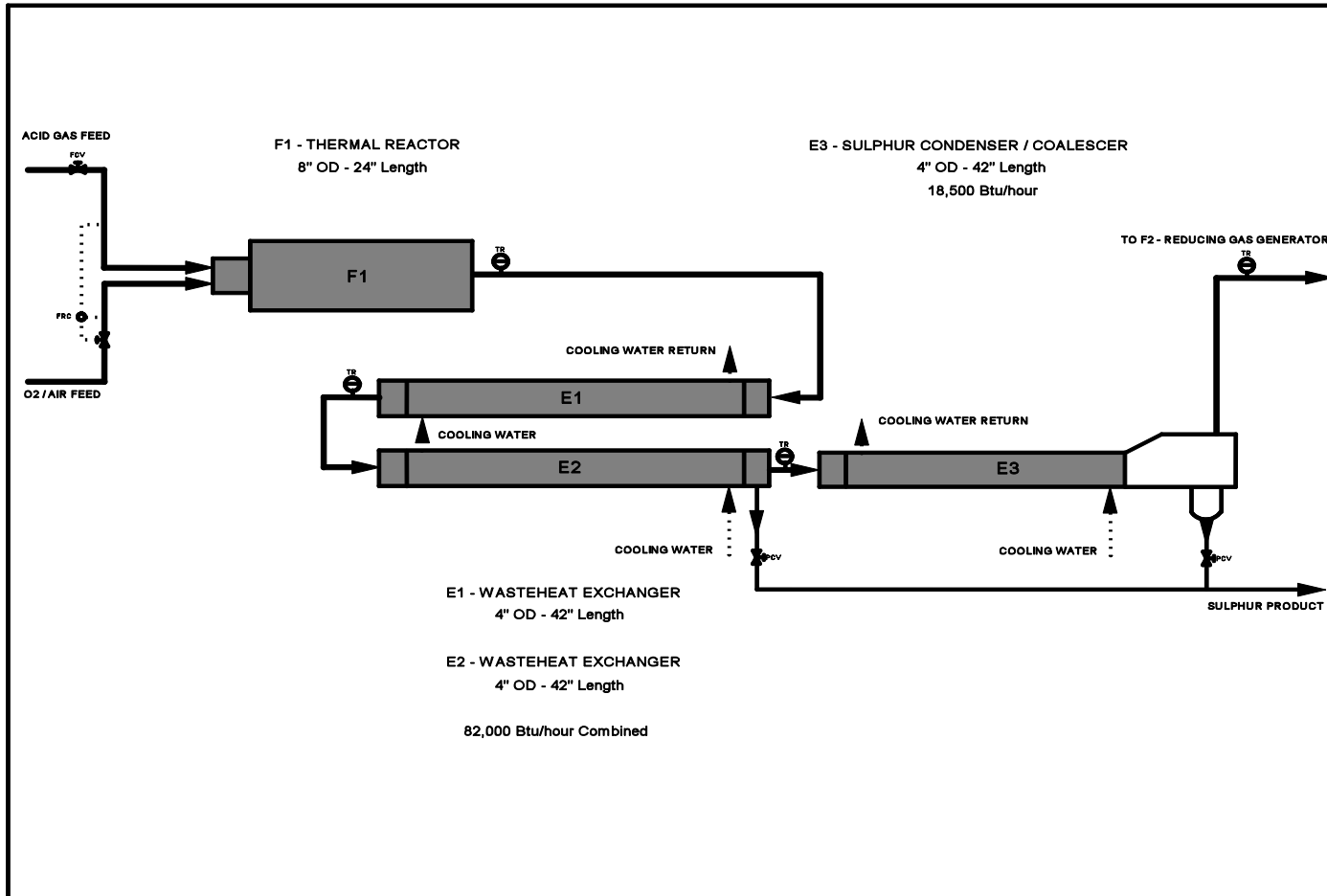**3.1.1 Sulfur Recovery Section**

Reaction Furnace

The H_2S oxidation reaction will occur in a free flame, single phase reactor modeled after a conventional modified Claus reaction furnace. In order to integrate efficiently with the upstream TPC separation unit several novel operation conditions have been proposed for the reaction furnace.

1. Oxygen Composition - In order to minimize the flow of unwanted inert components it is proposed to use a highly enriched air stream as the oxidant in the reaction furnace. For the purpose of the pilot plant design a 90 percent oxygen stream will be used.

2. Reaction Stoichiometry - A traditional modified Claus system calls for a 1/3 oxidation of the H_2S to SO_2. This product SO_2 then reacts with the remaining H_2S to form elemental sulfur. In a traditional modified Claus free flame reactor the typical unit conversion (yield) efficiency is 65 to 75 percent.

Figure 3.1

High Pressure SRU - Process Flow Diagram

ACID GAS FEED

FCV

F1 - THERMAL REACTOR
8" OD - 24" Length

E3 - SULPHUR CONDENSER / COALESCER
4" OD - 42" Length
18,500 Btu/hour

TO F2 - REDUCING GAS GENERATOR

TR

F1

TR

FRC

O2 / AIR FEED

COOLING WATER RETURN

TR

E1

COOLING WATER

COOLING WATER RETURN

TR

E2

TR

E3

COOLING WATER

PCV

COOLING WATER

PCV

E1 - WASTEHEAT EXCHANGER
4" OD - 42" Length

SULPHUR PRODUCT

E2 - WASTEHEAT EXCHANGER
4" OD - 42" Length

82,000 Btu/hour Combined

Figure 3.1

High Pressure SRU - Process Flow Diagram

F2 - REDUCING GAS GENERATOR

R1 - HYDROGENATION REACTOR
8" OD - 16" Height

V1 - WATER QUENCH TOWER
8" OD - 16" Height

FUEL GAS FEED

TRC

F2

FRC

O2 / AIR FEED

TR

TR

TR

TR

TREATED GAS

COOLING WATER

COOLING WATER RETURN

TR

COOLING WATER RETURN

E4

TR

COOLING WATER

E4 - WASTEHEAT EXCHANGER

4" OD - 42" Length

13,200 Btu/hour

For the CNG Claus system there is a need to minimize the SO_2 production and to control the potentially high reaction temperatures resulting from the use of enriched air as the oxidant. Therefore, it is proposed to operate the CNG Claus reaction furnace with a significantly lower reaction stoichiometry. For the design case an oxygen deficient operation of approximately 50 percent was used. This resulted in a decline in the predicted unit conversion efficiency to 50 percent and a predicted reaction temperature less than 2000°F. This also resulted in an SO_2 concentration of approximately 1.0 mole percent which is appropriate for the subsequent treating in the hydrogenation reactor

Wasteheat Exchanger

The partial oxidation of the H_2S in the reaction furnace is an extremely exothermic reaction which results in a very large energy release and high process temperatures in the reaction furnace. In order to recover the produced elemental sulfur it is necessary to cool the process gas significantly. This also allows the opportunity to recover a large amount of high quality energy usually in the form of high pressure steam.

The wasteheat exchanger is used to remove the bulk of that energy and cool the process gas to a lower intermediate temperature. This unit is a conventional shell and tube thermosyphon or kettle type boiler which will produce high pressure (600 psia) steam.

Sulfur Condenser / Collection Vessel

The sulfur condenser is used to further cool the process stream to a temperature (300°F) where essentially all of the sulfur vapor is condensed to liquid. The sulfur condenser heat exchanger has a traditional shell and tube configuration with the process gas on the tube side. This unit will also recover a significant amount of waste heat by producing steam.

The sulfur condenser vessel is equipped with a disengagement section on the outlet end in order to allow for efficient separation of the liquid sulfur from the process gas. A collection vessel equipped with continuous level control is used to store and remove the product sulfur from the process. This is effectively the final step in the true sulfur recovery portion of the plant. All of the subsequent units are used to treat the sulfur plant tail gas for recycle back to the TPC process.

3.1.2 Tail Gas Treating Section

In order to allow for a 100 percent recycle of the tail gas stream to the TPC system, it will be necessary to further treat the CNG Claus tail gas. The tail gas stream must meet some critical guidelines in terms of stream content to allow efficient processing in the TPC.

1. SO_2 Content - The SO_2 content in the tail gas must be essentially zero so that it does not react with H_2S to form sulfur in the TPC or its auxiliary systems.

2. Water Content - The tail gas must be dried to a very low dewpoint temperature to ensure that water does not freeze in the TPC system.

3. Process pressure - In order to return the treated tail gas to the TPC it will be necessary to re-compress back up to 100 psia.

The tail gas treating section is designed to perform the following specific process steps :

1. Heat the process gas and introduce reducing compounds into the process.
2. React all of the non-H_2S sulfur components back to H_2S via various reduction reactions.
3. Cool and remove the excess water.
4. Re-compress the cold, water free process gas which is primarily H_2S and CO_2 for recycle to the TPC separation process.

All of these functions are performed in units which have been used extensively in existing gas treating processes. Therefore, the design philosophy in general is based completely on existing technology.
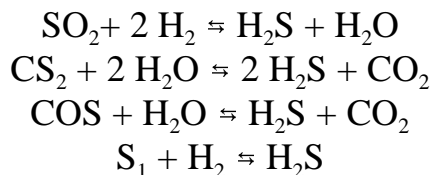

Reducing Gas Generator

This unit performs two functions simultaneously ; heating the process gas and introducing reducing compounds (H_2 and CO) into the process stream. The primary process unit is the reducing gas generator which is a direct fired hydrocarbon fuel gas burner. The burn products from this burner are mixed directly with the process gas to raise the process temperature to the desired value.

This burner system utilizes a controlled oxygen source (enriched air) and the burn stoichiometry is controlled such that the burner is 10 to 25 percent deficient in oxygen. This has the result of producing significant amounts of H_2 and CO which are needed in the subsequent processing step. The base design calls for a typical mixed outlet temperature of $500^\circ F$.

Hydrogenation / Hydrolysis Reactor

The next tail gas treating step is to convert all of the SO_2, COS, CS_2 and sulfur vapor to H_2S. This is completed in a fixed bed reactor over a cobalt - molybdenum catalyst. The main reactions which occur in this converter are :

$$SO_2 + 2\,H_2 \leftrightharpoons H_2S + H_2O$$
$$CS_2 + 2\,H_2O \leftrightharpoons 2\,H_2S + CO_2$$
$$COS + H_2O \leftrightharpoons H_2S + CO_2$$
$$S_1 + H_2 \leftrightharpoons H_2S$$

This reaction process system is utilized extensively in existing gas treating technology and all of these reactions go essentially to completion to ensure no SO_2. COS, CS_2 or S residual in the reactor effluent. The typical reaction temperature in this system is 650 to 750ºF.

Hydrogenation Reactor Cooler

In order to meet the water specification for the recycle stream it is necessary to remove all of the process water. As a preliminary step in the water removal process, the tail gas is cooled significantly from the 700ºF+ hydrogenation reactor temperature to approximately 300ºF. The initial cooling step is performed by a standard shell and tube heat exchanger with the process gas on the tube side. In a conventional design it is convenient to remove the excess energy in the form of steam.

Direct Water Quench / Water Removal

The first step in the water removal process is a direct contact water quench tower. In this unit the cooled tail gas is contacted directly with cooling water. The quench tower overhead gas is effectively cooled to 100ºF and the water content is dropped to the saturated value at that temperature. A typical water content of the quench overhead gas is 2 to 5 percent as compared to 25 to 35 percent in the inlet. This process produces a substantial mass of excess water which has a small sour component. This "sour water" must undergo additional treatment in order to allow for safe disposal. The sour water treatment system is described in a later section.

Tail Gas Dehydration

The final dehydration process must ensure that the water content in the recycled tail gas does not exceed 30 ppmv which translates to a -50ºF water dewpoint temperature. This step is completed in a dedicated molecular sieve dehydration system of conventional design.

Tail Gas Recompression

It is expected that the sulfur recovery and tail gas treatment processes will result in a system pressure loss between 5 and 10 psi. Therefore, the treated tail gas must be re-compressed to allow re-introduction back into the upstream TPC process. Based on the expected operating conditions of the system, the recompression ratio in this unit will have to be approximately 1.1 to 1.

3.2 Pilot Plant Description

The original design concept of the CNG Claus sulfur recovery process is based extensively on existing conventional Claus technology. However, the operating conditions will be substantially different from conventional Claus operations in the following areas :

1. Oxygen source - The primary oxygen source will be a highly O_2 enriched air stream in order to minimize the total process gas volume.

2. Reaction stoichiometry - The reaction will be completed with an oxygen flow of approximately 50 percent of the flow in a conventional Claus plant. This will ensure more moderate reaction temperatures and a low formation rate of SO_2.

3. Operating pressure - The normal operating pressure will be 100 psia as compared to a conventional Claus plant which operates at 20 to 25 psia.
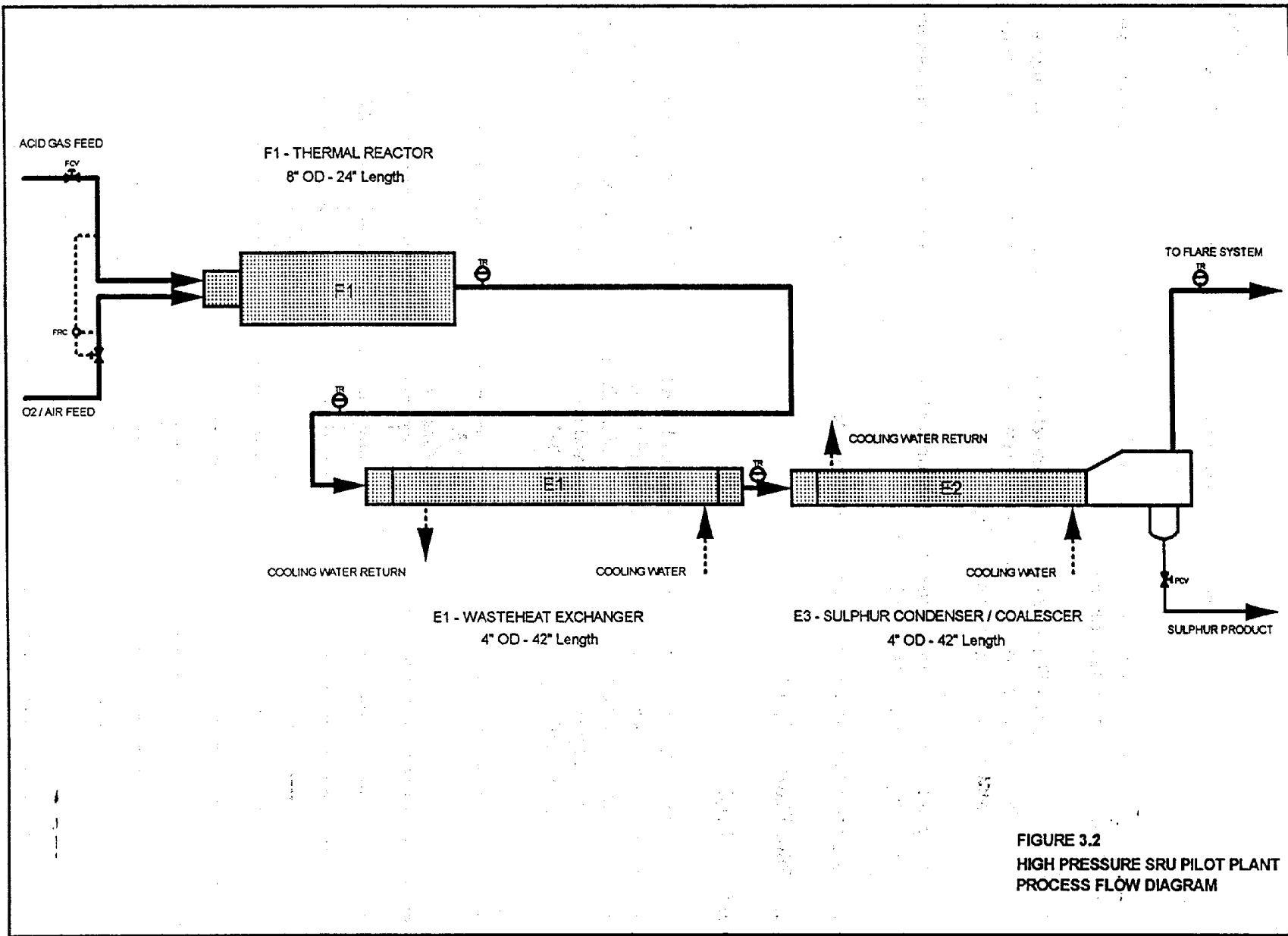
Figure 3.2 shows the process flow diagram for the CNG Claus pilot plant.

3.2.1 Pilot Plant Design Basis

Acid Gas Feed

Table 3.1 summarizes one of the typical acid gas and combustion "air" stream data cases. The acid gas composition was based on a preliminary estimated composition from the specified low quality raw gas stream. The "air" composition was chosen as typical for an enriched air stream from a pressure-swing O_2 enrichment plant. This acid gas flow rate and the target 50 percent unit recovery efficiency will result in a total sulfur production rate of 10.0 lb/h.

Table 3.1 Base Case Feed Gas Conditions			
		Acid Gas	Oxygen
Temperature	(°F)	50.0	50.0
Pressure	(psia)	100.0	100.0
Total Flow	(lbmol/h)	0.891	---
Composition	(mole %)		
	H_2S	69.7	
	CO_2	30.0	
	COS	0.3	
	O_2		90.00
	N_2		10.00

ACID GAS FEED

FCV

F1 - THERMAL REACTOR
8" OD - 24" Length

FRC

O2 / AIR FEED

F1

TR

TR

TO FLARE SYSTEM

TR

E1

TR

COOLING WATER RETURN

E2

COOLING WATER RETURN

COOLING WATER

COOLING WATER

FCV

E1 - WASTEHEAT EXCHANGER
4" OD - 42" Length

E3 - SULPHUR CONDENSER / COALESCER
4" OD - 42" Length

SULPHUR PRODUCT

FIGURE 3.2
HIGH PRESSURE SRU PILOT PLANT
PROCESS FLOW DIAGRAM

Reaction Furnace Operation

The reaction furnace operation has been devised to allow for stable operation while meeting the following criteria to ensure that a conventional furnace design (metallurgy etc) is adequate and that the downstream tail gas treating section can adequately handle the hydrogenation of SO_2 in a conventional manner.

1. The adiabatic reaction temperature must be maintained at or below 2500°F.
2. The overall conversion efficiency must be maintained at 50+ percent.
3. The SO_2 in the furnace outlet must be maintained at less than 2.0 mole percent.

These criteria are met by operating the furnace with a reaction stoichiometry significantly less than in conventional plants. Normally the H_2S to O_2 flow ratio is maintained at approximately 2 to 1. In the CNG Claus design an H_2S to O_2 flow ratio of approximately 4 to 1 is maintained. A full heat and material balance for the base pilot plant case is shown in Table 3.2. Under the original pilot plant base case operating conditions the adiabatic reaction furnace temperature is 1780°F. The SO_2 concentration in the furnace outlet is 1.0 mole percent and the conversion efficiency is 50.04 percent.

STREAM	Acid Gas	Oxygen	RF Outlet	WHE Outlet	Condenser Outlet
Table 3.2 — **Pilot Plant Material Balance**					
Temperature (°F)	50.0	50.0	1780.2	800.0	275.0
Pressure (psia)	100.0	100.0	99.0	98.5	98.0
Total Flow (lbmol/h)	0.8911	0.1654	1.0698	0.9629	0.9168
Composition (mole fraction)					
H_2			0.0175	0.0194	0.0204
Ar					
O_2		0.9000			
N_2		0.1000	0.0155	0.0172	0.0180
CH_4					
CO			0.0217	0.0242	0.0254
CO_2	0.3000		0.2281	0.2534	0.2661
H_2S	0.6970		0.2800	0.3111	0.3268
COS	0.0030		0.0024	0.0027	0.0028
SO_2			0.0086	0.0095	0.0100
CS_2			0.0001	0.0001	0.0002
H_2O			0.2830	0.3145	0.3303
S_{vapour} (as S_x)			0.1431	0.0479	trace
S_{liquid} as S_1 (lbmol/h)					0.3119
S_x number			2.040	6.768	7.537

**Sulfur Production and Collection**

In order to collect the elemental sulfur which is produced in the reaction furnace, it is necessary to condense the sulfur to the liquid phase and then complete a liquid separation from the main gas process stream. The process temperature needed to efficiently condense the elemental sulfur is approximately 300ºF. The cooling of the process gas is completed in two stages; the first stage cools the gas to approximately 800ºF (no sulfur condensation) and the second stage cools the process gas and condenses the elemental sulfur.

This heat exchange configuration is chosen to allow for efficient recovery of the high quality energy which is present in the process gas stream and matches the proposed heat exchange system for a commercial scale plant closely. This configuration also allows for condensation of the elemental sulfur only in the final cooling stage. The second process gas heat exchanger or sulfur condenser is designed to allow for efficient separation of the liquid sulfur from the process gas stream. The elemental sulfur is removed from the condenser at pressure and collected in a dedicated collection vessel. In the pilot plant design this vessel will be arranged to allow for collection of the total sulfur volume anticipated for a full test run.

4.0 Test Results - Data, Analysis and Methods

4.1 Experimental Test Plan

The fundamental question that must be answered by the experimental program is whether the Claus H_2S oxidation reactions will proceed to a sufficient degree under the proposed operating conditions. It is well known from the operation of conventional Claus Process Reaction Furnaces, at or near one atmosphere of pressure (15 psia), that one-third of the H_2S can be oxidized within 1 to 2 seconds at temperatures above 1700°F. It is also known that although all the O_2 is consumed in these Reaction Furnaces, the equilibrium yield of sulfur is not always achieved, particularly at the lower temperatures. That is, the reaction,

$$2\,H_2S + O_2 \leftrightharpoons S_2 + H_2O$$
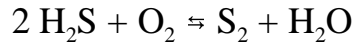
is often kinetically limited.

Since the proposed strategy for the CNG Claus is to oxidize only one-sixth of the H_2S at a higher system pressure (*ca.* 100 psia or 6 atmospheres) and a lower temperature (*ca.* 1500 to 2000°F) the first series of experiments is designed to determine if, indeed, the proposed strategy is practicable.

Critical Operating Variables

The critical operating parameters are related to two well-defined concepts; the chemical equilibria of the reaction system and the kinetic effects of the mechanical system. For test pilot plant test program it will be necessary to determine the impact of these parameters on the key reaction.

Chemical Equilibrium

The chemical equilibrium of the reaction system is affected and determined by :

- reaction pressure.
- reaction temperature.
- reactant composition.

The reaction pressure will be determined largely by the system pressure as defined in the process design. While it may be possible to determine the effect of reaction pressure on the reaction equilibrium, this parameter has not been identified as critical to the successful operation of the process.

The pilot plant has been designed for adiabatic operation in the thermal reactor. Therefore the reaction temperature will be set by the reactant composition and the extent of reaction of those reactants. This leaves the reactant composition as the most significant process variable and will be the focus of the pilot plant test plan. The following section discusses the composition variables which will be evaluated and presents the results from an array of simulated reaction runs which were completed using an equilibrium model based on a Gibbs free energy calculation technique.

Reaction Simulation Results

The work completed in the technical feasibility section was also used to evaluate the appropriate test variable matrix for the pilot plant tests. Those simulation results have been supplemented simulations which further define the range of potential reactant compositions.

The most significant reactant components are H_2S and O_2. There will also be CO_2 and N_2 in the feed gas which may have an effect on the reaction equilibrium. Table 4.1 on the following page summarizes an extensive set of equilibrium calculations completed for a range of inlet reactant compositions. This simulation matrix encompasses the full range of values expected for the acid gas and air compositions for the experimental test runs.

Mechanical Kinetic Effects

The reaction equilibrium can be significantly affected by kinetic effects in the thermal reactor. The kinetics of the reaction system can be affected by the following physical conditions :

- reaction residence time.
- reaction temperature.
- extent of mixing in the reaction section.

It is expected that the kinetic effects could have a measurable impact on the outcome of the reaction. It is expected that the effect of some kinetic limitation on the H_2S oxidation will not significantly affect the overall feasibility of the process, however, the test plan will include some studies to determine the potential effect of kinetics on the Claus reaction at the new operating conditions.

The reaction furnace design allows for a maximum residence time of 4 seconds (actual) which is significantly longer than in conventional Claus furnace design. The design also allows for decreasing the residence time substantially by altering the reaction volume. This will allow for some determination of the impact of residence time on the overall reaction. The mixing characteristics of the burner will be constant for all of the tests, therefore it will not be possible to determine the potential effects of mixing and turbulence on the reaction.

Acid Gas Composition H_2S (mole %)	Air Composition O_2 (mole %)	H_2S / O_2 Flow Ratio	H_2S Equilibrium Conversion	Reaction Temperature (ºF)	SO_2 Residual (mole %)
50	50	2.28	64.93	1987	4.03
50	50	2.92	58.59	1710	1.97
50	50	4.14	44.31	1382	0.77
50	90	2.36	65.57	2070	4.57
50	90	3	59.18	1776	2.13
50	90	4.19	44.57	1432	0.8
70	50	2.4	68.89	2335	4.51
70	50	3.1	62.22	2009	1.99
70	50	4.38	46.25	1649	0.66
70	90	2.51	69.59	2454	5.26
70	90	3.22	62.74	2091	2.21
70	90	4.49	46.5	1708	0.69
90	50	2.45	72.61	2714	4.62
90	50	3.21	65.21	2305	1.83
90	50	4.59	47.43	1883	0.53
90	90	2.58	73.68	2905	5.44
90	90	3.36	65.89	2424	2.02
90	90	4.74	47.72	1956	0.55

**Table 4.1
Experimental Test Plan - Simulation Summary**

Base Case Test Conditions

The pilot unit will be started up using sufficient O_2 to oxidize between one-third and one-half of the H_2S with a target residence time in the Thermal Reactor of 2 seconds. The temperature will be monitored to ensure that the Thermal Reactor does not become overheated. If necessary, the flow rates of the Acid Gas and O_2/Air Feeds, and/or their ratio, will be adjusted to prevent overheating. When stable operation is achieved, a routine sample set will be taken and analyzed to confirm the performance of the Thermal Reactor.

Once the operability of the pilot unit is established, the ratio of O_2/Air Feed to Acid Gas Feed will be adjusted, step wise, towards oxidation of one-sixth of the H_2S while monitoring the temperature and maintaining the residence time in the Thermal Reactor between 2 and 3 seconds. At each step, the unit will be allowed to stabilize (between 20 to 30 minutes should be sufficient since there is no catalyst present) as indicated by stable Thermal Reactor temperature(s) and a routine sample set will be taken and analyzed. When the target of one-sixth oxidation of the H_2S is reached (increasing the residence time if necessary), triplicate routine sample sets will be taken.

In addition, for each routine sample set, a set of quenched samples will be taken and analyzed. The analytical data from the routine sample set will be used to evaluate overall performance while the analytical data from the quenched samples set will be used for comparison with equilibrium-calculation results to determine the degree of approach to equilibrium in the Thermal Reactor.

Residence Time and Extent of Oxidation

Assuming that the feasibility and practicability of the fundamental operating strategy are established by the foregoing, the operation of the pilot unit will be characterized by the following series of tests.

a. Holding the O_2/Air to Acid Gas Feed ratio constant at one-sixth oxidation of the H_2S, the residence time in the Thermal Reactor will be varied from 1 to 4 seconds in one-second steps. Routine sample sets and quenched samples sets will be taken and analyzed at each step.

b. Holding the residence time constant at the value indicated by the foregoing as sufficient to reach equilibrium, the O_2/Air to Acid Gas Feed ratio will be reduced step wise to determine the practical lower limit of operation as indicated by analytical results, the Thermal Reactor temperature and stability of operation. Routine sample sets and quenched samples sets will be taken and analyzed at each step.

Feed Gas Compositions

Within the range of variation described above, tests will be carried out at the maximum and minimum attainable CO_2/H_2S ratios for the Acid Gas and the maximum and minimum attainable O_2/N_2 ratios for the O_2/Air Feed Streams. For these tests, the O_2/Air to Acid Gas ratio will be for one-sixth oxidation of the H_2S and the residence time in the Thermal Reactor will be that which in prior tests achieved the closest approach to equilibrium. Both a routine sample set and a quenched samples set will be taken and analyzed for each condition.

4.2 Test Results

Table 4.2 summarizes the set of operating conditions achieved for the initial successful test runs. These tests were conducted with a rich (90% H_2S) acid gas stream and normal ambient air for the combustion air source. The system pressure was varied between 14 and 40 psig during the test set and the full range of desired reaction stoichiometries was achieved.

Test	Acid Gas H_2S (mole %)	Acid Gas Flow (lbmol/h)	Combustion Air O_2 (mole %)	Combustion Air Flow (lbmol/h)	Furnace Pressure (psig)
1	89.45	0.583	20.81	0.851	14.3
2	89.40	0.695	20.81	1.192	17.0
3	89.40	0.600	20.81	0.597	40.0
4	89.40	0.600	20.81	0.679	40.0

Table 4.2
Pilot Plant Test Conditions

The results from these tests are summarized in Table 4.3 below and the full analytical results are presented in Appendix A. In general, the test run results matched the results generated with the equilibrium reaction model. Figure 4.1 shows the measured sulfur conversion in the reaction furnace as a function of reaction stoichiometry (excess air). Excess air is the measure of the deviation from the exact reaction stoichiometry required for full oxidation of H_2S to elemental sulfur (0% excess air). These results indicated an excellent match to the thermodynamic equilibrium data and indicated that a conversion efficiency in the 50% range can be maintained at very low reaction stoichiometries.

Table 4.3
Pilot Plant Test Results

Test	Acid Gas H_2S (mole %)	Combustion Air O_2 (mole %)	Excess Air (%)	H_2S Conversion (%)	SO_2 Residual (mole %)	Temperature Meas. / Theo ($^\circ$F)
Results Based on Furnace Samples						
1	89.40	20.81	-30.1	67.55	0.14	1770 / 1888
3	89.40	20.81	-49.2	49.70	0.14	1620 / 1702
4	89.40	20.81	-53.7	42.16	0.61	1618 / 1627
Results Based on Condenser Samples						
2	89.40	20.81	-21.3	65.17	1.48	1873 / 2127
1	89.45	20.81	-33.4	61.64	0.59	1770 / 1946
3	89.40	20.81	-48.9	47.65	0.34	1620 / 1764
4	89.40	20.81	-55.2	43.72	0.12	1618 / 1652

Figure 4.1
Reaction Furnace Evaluation
Sulfur Conversion vs. Reaction Stoichiometry
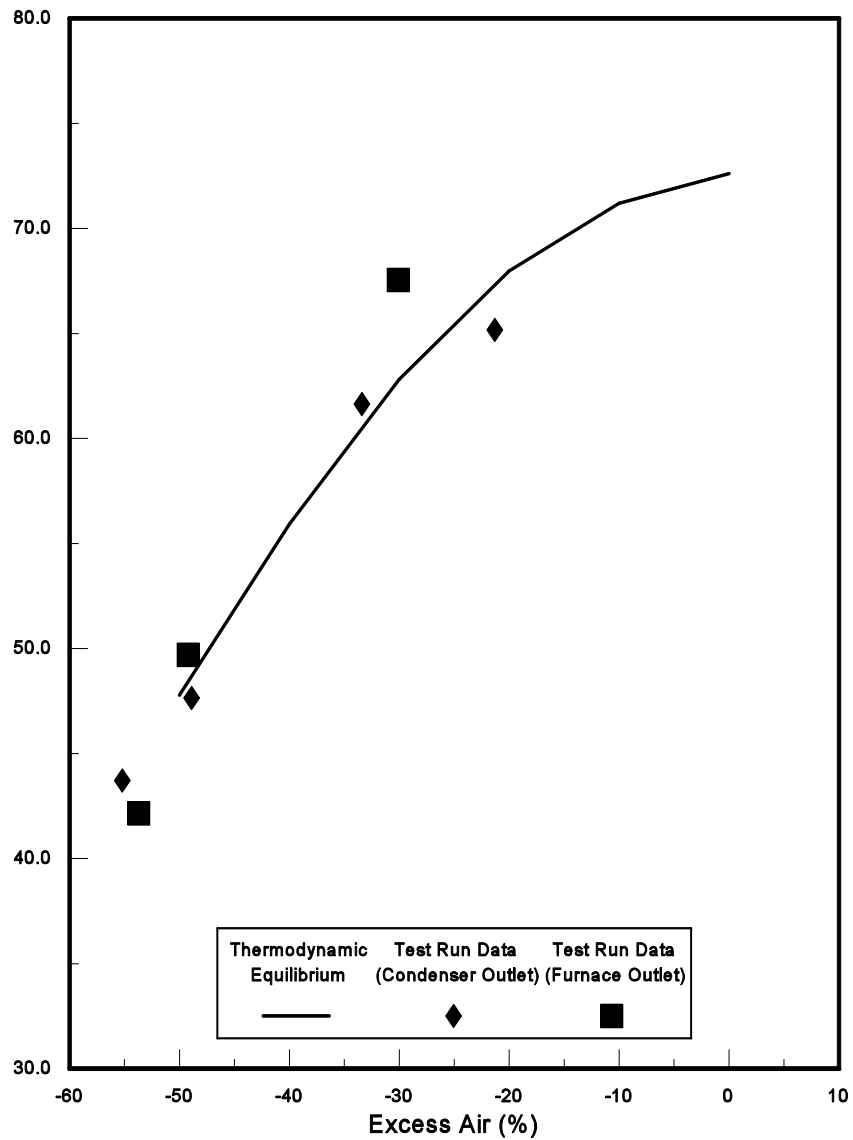
Notes :
1. Ambient air test set.
2. Thermodynamic equilibrium calculations completed using Sulsim(TM)

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Figure 4.2 shows the effect of reaction stoichiometry on the reaction furnace temperature. In this case there was a reasonable match between the actual and predicted value with the measured values generally lower than the predicted values. This can be attributed to heat losses from the reaction system.

Figure 4.3 shows the effect of system pressure on sulfur conversion for two levels of excess air. The predicted equilibrium indicate that system pressure does not significantly affect the conversion efficiency because the molar stoichiometry is similar between the reactants and the products. The test run data confirmed that system pressure does not have a significant impact on unit conversion efficiency.

Under all of the tested conditions the unit demonstrated good flame stability. This unit came to equilibrium (temperature, pressure and flow) very quickly after all of the feed gas flows and compositions were stabilized. This indicated that the conventional burner and furnace design was appropriate for use in the CNG Claus process in spite of the novel operating conditions presented.

Gas Sampling and Analysis Methods

All process gas samples were sampled and analyzed utilizing methods developed by BOVAR Western Research for use in conventional Claus plant analyses. For a standard test run the following samples were taken:

- Combined feed gas stream (H_2S and CO_2 mixture)
- Combustion "air" stream (ambient air and O_2, N_2 mixture)
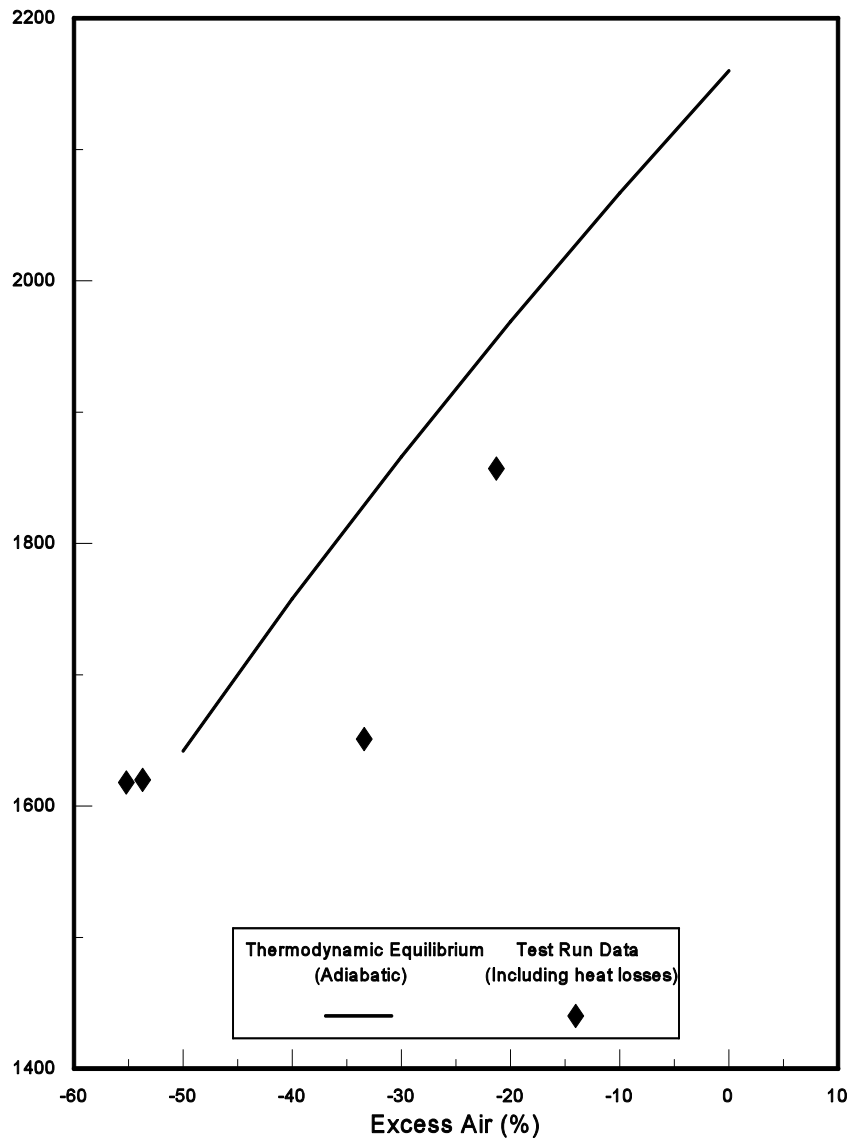- Reaction furnace stream
- Tail gas stream

The feed gas samples were taken directly into glass sampling envelopes. These samples are very clean and at low temperature and therefore no special sampling techniques are required. However, sampling of gas streams in sulfur plant situations requires that special precautions be taken to ensure a representative sample and to ensure that there is no reaction of the process gas in the sampling train itself. Our experience, indicates that typical sulfur plant process gases must be sampled through an inert sampling train to ensure that there is no continued reaction. Extensive research into this problem has indicated that sampling through anything other than a glass or Teflon-lined probe tube results in catalysis of various reactions which results in a change in the composition of the sampled gas.

Also, samples of the gas stream taken at the wall of the pipe are not representative of the bulk gas stream, therefore the use of a sample probe is mandatory. Conditioning of the sample requires removal of water and entrained sulfur. Water is removed by passing the gas through tubes of powdered P_2O_5 which does not react with the acid gas species in the process streams. Glass wool plugs in the conditioning tubes are used to trap the entrained sulfur.

The reaction furnace sample was taken through a glass lined, water cooled probe in order to quench the gas and ensure no unwanted reaction of the gas in the sampling probe. The process gas was quenched to ambient temperature in less than 20 ms. The tail gas was sampled through a standard Teflon lined sample probe system.

The gas analytical work was performed on site by BOVAR Western Research personnel using a gas chromatograph together with ancillary equipment. The chromatographic methods used are described in Appendix B.
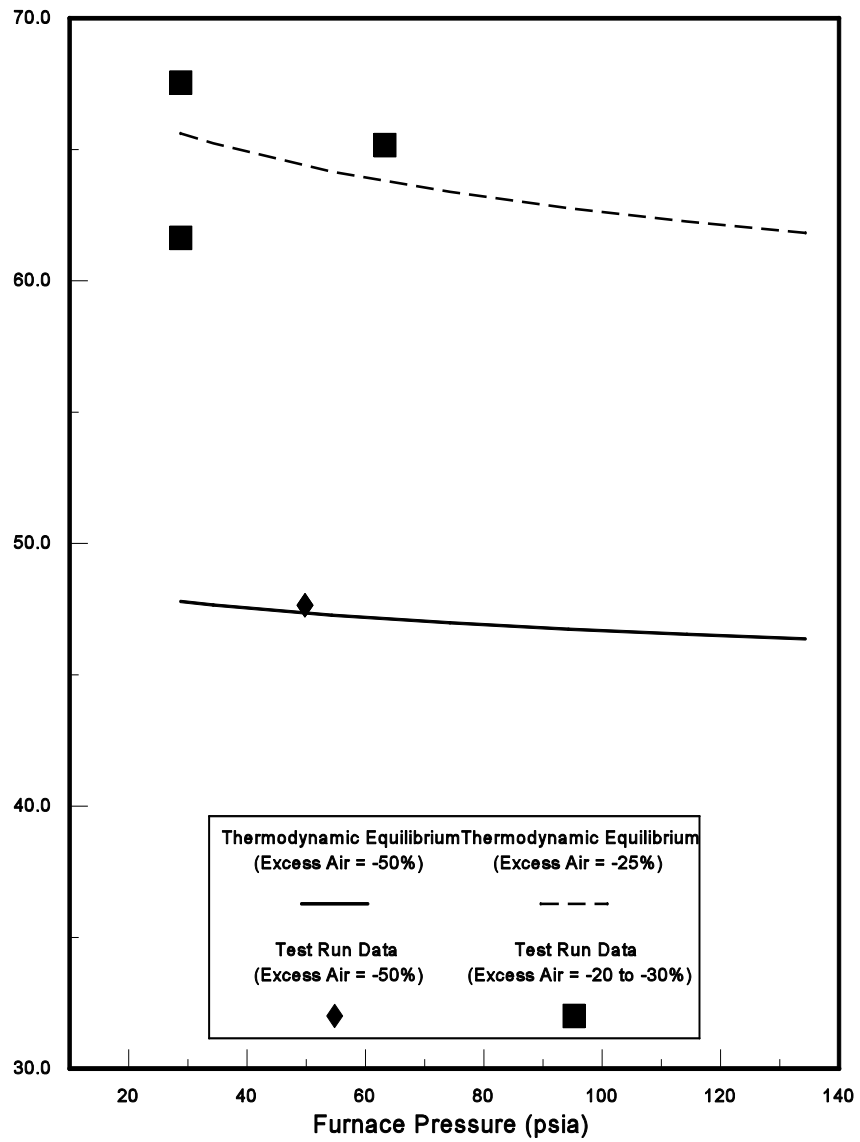
Figure 4.2
Reaction Furnace Evaluation
Temperature vs Reaction Stoichiometry

Notes :

1. Ambient air test set.

2. Thermodynamic equilibrium calculations completed using Sulsim(TM)

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Figure 4.3
Reaction Furnace Evaluation
Sulfur Conversion vs. Reaction Furnace Pressure

	Thermodynamic Equilibrium (Excess Air = -50%)	Thermodynamic Equilibrium (Excess Air = -25%)
	————	— — —
	Test Run Data (Excess Air = -50%)	Test Run Data (Excess Air = -20 to -30%)
	◆	■

Furnace Pressure (psia)

Notes :
1. Ambient air test set.
2. Thermodynamic equilibrium calculations completed using Sulsim(TM)

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5.0 Conclusions

The test results generated to date gave clear indication of the following:

1. The Claus reaction proceeds successfully in a free flame reactor under all of the tested conditions.

2. The sulfur conversion yields in the pilot plant closely match the expected results as indicated by thermodynamic equilibrium calculations for all of the tested conditions.

3. The Claus reaction (H_2S oxidation) proceeds successfully at pressures of 50 psia and greater.

4. The Claus reaction is not significantly affected by operating pressures over the operating range tested. This is consistent with predicted results.

5. The Claus reaction continues successfully at very low oxidation reaction stoichiometries.

6. The results from the test runs indicated that the effect of reaction stoichiometry on sulfur conversion closely matches the predicted results.

7. The observed reaction furnace temperatures were well within acceptable ranges.

Gas Chromatographic Analyses
(Mole Percent)

Fuel Gas Runs

CONSOLIDATED NATURAL GAS   **Feb 23, 1997**
DAVIS, OKLAHOMA   File Number: 4309

Sample No:	1	2	3
Site:	TAIL GAS	TAIL GAS	TAIL GAS
Time:	14:28	15:42	16:02
H_2	0.000	0.000	0.000
Ar	0.959	0.985	0.984
O_2	15.170	9.838	10.122
N_2	80.214	82.369	82.243
CH_4	0.000	0.000	0.000
CO	0.000	0.000	0.000
CO_2	3.657	6.808	6.651
C_2H_4	0.000	0.000	0.000
C_2H_6	0.000	0.000	0.000
H_2S	0.000	0.000	0.000
COS	0.000	0.000	0.000
C_3H_8	0.000	0.000	0.000
SO_2	0.000	0.000	0.000
CS_2	0.000	0.000	0.000
iC_4H_{10}	0.000	0.000	0.000
nC_4H_{10}	0.000	0.000	0.000
iC_5H_{12}	0.000	0.000	0.000
nC_5H_{12}	0.000	0.000	0.000
$C_6H_{14}+$	0.000	0.000	0.000
	100.000	100.000	100.000
H_2S/SO_2:	---	---	---
C/S Ratio:	---	---	---

Zero means not detected.

Sampled water- and   **BOVAR Western Research**
sulfur-free.   Houston, TX

TABLE A-2

Gas Chromatographic Analyses
(Mole Percent)

Pre-test Runs

CONSOLIDATED NATURAL GAS   **Feb 24, 1997**
DAVIS, OKLAHOMA   File Number: 4309

Sample No:	4	5	6
Site:	ACID GAS	ACID GAS	TAIL GAS
Time:	15:41	16:02	16:35

H_2	0.000	0.000	0.184
Ar	0.000	0.000	0.992
O_2	0.000	0.000	7.812
N_2	0.000	0.000	82.946
CH_4	0.000	0.000	0.000
CO	0.000	0.000	0.045
CO_2	66.500	75.454	5.603
C_2H_4	0.000	0.000	0.000
C_2H_6	0.000	0.000	0.000
H_2S	33.389	24.440	0.414
COS	0.002	0.001	0.011
C_3H_8	0.109	0.085	0.000
SO_2	0.000	0.000	1.991
CS_2	0.000	0.000	0.002
iC_4H_{10}	0.000	0.000	0.000
nC_4H_{10}	0.000	0.000	0.000
iC_5H_{12}	0.000	0.000	0.000
nC_5H_{12}	0.000	0.000	0.000
$C_6H_{14}+$	0.000	0.000	0.000
	100.000	100.000	100.000
H_2S/SO_2:	---	---	0.208
C/S Ratio:	2.001353	3.097559	2.338130

Zero means not detected.

Sampled water- and   **BOVAR Western Research**
sulfur-free.   Houston, TX

TABLE A-3

Gas Chromatographic Analyses
(Mole Percent)

Test 1

CONSOLIDATED NATURAL GAS   **Feb 25, 1997**
DAVIS, OKLAHOMA   File Number: 4309

Sample No:	15	7	8
Site:	ACID GAS	WHB	TAIL GAS
Time:	12:41	12:58	12:58
H_2	0.000	2.924	1.728
Ar	0.013	0.850	0.827
O_2	0.000	0.343	0.019
N_2	1.110	71.080	69.116
CH_4	0.000	0.000	0.000
CO	0.000	0.246	0.158
CO_2	9.101	5.845	6.020
C_2H_4	0.000	0.000	0.000
C_2H_6	0.000	0.000	0.000
H_2S	89.454	17.942	20.810
COS	0.005	0.153	0.170
C_3H_8	0.307	0.000	0.000
SO_2	0.010	0.235	0.943
CS_2	0.000	0.382	0.209
iC_4H_{10}	0.000	0.000	0.000
nC_4H_{10}	0.000	0.000	0.000
iC_5H_{12}	0.000	0.000	0.000
nC_5H_{12}	0.000	0.000	0.000
C_6H_{14}+	0.000	0.000	0.000
	100.000	100.000	100.000
H_2S/SO_2:	9202.129	76.367	22.072
C/S Ratio:	0.112086	0.347066	0.293480

Zero means not detected.

Sampled water- and   **BOVAR Western Research**
sulfur-free.   Houston, TX

TABLE A-4

Gas Chromatographic Analyses
(Mole Percent)

Test 2

CONSOLIDATED NATURAL GAS   **Feb 25, 1997**
DAVIS, OKLAHOMA   File Number: 4309

Sample No:	15	9	10
Site:	ACID GAS	WHB	TAIL GAS
Time:	12:41	13:10	13:36

H_2	0.000	1.629	0.917
Ar	0.013	0.970	0.901
O_2	0.000	0.454	0.017
N_2	1.110	81.115	75.318
CH_4	0.000	0.000	0.000
CO	0.000	0.232	0.164
CO_2	9.101	5.451	5.639
C_2H_4	0.000	0.000	0.000
C_2H_6	0.000	0.000	0.000
H_2S	89.454	9.549	14.543
COS	0.005	0.348	0.196
C_3H_8	0.307	0.000	0.000
SO_2	0.010	0.017	2.206
CS_2	0.000	0.235	0.099
iC_4H_{10}	0.000	0.000	0.000
nC_4H_{10}	0.000	0.000	0.000
iC_5H_{12}	0.000	0.000	0.000
nC_5H_{12}	0.000	0.000	0.000
$C_6H_{14}+$	0.000	0.000	0.000
	100.000	100.000	100.000
H_2S/SO_2:	9202.129	547.083	6.592
C/S Ratio:	0.112086	0.603395	0.355717

Zero means not detected.

Sampled water- and   **BOVAR Western Research**
sulfur-free.   Houston, TX

Gas Chromatographic Analyses
(Mole Percent)

Test 3

CONSOLIDATED NATURAL GAS   **Feb 25, 1997**
DAVIS, OKLAHOMA   File Number: 4309

Sample No:	16	11	12
Site:	ACID GAS	WHB	TAIL GAS
Time:	14:00	14:06	14:06

H_2	0.000	1.634	0.957
Ar	0.000	0.762	0.732
O_2	0.000	0.045	0.000
N_2	0.188	63.700	61.369
CH_4	0.000	0.000	0.000
CO	0.000	0.125	0.081
CO_2	10.094	6.904	6.219
C_2H_4	0.000	0.000	0.000
C_2H_6	0.000	0.000	0.000
H_2S	89.396	26.771	29.947
COS	0.006	0.245	0.227
C_3H_8	0.307	0.000	0.000
SO_2	0.009	0.185	0.207
CS_2	0.000	0.439	0.261
iC_4H_{10}	0.000	0.000	0.000
nC_4H_{10}	0.000	0.000	0.000
iC_5H_{12}	0.000	0.000	0.000
nC_5H_{12}	0.000	0.000	0.000
$C_6H_{14}+$	0.000	0.000	0.000
	100.000	100.000	100.000
H_2S/SO_2:	9921.754	144.617	144.669
C/S Ratio:	0.123275	0.245819	0.219660

Zero means not detected.

Sampled water- and   **BOVAR Western Research**
sulfur-free.   Houston, TX

Gas Chromatographic Analyses
(Mole Percent)

Test 4

CONSOLIDATED NATURAL GAS   **Feb 25, 1997**
DAVIS, OKLAHOMA   File Number: 4309

Sample No:	16	13	14
Site:	ACID GAS	WHB	TAIL GAS
Time:	14:00	14:08	14:08

H_2	0.000	1.699	0.901
Ar	0.000	0.730	0.755
O_2	0.000	0.016	0.030
N_2	0.188	61.019	63.087
CH_4	0.000	0.000	0.000
CO	0.000	0.115	0.086
CO_2	10.094	5.847	6.308
C_2H_4	0.000	0.000	0.000
C_2H_6	0.000	0.000	0.000
H_2S	89.396	29.169	27.730
COS	0.006	0.202	0.226
C_3H_8	0.307	0.000	0.000
SO_2	0.009	0.732	0.626
CS_2	0.000	0.471	0.251
iC_4H_{10}	0.000	0.000	0.000
nC_4H_{10}	0.000	0.000	0.000
iC_5H_{12}	0.000	0.000	0.000
nC_5H_{12}	0.000	0.000	0.000
$C_6H_{14}+$	0.000	0.000	0.000
	100.000	100.000	100.000
H_2S/SO_2:	9921.754	39.822	44.299
C/S Ratio:	0.123275	0.213705	0.236244

Zero means not detected.

Sampled water- and   **BOVAR Western Research**
sulfur-free.   Houston, TX

TABLE A-7

Gas Chromatographic Analyses
(Mole Percent)

Feed Gas Supply Samples

CONSOLIDATED NATURAL GAS   **Feb 26, 1997**
DAVIS, OKLAHOMA   File Number: 4309

Sample No:	17	18
Site:	CO2 TANK	O2 N2 MIX 50-50
Time:	10:16	00:00

H_2	0.000	0.000
Ar	0.016	0.000
O_2	0.366	50.450
N_2	1.303	49.550
CH_4	0.000	0.000
CO	0.000	0.000
CO_2	98.315	0.000
C_2H_4	0.000	0.000
C_2H_6	0.000	0.000
H_2S	0.000	0.000
COS	0.000	0.000
C_3H_8	0.000	0.000
SO_2	0.000	0.000
CS_2	0.000	0.000
iC_4H_{10}	0.000	0.000
nC_4H_{10}	0.000	0.000
iC_5H_{12}	0.000	0.000
nC_5H_{12}	0.000	0.000
$C_6H_{14}+$	0.000	0.000
	100.000	100.000
H_2S/SO_2:	---	---
C/S Ratio:	---	---

Zero means not detected.

Sampled water- and   **BOVAR Western Research**
sulfur-free.   Houston, TX

ANALYTICAL METHODS

Sample Analysis

Gas chromatographic analysis is the most common method used because it is the only method that conveniently yields multicomponent analyses with a reasonable degree of accuracy on each component. A single run will yield results for each of the four sulphur species H_2S, SO_2, COS and CS_2, and give CO_2 and the N_2+ - group. A further run on another column will split the N_2+ - group yielding H_2, Ar, O_2, CH_4 and CO. Such detailed analyses are necessary for accurate efficiency determinations and for constructing heat and material balances.

The H_2O and elemental sulphur are removed from the sample for two reasons. Firstly, to prevent reaction among sulphur gases while obtaining and transporting the sample and secondly, because both H_2O and sulphur are detrimental to most gas chromatograph column packings.

Analysis of these gases required suitable packings, adequate calibration techniques, and methods of eliminating, or minimizing:

- adverse interactions between the sulphur gases and the column packing;

- reactions among the sulphur gases on the column surface; and

- adverse interactions of the sulphur gases with the detector of the chromatograph.

When all of the above factors have been optimized, uncertainties of the major and intermediate component concentrations are estimated to be ± 1 to ± 2 percent of value, or better. Minor component uncertainties are in the ± 5 to ± 10 percent of value range.

It is a simple matter to develop a conversion profile for the plant using a carbon balance with the dry steam compositions above.