DE-FG22-93PC93220--0

DOE/PC/93220--0

RECEIVED
AUG 11 1998
OSTI

Production of Elemental Sulfur and Methane From H_2S and $C0_2$ Derived From a Coal Desulfurization Process

Final Report
September 1, 1993 - March 31, 1997

By:
Xueyu Jiang
Soon-Jai Khang
Timothy C. Keener

Work Performed Under Contract No.: DE-FG22-93PC93220

For
U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
University of Cincinnati
Department of Civil and Environmental Engineering
Cincinnati, Ohio 45221-0171

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

ABSTRACT

The purpose of this study was to experimentally and theoretically investigate the feasibility of producing elemental sulfur, carbon monoxide (CO), hydrogen (H_2) and possibly methane (CH_4) from hydrogen sulfide (H_2S) and carbon dioxide (CO_2) through catalytic reactions. A novel experimental system that could evaluate potential catalysts and adsorbents under controlled laboratory conditions was designed and constructed. Additionally an effective simulation program capable of providing valuable thermodynamic information on the reaction system was compiled.

The following tasks have been performed: (1) design and construction of an experimental system for the catalyst preparation and catalyst screening studies including frequent modifications of the experimental setup to meet specific application needs; (2) installation and calibration of related analytical instruments, and investigation of the temperature distribution profile inside the reactor; (3) preparation, reduction, sulfidation of potential catalysts, and measurements of specific surface area of catalysts; (4) decomposition of H_2S under both non-catalytic condition and catalytic condition with the CoO-MoO_3-alumina catalyst at moderate temperatures around 550°C. Analyses of the product gas by gas chromatograph; and (5) thermodynamic studies on the theoretical conversions of H_2S for various temperatures, pressures and ratios of H_2S to CO_2.

Based on the results of the above tasks, bench scale experiments were performed with the CoO-MoO_3-alumina catalyst at moderate temperatures around 550°C to investigate the adsorption effects of solid sorbents in order to remove sulfur from the reaction environment. Four kinds of adsorbents have been tested along with several designs of solid adsorbent feed systems.

The following results were obtained: (1) it was experimentally demonstrated that the Co-Mo sulfided catalyst was a good candidate for the decomposition of H_2S to elemental sulfur. In the presence of CO_2, the conversion of H_2S to elemental sulfur increased significantly. The experimental values were reasonably close to the thermodynamic equilibrium limits; (2) it was experimentally shown that the present catalytic process produced a significant amount of sulfur, CO and H_2. However, the H_2S conversion level of about 4.3% at 550°C was not sufficient enough for commercial applications. A recycle and/or a hybrid system of catalysis and adsorption may be required; (3) the thermodynamic simulation showed that at least two reaction zones were required for production of any appreciable amount of methane. The first reaction zone should be composed of multiple stages to recover the elemental sulfur in order to avoid the equilibrium limitations. With an optimum temperature in each zone, the conversion could be increased significantly and less amount of by-products such as COS, CS_2 and SO_2 would be produced. The results illustrated that the number of stages needed for recovering sulfur could be greatly affected by the sulfur vapor pressure which followed a logarithmic relationship with the system temperature. The H_2S conversion and sulfur yield increased following a logarithmic pattern with the number of stages. The simulation also indicated that a multiple stage system became less effective at high reaction temperatures; (4) although the experimental results indicated that activated carbon was the best of four tested adsorbents based on the adsorption experiments of sulfur vapor, it may be a poor choice of adsorbent since the activated carbon in the reacting environment may participate in the reaction moving the equilibrium in an unfavorable direction. Other non-reacting sorbents might still be applicable since solid powders could easily be transported through the catalytic packed-bed with the proper use of vibrators.

1. INTRODUCTION

1.1 Problem Statement

Elemental sulfur is an important ingredient in the chemical industry and is produced or recovered from Frasch process, pyrites, hydrocarbon operations and other forms (Oil & Gas Journal, 1993). Elemental sulfur is also one of the largest single chemicals produced in the United States today. This country consumed over 11 million tons of elemental sulfur in 1988 (Gangwal et al., 1991), 13.7 million tons in 1991 (Chemical and Engineering News, 1992) and 12.7 million tons in 1992 (Chemical Engineering, 1994). In 1991, only 26.7% of all sulfur consumed in the United States was produced by Frasch process, whereas 62.1% was from various types of sulfur recovery processes. In 1992, the total amount of elemental sulfur produced in the United States was 10.7 million tons, of which 7 million tons were recovered elemental sulfur from petroleum refineries and only 2.3 million tons were from sulfur mines (Figure 1). Canada and the United States dominate petroleum-derived sulfur recovery and produce more than 56% of the world's supply (True, 1993 and Swain, 1995).

Utilization of high sulfur feed stocks in sour natural gas, residual crude oils and high sulfur coal in petro-chemical and energy industries is increasing today. In most situations, sulfur must be removed before combustion or utilization to comply with environmental and emission regulations, and to protect catalysts used in the downstream processes. However, the sulfur removed from natural gas, crude oil, coal gasification and other industrial hydrodesulfurization process is usually in the form of gaseous H_2S. Since the New Clean Air Amendment allows only moderate sulfur dioxide emissions from existing power plants (Lee, 1991 and Kwong, 1995), developments have emphasized the importance of effective technologies for treating the contaminated air. Because the air pollution control systems and the processes for removing H_2S from gas streams are generally both capital and energy intensive, the recovery of sulfur from fossil fuels is important in the petro-chemical and energy industries to offset the pollution control cost. Furthermore, cold gas cleanup systems in use today normally require a liquid absorbent and are unable to completely remove the noxious smell of H_2S. The odor is not only a nuisance but also toxic and health hazard to people involved at various facilities and treatment plants (Bhambhani el al., 1994; Fire, 1991; Rapaport, 1990 and Weil, 1983).

It is possible to partially offset the cost of sulfur removal by recovering sulfur in a marketable form if catalytic reaction based processes are developed. In the past several decades, many researchers have studied methods for production of hydrogen, elemental sulfur or both by decomposition of H_2S. The most popular process is the Claus process. In this process, H_2S is partially oxidized to sulfur dioxide, which then reacts with H_2S to produce elemental sulfur.

$$2\,H_2S + SO_2 \rightleftharpoons 3\,S + 2\,H_2O$$

Unlike the Claus process which uses oxygen to form SO_2, CO_2 can act as an oxidizing reactant to react with H_2 that is produced during the H_2S decomposition reaction. Bowman (1991) studied the thermodynamic possibilities of reaction of H_2S with CO_2 within three temperature regions under various pressures. However, no experimental data were presented to verify the equilibrium calculations.

Liptak (1974) first proposed the following reaction at a high temperature with catalysts to produce methane and sulfur:

$$4\ H_2S + CO_2 \rightleftharpoons 4\ S + CH_4 + 2\ H_2O$$

Paushkin (1988) also proposed the following reaction to produce sulfur and ethylene:

$$6\ H_2S + 2\ CO_2 \rightarrow 6\ S + CH_2{=}CH_2 + 4\ H_2O$$

The above reactions have been described to be potentially effective but actual reaction kinetics and the effects of temperature and residence time on the conversion and selectivity have not been reported in the literature.

The idea of producing elemental sulfur by reacting H_2S with CO_2 is particularly appealing because: (1) both CO_2 and H_2S occur commonly in the utilization of fossil fuels where H_2S is a by-product of hydrodesulfurization process of crude oil and natural gas; (2) H_2S, which would be converted into sulfur dioxide during combustion, must be removed to comply with environmental legislation; and (3) CO_2 is a known greenhouse gas.

1.2 Objective

The overall objective of the project was to study the feasibility of such a process where H_2S and CO_2 would be directly converted into elemental sulfur and a mixture of CO, H_2 and possibly CH_4 by using appropriate catalysts, adsorbents and operating conditions. The specific tasks consisted of the following:

(1) To perform thermodynamic analyses in order to determine the extent of conversion, and assess the effect of various parameters and the possibility of formation of

undesirable side-products.

(2) To establish a preparation procedure for the sulfidation of the CoO-MoO_3-alumina catalyst from its oxide form in which the catalyst was supplied by the vender.

(3) To test the sulfided CoO-MoO_3-alumina catalyst and to determine its feasibility in producing elemental sulfur from the H_2S and CO_2 gas mixture. This task included the design and construction of a reactor for conducting these tests as well as the development of experimental procedures for these tests.

1.3 Work Performed

In order to achieve the above objective, the following research tasks have been performed:

(1) *Thermodynamic Analysis and Simulation*

The simulation results of thermodynamic analyses for the equilibrium behavior of H_2S and CO_2 at different temperatures and pressure ranges were obtained based on possible experimental conditions by using the JANAF Thermodynamic Tables (Stull, 1971) and the Stanjan method (Reynolds, 1987), which provided important information for process development. Theoretical equilibrium conversions were calculated and analyses were carried out varying three system parameters: temperature, pressure, and the ratio of H_2S to CO_2.

(2) *Experimental System*

An experimental system was designed and constructed for the catalyst preparation and catalyst screening studies. Potential catalysts and relevant experimental materials for the experiments were selected. Analytical instruments were installed and the temperature profile inside the reactor was measured. Catalyst preparation tests were first performed in the TGA and the catalyst performance studies were carried out in the packed-bed reactor.

(3) *Catalyst Preparation*

A specific method of sulfidation of commercial CoO-MoO$_3$-alumina catalyst was obtained using a thermogravimetic analyzer (TGA). Separate CoO-MoO$_3$-alumina catalyst was also synthesized in our laboratory as a base-line test. The catalysts were subsequently reduced, sulfided and the specific surface area of the catalysts were measured as a part of the catalyst characterization.

(4) *Packed-Bed Catalytic Reactor*

Experiments were conducted in the tubular reactor packed with CoO-MoO$_3$-alumina catalyst. The results showed that higher sulfur conversions could be obtained by using a mixture of H_2S and CO_2 instead of H_2S alone. The results also showed that sulfur conversion increased with increasing temperature. H_2S was decomposed under both non-catalytic and catalytic (with CoO-MoO$_3$-alumina catalyst) conditions. The product gas was analyzed using a dual-column gas chromatograph.

(5) *Sulfur Adsorption on Various Adsorbents*

Bench-scale experiments were performed to find out the feasibility of sulfur vapor condensation and adsorption on various adsorbents. The relationship between the reaction temperature and the sulfur recovery efficiency was studied. A hybrid process of catalysis and adsorption was investigated.

This report describes the feasibility study of a process that H_2S and CO_2 would be directly converted into elemental sulfur and a mixture of CO, H_2 and possibly CH_4 using appropriate catalysts. The report also includes detailed results of thermodynamic analyses for the equilibrium behavior of CO_2 and H_2S at different temperature and pressure ranges, and summarizes the current techniques and background of the sulfur recovery. The results of this project will be useful in conjunction with the novel coal feeder to pretreat coal for coal-fired power plants which provides a continuous supply of hydrogen sulfide which could offset the costs of producing clean energy.

2. LITERATURE REVIEW

The feasibility of production of elemental sulfur and hydrogen by decomposition of H_2S has been well established in the literature. As early as 1950's, Gamson and Elkins (1953) had already pointed out that the depletion of pure sulfur deposits mined by the Frash process would encourage augmented sulfur supplies from hydrogen sulfide generated from the accelerated use of high sulfur-bearing petroleum crude oil and natural gas. In their research, they thoroughly investigated the kinetics and thermodynamics of the reactions in the Claus process with detailed calculations.

In addition to the Claus process, many processes have been developed in the last decade such as thermal decomposition of H_2S, catalytic decomposition of H_2S, thermal decomposition of H_2S while products were continually removed, oxidization of H_2S by O_2, and partial oxidization of H_2S by CO_2. However, only Claus process is considered commercially viable today. Zaman and Chakma (1995) have provided an updated summary of various technologies in the area of hydrogen and sulfur recovery from H_2S.

2.1 Claus Process

Claus process is the most widely used modern process in industry for sulfur recovery. According to the estimation by Goar et al. (1986), some 90 to 95% of recovered sulfur in the world was produced by the Claus process. Since the Claus process was invented in 1883, significant modifications have been made on the commercial Claus process used today, but the principal mechanisms of the process are the same as one hundred years ago, that is, about one third of the H_2S needs to be burned in the air to form SO_2 which subsequently reacts with H_2S to produce elemental sulfur as shown below.

$$2\,H_2S + 3\,O_2 \rightarrow 2\,SO_2 + 2\,H_2O \qquad \text{(Combustion Process)}$$

$$2\,H_2S + SO_2 \rightleftharpoons 3\,S + 2\,H_2O \qquad \text{(Claus Process)}$$

$$2\,H_2S + O_2 \rightarrow S_2 + 2\,H_2O \qquad \text{(Overall Process)}$$

As the Claus Process is equilibrium limited, the stream of tail gas contains appreciable amounts of SO_2 (Caruana, 1996). In order to comply with the air pollution regulations, the modern Claus Process consists of a combustion stage, one to four catalytic converters, and a tail-gas clean-up unit (Figure 2). A detailed review of commercial developments in Claus process technology was discussed by Goar (1986). Since there is 79% nitrogen in the air, the use of air in the Claus process requires that the inert N_2 must be treated in a tail gas plant to meet the environmental regulation before it is released to the atmosphere. Tail gas treatment increases the sulfur recovery cost. Several tail gas clean-up processes are reviewed by West (1984). In early 1990's, Khudenko et al. (1993) proposed a novel oxygen-based modifications of the Claus process. The major finding of the work was that oxygen-based Claus systems could be used for upgrading the existing system to reduce the equipment size requirement.

By the nature of the Claus process, hydrogen cannot be recovered and is finally wasted in the form of water, making the process less attractive for hydrogen economy. Because the Claus process is a highly optimized technology, it will be an outstanding revolution to the existing technology if any further development is made to reduce both the capital cost and the sulfur emissions, and simultaneously recover the elemental sulfur and hydrogen in a usable form.

2.2 Thermal Decomposition of H_2S without Catalyst

The idea of producing elemental sulfur and hydrogen by direct decomposition of H_2S has been well discussed in the literature (Kaloidas and Papayannakos, 1989 and 1991; Roth et al., 1982; Raymont, 1975). The original purpose was to produce H_2 but it has been used to produce sulfur as well.

$$H_2S \rightleftharpoons H_2 + 0.5\ S_2$$

Studies of determining the mechanism and kinetics for the decomposition have been reported by a number of researchers. Kaloidas and Papayannakos (1989, 1991) studied the kinetics of the non-catalytic thermal decomposition of H_2S. The reactions were carried out in the temperature range of 600 to 860°C, and the pressure range of 1.3 to 3.0 atm. The proposed rate-limiting mechanism was the initial step of the splitting H_2S into intermediate free-radicals. Statistical analyses indicated that the proposed kinetic model and the experimental data agreed well with each other.

Roth et al. (1982) carried out the thermal decomposition of H_2S in the temperature range of 1965 to 2560 K, pressure between 1.8 to 2.0 bars, and H_2S concentration as low as 25 to 200 ppm. Argon (Ar) was used as an inert gas. The primary reaction mechanism was found to follow second-order kinetics with respect to H_2S concentration:

$$H_2S + Ar \rightarrow HS + H + Ar$$

$$H_2S + H \rightarrow HS + H_2$$

The required experimental temperature was much higher than that commonly used by the sulfur recovery industry, requiring an expensive plasma operation, thus making this technology economically unattractive.

Raymont (1975) found that H_2S could be thermally decomposed. However, it was thermodynamically unfavorable below 1800K (1527°C) due to the endothermic nature of the reaction. He established three different reaction systems: an empty uncatalyzed reactor, a reactor filled with blank pellets and a reactor packed with active catalyst pellets. He found that certain metal catalysts were very effective for both the hydrogen yield and the rate of H_2S decomposition. He pointed out that, above 1250 K, the yields became the same for both catalytic and non-catalytic reactions.

2.3 Thermal Decomposition of H_2S with Catalyst

There have been several works in the efforts to increase the rate of reaction at relatively lower temperatures using catalysts. Fukuda et al. (1978) decomposed H_2S on molybdenum disulfide (MoS_2) and tungsten disulfide catalysts at 500-800°C. They found that MoS_2 decomposes H_2S more effectively into hydrogen and elemental sulfur than tungsten disulfide over the entire range of temperature. Megalofonos and Papayannakos (1991) tried to produce hydrogen from natural gas and H_2S over the temperature range of 973K (700°C) to 1098K (825°C) under 0.1 M Pa. Experiments were carried out in both a non-catalytic reactor and a catalytic tubular reactor filled with MoS_2 catalyst. It was shown that the catalytic reaction rates were much greater than the thermal reaction rates.

Chivers et al. (1980) found that MoS_2 was the most effective catalyst above 600°C, but WS_2 and Cr_2S_3 gave higher H_2 yields than MoS_2 below 600°C. They also found that FeS, CoS, NiS, CuS, C_2S and Cu_9S_5 were not effective for the decomposition of H_2S and only a trace amount of elemental sulfur was produced using these metal sulfides. Among all the catalysts tested to date, MoS_2 has been proven to be the most effective over a wide range of temperature. The catalyst properties of MoS_2 and possible mechanisms for H_2S decomposition were described by Katsumoto et al. (1973), Kotera (1976), Mitchell (1981) and, Sugioka and Aomura (1984) over various ranges of reaction temperature and pressure.

Chivers and Lau (1985) screened the alkali metal sulfides and polysulfides group and found that sodium polysulfides were not catalytically active for H_2S decomposition. The most significant result in their study was the discovery that Li_2S acted as a catalyst for the thermal decomposition of H_2S at 500 to 800°C. But its application was limited due to the sensitivity of Li_2S towards impurities, CO_2 and water. Chivers and Lau (1987) continued their investigation on vanadium sulfide and mixed catalysts. The mixture of V_2S_3/Cu_9S_5 which formed Cu_3VS_4 at elevated temperatures was shown to have a higher catalytic activity than MoS_2 in a closed circulating system using a quartz reactor in the temperature range of 400 to 800°C, whereas MoS_2 was found to be a better catalyst in a thermal diffusion column reactor. However, the cost (per unit weight) of commercial V_2S_3 was about 30 times greater than that of MoS_2. They suggested that the catalytic mechanism of vanadium sulfide in H_2S decomposition was via a two-step process shown below:

$$2\ VS + H_2S \rightarrow V_2S_3 + H_2$$

$$V_2S_3 \rightarrow 2\ VS + S^*$$

Al-Shamma and Naman (1989 and 1990) investigated the use of V_2S_3, V_2O_5/Al_2O_3 and V_2S_3/Al_2O_3 catalysts. In the once-through flow reactor, the concentration of H_2 increased during the first 150 to 200 minutes, then it went down without reaching a steady-state value. All their experiments were carried out in the temperature range of 723K (450°C) to 873K (600°C) with various vanadium oxide/alumina oxide percentages. The suggested main reaction mechanism was:

$$V_2O_5 + 5\ H_2S \rightarrow V_2S_3 + 5\ H_2O + 2\ S^*$$

The subsequent reactions of V_2O_5 were the same as those by Chivers and Lau (1987). The reaction order was between zero and one depending on the composition of catalysts and the reaction temperature.

Bagajewicz et al. (1988) found that H_2S was chemisorbed reversibly on a nonstoichiometric vanadium oxide and bulk sulfide was not formed at the temperature range of 650-700°C. Li et al. (1996) also studied using vanadium-based mixed oxide catalyst for selective oxidation of H_2S to elemental sulfur. The catalytic reaction was carried out in a fixed-bed reactor in the temperature range of 200-300°C which was lower than Chivers and Lau's (1987). The vanadium-based binary mixed-oxide catalysts performed much better than the pure vanadium oxide. The maximum sulfur yield was 97% when vanadium-based binary mixed-oxide catalysts were used.

Ross and Jeanes (1974) found out that cobalt molybdate catalysts had a high efficiency to oxidize H_2S when the concentration of H_2S was below 4000 ppm and the reaction temperature was kept below 300°C. The main propose of the research was to reduce the H_2S level below its odor threshold.

Research Triangle Institute (RTI) developed a direct sulfur recovery process (DSRP), which would convert SO_2 directly to elemental sulfur by using the coal gas and a catalyst (Gangwal et al., 1991). They claimed that the conversion could reach above 95% with the following series of reactions.

$$2\ H_2 + SO_2 \rightarrow 2\ H_2O + 1/n\ S_n$$

$$2\ CO + SO_2 \rightarrow 2\ CO_2 + 1/n\ S_n$$

$$SO_2 + 3\ H_2 \rightarrow H_2S + 2\ H_2O$$

$$2\ H_2S + SO_2 \rightarrow 2\ H_2O + 3/n\ S_n$$

They also found that pressure had a significant effect on the conversion of H_2S to elemental sulfur. Increasing reaction pressure from 1.5 to 20 atm quadrupled the sulfur recovery when the space velocity was kept at the same level. The work was focused on the conversion of dilute SO_2 to elemental sulfur.

Although metal oxides were commonly used for the decomposition of H_2S and for many other applications in a wide range of industries, Yang and Kung (1994) used platinum sulfide as a catalyst for their hydrogen recovery experiments to oxidize and decompose H_2S. The metal oxide catalysts were tested and characterized by a number of researchers during the past decades (Bartholomew et al., 1979; Beer et al., 1974 and 1976; Berk et al., 1991; Fellmuth et al., 1987;

Gai, 1979; Sivasanker et al., 1979; Twigg, 1989; Xu et al., 1991).

2.4 Thermal Decomposition of H_2S while Products are Continually Removed

Even though the usage of catalysts can increase the rate of reaction, the yield of sulfur is still limited by the equilibrium of H_2S decomposition. For this reason, some researchers have studied the ways to continually remove either H_2 or S_2 from reaction zone in order to shift the equilibrium to the product side, thus promoting further decomposition of H_2S. The study of Raymont (1975) was focused on the recovery of H_2. The use of platinum or palladium alloy membranes was suggested and a diagrammatic representation of the proposed process was also made. The idea of selective hydrogen removal by platinum-based metal-membrane was experimentally tested by Edlund and Pledger (1993 and 1994). They showed that the removal of hydrogen during thermal decomposition of hydrogen sulfide resulted in higher conversions of H_2S than that could normally be obtained by equilibrium. Kameyama et al. (1979, 1981, 1983) used both a microporous Vycor type glass membrane having a mean pore diameter of 45 Å and a microporous alumina membrane having a mean pore diameter of 1000 Å for the H_2-H_2S separation system. The use of membrane at 800°C or higher increased the yield of hydrogen by about two times that obtained by equilibrium only.

However, the limitations of membrane selectivity and permeability, and the severely corrosive nature of H_2S to the membrane material made the industrial membrane application difficult. Due to the unavailability of pactical membranes for removal of H_2 from the product stream, Banderman and Harder (1982) used the pressure swing adsorption on zeolite or carbon molecular sieve and found that the adsorption method was competitive to the Claus process.

2.5 Oxidization of H_2S by O_2

The processes using catalytic oxidation of H_2S by molecular oxygen (O_2) over an activated carbon bed or a molecular sieve column have been studied by a number of researchers (Chowdury and Tollefson, 1990; Coskun and Tollefson, 1980; Dalai et al., 1993; Ghosh and Tollefson, 1986; Kaliva and Smith, 1983; Sreeramamurthy and Menon, 1975; Steijns et al., 1974 and 1976; Zhenglu et al., 1984). In these process, the sulfur is produced by the selective oxidation of H_2S:

$$H_2S + 0.5\ O_2 \rightarrow S + H_2O$$

or

$$H_2S + 0.5\ O_2 \rightarrow 1/n\ S_n + H_2O$$

The conversion of H_2S to elemental sulfur with dilute oxygen at 20 atm near 635K (362°C) was above 98% and decreased when the pressure and the temperature were lowered (Gangwal et al., 1991 and 1995). The inlet gas contained 6.46% H_2S, 3.23% O_2 and 8.14% H_2O in N_2. Tsuchiya et al. (1994) investigated the reaction of atomic oxygen with H_2S by the shock tube/laser photolysis method in the very high temperature range of 1100 to 2000K (827 to 1727°C). The concentration of H_2S was at ppm level. The activity of potential catalysts for the oxidation of H_2S with molecular oxygen was investigated in detail by Marshneva and Mokrinskii (1989). The importance of catalyst carrier affecting the performance of the catalyst was experimantally demonstrated by Terorde et al. (1993). They tested the iron oxide catalysts supported on titania, zirconia, magnesia, θ-alumina and silica for selective oxidation of the stream containing 3 to 5% H_2S which was not converted into sulfur in Claus process and remained in the tail gas due to thermodynamic limitations. Their results showed that the silica-supported iron oxide catalyst exhibited the best performance with stable activity and selectivity, and the magnesium-supported iron oxide showed worst performance. The selective-oxidation method with molecular O_2 has been shown to be more effective for treating lower concentration H_2S (<10 volume %) especially removing trace quantities of H_2S from a gas stream rather than for producing a large amount of sulfur, which could be efficiently accomplished by the Claus process (Steijns and Mars, 1974; Ghosh and Tollefson, 1986).

2.6 Partial Oxidization of H_2S by CO_2

Another way of effectively decomposing H_2S is to add oxygen-rich reactants such as CO_2 to react with H_2. Bowman (1991) studied the thermodynamic possibilities of reaction of H_2S with CO_2 under various reaction conditions. He divided his thermodynamic calculations into three temperature regions. Although no experimental data were presented to verify the equilibrium calculations, he considered the following reaction of H_2S and CO_2 in the temperature range of 900-1300 K (627-1027°C):

$$H_2S + CO_2 \rightleftharpoons CO + H_2O + 0.5\ S_2$$

Towler et al. (1993) proposed the following reaction mechanism for the production of elemental sulfur from H_2S and CO_2 in the temperature range of 900-950°C:

$$H_2S \rightleftharpoons H_2 + 0.5\ S_2$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

They found that the presence of CO_2 had the effect of shifting the H_2S decomposition reaction to the product side by reacting the produced H_2 with CO_2 to form CO and H_2O via the water-gas shift reaction. The catalyst tested was MoS_2. Liptak (1974) proposed the following reaction at a high temperature with catalysts:

$$4\ H_2S + CO_2 \rightleftharpoons 2\ S_2 + CH_4 + 2\ H_2O$$

Paushkin (1988) also proposed the following additional reaction:

$$6\ H_2S + 2\ CO_2 \rightarrow 6\ S + CH_2{=}CH_2 + 4\ H_2O$$

These reactions have been described to be potentially effective but actual reaction kinetics have not been reported in the literature.

Fellmuth et al. (1987) tried to react H_2S with CO_2 through the following catalytic reaction.

$$H_2S + CO_2 \rightleftharpoons COS + H_2O$$

They found that the presence of A- and X-type zeolites lead to H_2S conversions up to 70% at room temperature. The results obtained at different residence times illustrated the dual function of the zeolites as catalyst and as selective sorbents causing a shift in reaction equilibrium. Randall et al. (1992) patented a process in which a multicomponent feed stream containing H_2S and CO_2 was passed through a reactor filled with alumina or molecular sieve catalysts to produce COS. The COS was then carried into another reactor packed with alumina, metal sieves or transition metal sulfides, and decomposed to elemental sulfur and CO. George (1974) also presented a similar process where the reaction would require an additional step to decompose the carbonyl sulfide

(COS) to form elemental sulfur.

2.7 Other Miscellaneous Processes

A process combining absorption of H_2S with I_2 (aqueous) and photoelectrochemical decomposition of the resulting HI (aqueous) by using solar energy was proposed by Oosawa et al. (1987). The reaction was occurring at room temperature and the overall reaction was as simple as:

$$H_2S(g) + I_2aq \rightarrow 2\,HIaq + S(s)$$

$$2\,HIaq \rightarrow I_2aq + H_2(g)$$

Barbeni et al. (1985) used the principle of visible light irradiation on CdS dispersions in alkaline aqueous media containing hydrogen sulfide which led to efficient hydrogen evolution. Linkous et al. (1994) also tried to decompose H_2S in solar-driven photoelectrochemical cells to produce hydrogen and elemental sulfur.

Helfritch (1993) designed a pulsed corona discharge reactor and tested it to decompose H_2S at room temperature. His results indicated that the corona discharge reactor could drive the H_2S concentration to extremely low levels. The product of the decomposition was elemental sulfur and the energy efficiency was good.

Bagautdinov et al. (1991) investigated the microwave discharge dissociation process with gas mixtures of H_2S and CO_2. They concluded that the process was effective and could be scaled up by increasing the discharge power to 300 kW and the pressure to 500 torr. Traus and Suhr (1992 and 1993) used a high-temperature ozonizer and an atmospheric-pressure glow discharge to study the dissociation of H_2S into elemental sulfur and hydrogen. The potential of these techniques were to comply with economic and physicochemical characteristics for the H_2S/H_2 system.

Petrov and Srinivasan (1996) studied the prospects for the development of chemical-electrochemical plants to remove H_2S from sour gas and production of high quality hydrogen and sulfur at low temperatures. They claimed that extremely pure hydrogen and sulfur were produced at a low cell voltage (1.0 V) and a high current density (300 mA/cm^2). In Japan, Mizuta et al. (1991) was using a hybrid Fe-Cl process consisting of the adsorption of H_2S by $FeCl_3$ aqueous solution and subsequent electrolysis of $FeCl_2$ solution to produce H_2 and elemental sulfur. Their bench-scale plant was successfully operated for 1000 hours.

2.8 Summary and Choice of Methods

As reviewed in the pervious sections on thermal decomposition of H_2S, more investigation is needed for kinetics measurements, mechanism studies and catalyst development. The results of kinetic studies are mostly empirical, and there are significant disagreements in the parameter values as the order of reaction was reported between one and two, and the activation energies for the catalytic reaction was reported from 50 to 112 kJ/mol. Among the catalysts, only MoS_2 has been investigated in significant details. Even in this case, information how to improve the catalyst by adding additional components is scarce (Zaman and Chakma 1995).

The main purpose of decomposition of H_2S was to produce S_2 from H_2S. Since the decomposition is endothermic, the reaction is unfavorable at lower temperatures. This is the reason why many catalytic reactions have been investigated to increase the reaction rate. Molybdenum sulfide (MoS_2) has been proved to be the most effective catalyst among those investigated for the H_2S decomposition reaction.

Even though an effective catalyst could increase the rate of decomposition, the yield of elemental sulfur was still limited by the low equilibrium conversion of H_2S even at an elevated temperature. Therefore it was necessary to remove the product, H_2 or S_2, to shift the equilibrium in order to promote the decomposition of H_2S. Both Bowman (1991) and Towler et al. (1993) proposed that the presence of CO_2 had the effect of promoting the H_2S decomposition by reacting with H_2 to form CO and H_2O. It is the reaction which produces a mixture of CO and H_2 as well as elemental sulfur in a single step.

Since the H_2S decomposition reaction could be effectively catalyzed by MoS_2 at temperatures between 900 and 950°C, it would be interesting to develop catalysts which work effectively at a lower temperature around 550°C. The CoO-MoO_3-alumina catalyst is a good candidate for the H_2S and CO_2 system because: (1) Mo is an active catalyst for oxidizing H_2S as proved by previous researchers and, (2) Co-Mo is a known catalyst for the water-gas shift reaction which may take place in the H_2S and CO_2 system. Furthermore, the CoO-MoO_3-alumina catalyst is also a hydrodesulfurization catalyst routinely used in the petroleum industry and is readily available from commercial sources.

3. EXPERIMENTAL SYSTEM

3.1 Design and Construction of Experimental Systems

3.1.1 Experimental Apparatus for the Synthesis of Catalyst

An experimental system for preparing catalysts by precipitation was set up as shown schematically in Figure 3. Flow rates of air and nitrogen were controlled by rotameters and needle valves. The stock solution which was used to prepare catalyst was kept in a 2000 ml beaker. The temperature of the solution was controlled by a hot plate equipped with a 9"x9" magnetic stirrer and water bath. The pH value of the solution was adjusted by adding 3.0M NaOH solution and measured by an Accumet-900 pH-Meter.

3.1.2 TGA System for Sulfided Catalyst Preparation

A standard method for preparation of Co-Mo sulfide catalyst could not be found in the open literature. However sulfide catalysts could be prepared by a series of procedures under special conditions. The Du Pont Instrument 951 TGA (thermogravimetric analyzer) was used for establishing the sulfidation procedure from the oxide form of the Co-Mo catalyst (CoO-MoO_3-alumina) which was supplied by Crosfield Catalysts (4099 West 71st Street, Chicago, Illinois 60629). Approximate by 40 mg of Co-Mo oxide catalyst was used each time to determine the extent of reduction and sulfidation. The supplied catalyst was reported to contain 7% cobalt oxide and 22% molybdenum oxide by weight with the balance of alumina.

3.1.3 Packed-Bed Reaction System for Catalyst Screening Studies

The initial experimental reactor setup was shown schematically in Figure 4. Flow rates of H_2S, CO_2, H_2 and N_2 were controlled by needle valves and measured by rotameters. Before entering the reactor the inlet gases were first passed through a stainless steel manifold to obtain a well-mixed feed stream. The mixture flowed through a 6.35×10^{-3} m (1/4 inch) I.D. stainless steel tube and then into a 7.62×10^{-1} m (30 inch) long, 3.18×10^{-2} (1.25 inch) I.D. quartz tube reactor. The middle section of the reactor (3.05×10^{-1} m or 12 inch) was heated by a tubular furnace while the rest of the reactor extended out of the furnace and exposed to ambient air. One end of the exposed section was packed with quartz wool as a sulfur condenser. The catalyst bed was packed with approximately 40 grams of catalyst pellets and was supported on both sides by a plug of quartz wool. The exhaust gas from the reactor was flushed into a Bunsen burner and combusted before venting into the fumehood in order to destroy the odor of unreacted H_2S and other potentially hazardous chemicals. Five type-K thermocouples were inserted through the two ends of the reactor and were located at different positions of the reactor in order to monitor the temperature distribution inside the reactor. An additional thermocouple, which measured the temperature of the reactor tube wall, was connected to a temperature controller which could turn the furnace on and off according to a desired set-point temperature. The temperature distribution inside the reactor was recorded by a computer data acquisition system. During the course of experiments, gas products and unreacted reactants were analyzed by a gas chromatograph equipped with two different columns, one for sulfur compounds and the other for hydrocarbons. Elemental sulfur was collected from the condenser and weighed.

After using the reactor for several months, it was found that some modifications on the structure of the reactor were necessary in order to achieve better experimental results. The motivation was based on the fact that there was a significant temperature variation within the reactor, making the reactor non-isothermal. It was more obvious at the cooling zone which exposed to the ambient air. The temperature profile caused more quenching of sulfur vapor near the wall and less quenching at the centerline. It was observed that the sulfur did not condense uniformly in the cooling zone: more sulfur gathered on the wall. It was suspected that some sulfur vapor passed though the quartz wool (cooling zone) and condensed on the cooling tubes located downstream where the sulfur could not be collected. Because of the reversible nature of the H_2S decomposition mechanism, it was even possible that some degree of re-equilibration took place when the product gases were gradually cooled at the cooling zone of the reactor and some of the sulfur vapor might have recombined with H_2 to reform H_2S. This effect would be more significant to the reactor having larger dimensions. Also caused by a radial temperature profile inside the reactor, the temperature of the bed was higher at the wall and lower close to the center line of the reactor due to the heat transfer resistance of the porous catalyst pellets which are poor heat conductors. Since the thermocouple inside the catalyst bed was located close to the center of the reactor, it was measuring the lowest radial temperature of the catalyst bed. The best way to eliminate the temperature profile in this type of laboratory reactor was to reduce the reactor diameter.

With these considerations, siganificant modifications have been made on the experimental reactor system. By placing an appropriate condenser at the exit of the reactor, the possibility of re-equilibration was eliminated since the quench rate became significantly higher. The reactor satisfied the following specifications:

(1) It should be an once-flow reactor (no recycle).

(2) The temperature inside the catalytic reaction zone should be uniform radially as well as axially.

(3) The reactor wall is preferably transparent so that the catalyst color change or other phenomena can be observed during the experiment.

(4) It should be easy to load or unload catalysts.

(5) The results obtained from the reactor should be straight forward for analysis and should have a minimum interference due to structure or configuration.

(6) It should have a smooth connection with the quench zone.

(7) It should have a good sealing to prevent H_2S leakage in compliance with laboratory regulations.

(8) It should have a better heat transfer capability.

(9) It should be easy to monitor the reactor temperatures inside and outside the reactor tube.

The modified reactor design is shown schematically in Figure 5. The reactor was fabricated from a quartz tube of internal diameter $d_i = 1.27 \times 10^{-2}$ m (0.5 inch) and length $L = 3.048 \times 10^{-1}$ m (12 inch). The tubular Lindberg furnace which could raise temperature up to 1010°C was controlled by a standard temperature controller. Three type-K thermocouples were inserted into the quartz reactor and located at different positions of the reactor so that axial temperatures along the reactor could be measured simultaneously.

A schematic diagram of the overall modified experimental setup is shown in Figure 6. As the original experimental setup, the flow rates of H_2S, CO_2, H_2 and N_2 were controlled by needle valves and rotameters. The gases were first passed through a stainless steel manifold to obtain a mixture of reactants. The mixture was then flushed into the quartz tube reactor through $6.35x10^{-3}$ m (1/4 inch) stainless steel tube. The middle section of $2.54x10^{-1}$ m (10 inch) of the reactor was heated by a horizontal tubular furnace while the remaining length of the reactor was directly connected to a sulfur condenser. The catalyst bed contained approximately 5 grams of catalyst pellets and was constrained on both sides by a plug of quartz wool. The rest of the experimental setup was kept the same as the original setup. Water vapor was separated from the gas mixture by a water condenser. Separation of unreacted H_2S was made by using a 30 wt% diethanolamine bath. The exhaust gas was then flushed into a Bunsen burner and combusted before venting to the fumehood. Two K-type thermocouples, which measured the surface temperature of the reactor, were connected to a temperature controller which could turn the heater switch on and off according to a desired set-point temperature. The history of temperature distribution inside the reactor was recorded by a computer data acquisition system. The composition of the exit gas stream was analyzed by a gas chromatograph.

3.1.4 Apparatus for Absorption Test of Sulfur Vapor

The investigation was performed using two experimental systems. The first experimental system for adsorption of sulfur vapor on selected materials was schematically shown in Figure 7. Elemental sulfur was loaded in a Pyrex glass tube which was 1 inch in I.D. and 10 inches in length.

A total amount of sulfur was approximately 30 grams. Oxygen free nitrogen was used to purge the glass tube to maintain an inert environment. The flowrate was controlled by a rotameter with a needle valve. The adsorbents were loaded into a small basket made of stainless steel screen. The amount of adsorbent used in each run was approximately 400-500 mg. The Pyrex glass tube, containing the adsorbent basket and sulfur, was heated by a tubular furnace to reach the expected experimental temperature. Two K-type thermocouples were used in the system. One measures the temperature of the adsorbent basket, the other was connected to the tubular furnace which monitored the upper temperature limit.

All adsorbents were obtained from commercial sources. The adsorbents tested were alumina (two kinds of shape), CoO-MoO_3-alumina and activated carbon. Oxygen free nitrogen was purchased from Wright Brothers Inc., a distributor for the Matheson Gas Products. Sublimed sulfur powder was obtained from Fisher Scientific Inc. Cobalt-molybdenum (CoO-MoO_3-alumina, Crosfield 465, 1/20" extruded) was obtained from Crosfield Catalysts (4099 West 71st Street, Chicago, Illinois 60629). The alumina was purchased from Engelhard Corporation (120 Pine Street, Elyria, Ohio 44035). The activated carbon (mesh 12 x 40) was obtained from Autochem North America (Mineral Products Division, Three Parkway, Philadelphia, PA 19102).

The second experimental system for investigating adsorption of sulfur vapor is schematically shown in Figure 8. The system consists of two sulfur vaporizers, three temperature controllers and an adsorption bed. The vaporizers were made of stainless steel with the dimension of 2.5 inches in O.D. and 7 inches in height. The tube and connections were all made of 1/4 inch stainless steel. The temperature controllers (Omega, CN 9000A) and K-type thermocouples (O.D.

1/16") were obtained from the Omega Technologies Company (One Omega Drive, Box 4047, Stamford, Connecticut 06907). Flexible electric heating tapes (AWH-051-060DSP) were purchased from Amptek Company (P.O. Box 1381, Stafford, Texas 77497). During the experiment, the temperature of the first sulfur vaporizer was always set higher than that of the second one in order to generate completely saturated sulfur vapor. The saturated sulfur vapor pressure was estimated based on the relationship between the sulfur vapor pressure and temperature diagram shown in Figure 9.

3.1.5 Hybrid Reaction System - Catalytic Decomposition and Adsorption

The experimental setup for the hybrid reaction system was shown in Figure 10. The flow rates of H_2S, CO_2, H_2 and N_2 were controlled by needle valves and rotameters. The gases were then flown into the quartz tube reactor through 6.35×10^{-3} m (1/4 inch) stainless steel tube. The middle section of the reactor, 2.54×10^{-1} m (10 inch), was heated by a tubular Lindberg furnace which could achieve temperatures up to 1010°C. The remaining length of the reactor was directly connected to a sulfur condenser which was equipped with a water-cooled jacket. The catalyst bed contained approximately five grams of catalyst pellets and was supported by a stainless steel screen at the bottom. The adsorbents in the powder form could freely pass through the stainless steel screen support with the help of a mechanical vibrator. Separation of the unreacted H_2S was made by using a 30 wt% diethanolamine bath. The exhaust gas was then flushed into a Bunsen burner and combusted before venting to the fumehood. The system temperatures were monitored and controlled by K-type thermocouples. One thermocouple was used to measure the surface temperature of the reactor and the other was connected to a temperature controller which could turn the heater switch on and off according to a desired set-point temperature.

The most significant feature of the current setup was that the reactor was mounted on a frame structurally separated from the rest of the system and was driven by an electromagnetic vibrator purchased from Magic Flow Products Company (a Vibratory Equipment Division, 3105 Avalon Road, Carronlton, Ohio 44615). The added power of vibration made the adsorbents pass through the catalytic bed smoothly. At the bottom of the reactor, the reacted adsorbent was collected and then analyzed by the thermogravimetric analyzer (TGA) and total sulfur analyzer (TSA).

The detailed reactor structure is shown in Figure 11. The reactor was fabricated from a quartz tube of internal diameter $d_i = 1.27\times10^{-2}$ m (0.5 inch) and length $L = 3.048\times10^{-1}$ m (12 inches) and mounted on a metal frame connected with the electromagnetic vibrator. Three type-K thermocouples were inserted into the quartz reactor and located at different positions of the reactor so that axial temperatures in the reactor could be measured simultaneously.

3.2 Experimental Procedures

3.2.1 Synthesis of Catalyst

A Co-Mo catalyst was synthesized in our laboratory (in addition to that obtained from a commercial source). The catalyst was prepared by first dissolving ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot4H_2O$, 50.0 gram) and cobalt(II) nitrate ($Co(NO_3)_2\cdot6H_2O$, 20.0 gram) in 1000 ml water for 2 hours. The pH value of the solution was adjusted to 5.5 by adding 0.5M HNO_3.

Alumina pellets (100 gram, size of 1/8") were dried at 100°C in an oven in order to remove adsorbed vapors and then added to the solution. The temperature of the solution was kept at 25°C, and the pH value of the solution was always kept at 5.5 by using 0.5M HNO_3. The solution was brown-red in color and continually stirred by a magnetic stirrer. After 10 hours of mixing, the supported catalyst was collected by decantation. Then the catalyst was calcinated at 550°C for 5 hours under 1.18×10^{-5} m^3/sec (1.5 ft^3/h) of air flow in a quartz reactor in order to obtain a mixture of metal oxides CoO-MoO_3-alumina. A purple color was obtained in the catalyst indicating that both CoO and MoO_3 were deposited on the surface of alumina.

3.2.2 Preparation of Sulfided Catalyst

The preparation of sulfide catalyst is usually carried out by special preparation methods depending on the actual experimental conditions (Weisser et al., 1983). In most situations, an active sulfide catalyst is prepared by converting the corresponding oxide into the sulfide form.

For this process, the CoO-MoO_3-alumina was obtained from a commercial source (Crosfield Catalysts, 4099 West 71st Street, Chicago, Illinois 60629). The weight percentages of the ingredients were: 7% CoO, 22% MoO_3, and 71% alumina. A test was performed by using the thermogravimetric analyzer (TGA) to set up a procedure that the sulfide catalyst could be prepared by first reducing, then sulfiding the oxide catalyst into the sulfided form. Approximately 40 mg of the catalyst pellet was placed onto the weighing pan of the TGA. The catalyst was purged under oxygen-free N_2 (100 cm^3/min) at 200°C for 2 hours in order to remove any moisture and other possible adsorbed substances on the pellets. The purging step was stopped when the recorded weight reached a steady value after 40 to 50 minutes. Then, the pellets were reduced by using a pure hydrogen flow (50 cm^3/min) at 500°C for 24 hours to reduce CoO and MoO_3 into the metallic states of Co and Mo. The H_2 flow was turned off after the weight of the sample reached a steady value in about 10 hours. (The reduction time for the actual reactor was set to 24 hours to insure a thorough reduction.) After the reduction procedure, the catalyst changed its color from light blue to dark black. Finally, the pellets were sulfided by using a pure hydrogen sulfide flow (5 cm^3/min) at 500°C for one hour. The flow was turned off when the weight reached a steady value. The completion of sulfidation was also confirmed from the appearance of condensed bright yellow elemental sulfur on the tube wall at the exit of the TGA. According to the results of the material balance calculation, approximately 90% sulfidation was obtained in 20 minutes and the rest 10% sulfidation required another 60 minutes. It seemed that a longer time was needed to sulfide inside the pores of the catalyst pellets, and it was not clear when the sulfidation completed. Based on this TGA experiment, the period of 45 to 50 minutes was set as the time needed for sulfidation in the reactor. During the bench scale experiment which was carried out in the quartz reactor, visual method was also used to determine whether the sulfidation had been finished by observing the cold reactor section near the exit. When a trace amount of elemental sulfur was observed, it was assumed that the sulfidation was over and the catalytic reaction started.

3.2.3 Catalyst Screening Studies in Packed-Bed Reactor

One of the specific considerations for the catalytic sulfur recovery reaction was to operate the reactor at a temperature as low as possible to avoid sintering of the catalyst. As the vaporization temperature of elemental sulfur is approximately 444.6°C (Perry and Green, 1984), an operation below this temperature would result in deposition of elemental sulfur on the catalyst pellets as the reaction proceeded. In order to avoid both catalyst sintering and sulfur condensation on the catalyst, experiments were carried out at temperatures from 500 to 600°C. The overall system shown in Figure 6 was employed to measure the conversion of H_2S to elemental sulfur as a function of reaction temperature and operation time. The performance of a specific catalyst was evaluated by measuring the rate of conversion of H_2S as a function of H_2S feed concentration per unit time per catalyst weight in the reactor. The feed compositions were selected according to the results of thermodynamic analyses. The space time of the catalyst bed was varied from 0.5 to 2.0 minutes for a fixed bed with catalyst weighing approximately 5 grams. (The space time of the original catalyst bed was also varied from 0.5 to 2.0 minutes but contained approximately 40 grams of catalyst.) The catalyst bed temperature was varied from 500 to 600°C in order to evaluate the temperature effects on the equilibrium and the reaction rate. The following procedures were carried out.

(1) Nitrogen purge through the catalytic bed

The reactor was packed with approximately 5 grams of catalyst which occupied about one third of the heated zone of the reactor. At the beginning, a dry stream of oxygen-free N_2 (50 cm^3/min) passed through the catalyst bed at 200°C for about 1 hour in order to purge moisture and other adsorbed species on the catalyst. When the catalyst had been completely purged, while still maintaining the N_2 flow, the end of the cooling zone of the reactor was disconnected and the collected water droplets were removed. After the moisture was removed, a plug of quartz wool was placed in the cooling zone of the reactor so that it would act as a sulfur condenser to collect the elemental sulfur produced.

(2) Reduction of catalyst with H_2

The catalyst bed was heated to 500°C and the gas flow was switched from N_2 to H_2. Pure H_2 passed through the catalyst bed at a flow rate of 50 cm^3/min for 24 hours in order to reduce the metal oxides.

(3) Sulfidation of catalyst with H_2S

Once the catalyst had been reduced to its elemental form, the H_2 flow to the reactor was stopped and the temperature was adjusted to the sulfidation temperature of 500°C. During this period of time, the catalyst bed was kept under the dry oxygen-free N_2 flowing at 50 cm^3/min. Once the desired temperature was reached in the reactor, pure H_2S flowed through the reactor at the rate of 50 cm^3/min until the catalyst was totally sulfided. It took approximately 45 minutes to achieve full sulfidation.

(4) Production of elemental sulfur and synthesis gas from H_2S and CO_2

Once the catalyst had been fully sulfided, the H_2S flow to the reactor was stopped and the temperature was adjusted to a desired temperature from 500 to 600°C for H_2S decomposition reaction while maintained under the dry oxygen-free nitrogen purge gas. After the temperature had reached the desired value in the reactor, the mixture of H_2S and CO_2 flowed into the reactor and through the catalyst bed for 3 hours. The total flow rate and the ratio of H_2S to CO_2 were predetermined based on different experimental requirements. The elemental sulfur was condensed in the cooling section of the reactor. Gas products and unreacted reactants were analyzed by a gas chromatograph. A sample volume of 0.3 to 0.4 ml was taken at regular intervals from the reactor exit and injected into the GC for analysis. A number of tests were conducted for each set of experimental configuration in order to determine if any sulfur was produced. During the experiments, the reactor was also visually observed to monitor if any unexpected experimental phenomenon occurred.

(5) Collection of the sulfur product

At the end of each experiment, the reactant gases were turned off and the reactor was cooled down to room temperature under the dry oxygen-free nitrogen purge. Then the end of cooling zone of the reactor was opened to take out the quartz wool plug. The produced sulfur that had condensed on the quartz wool plug and inside wall of the reactor was washed by carbon disulfide (CS_2). The CS_2 solution containing the sulfur was collected in a beaker. And the CS_2 was evaporated in the fumehood and the sulfur in beaker was weighed. The quartz wool and the catalyst were weighed before and after each experiment as an additional method of determining if any sulfur was left behind.

3.2.4 Adsorption Test of Sulfur Vapor

Figure 9 shows the relationship of sulfur vapor pressure with temperature at 1 atm from three independent sources (Perry et al. 1984, Hultgren et al. 1973 and Barin et al. 1977). Due to the different research interests of the investigators, the sulfur vapor pressure data in these sources do not cover the same temperature range. However, they are consistent with each other in their tendencies and overlap areas within the temperature range of our interest and are sufficient for the present purpose. The figure shows that sulfur vapor pressure increases exponentially with the temperature. This feature makes the operating temperature of condenser very sensitive to the efficiency of sulfur removal from vapor phase. In order to experimentally investigate the effects of the different types of material on sulfur vapor condensation and adsorption, the following experimental procedures were performed during the tests.

(1) Sulfur was loaded into the Pyrex glass tube.

(2) The tube was purged with oxygen free nitrogen to make an inert environment.

(3) The furnace temperature was raised to 150°C. This step was necessary to minimize the initial condensation of sulfur vapor on adsorbent surface. Additional condensation might occur when there was a temperature difference between the hot glass tube and adsorbent basket containing the adsorbents.

(4) The adsorbent weighing 400-500 mg was loaded on to a small basket made of stainless steel screen. The basket was inserted into the tube.

(5) The furnace temperature was raised to the desired experimental value.

(6) Purging with oxygen-free N_2 was stopped when the desired temperature was reached.

(7) After a predetermined duration of time, the basket was removed and measured the weight change of the adsorbent.

3.2.5 Decomposition of H_2S with Adsorption of Sulfur

To investigate whether H_2S decomposition was enhanced by adsorbing sulfur away from the reaction zone, a series of experiments were performed using three different kinds of adsorbents in the reactor packed with catalyst according to the procedures described below.

(1) The catalyst bed was purged with N_2 (50 cm^3/min) at 120°C for 1 hour.

(2) The collected moisture was removed from the condenser.

(3) The bed was heated to 500°C while purging with N_2 (50 cm^3/min).

(4) The Co-Mo-alumina pellets were reduced for 24 hours under H_2 (50 cm^3/min).

(5) Inlet flow was switched to H_2S (50 cm^3/min) and the catalyst pellets were sulfided for 45 minutes.

(6) H_2S flow was regulated to 25 cm^3/min and CO_2 flow (25 cm^3/min) was switched on and the temperature was set to a desired level (450-550°C).

(7) The adsorbent feeder and the electromagnetic vibrator were turned on.

(8) The reaction was carried out for 20-30 minutes.

(9) The adsorbent was collected at the bottom of the reactor.

(10) The reaction was shut down by turning off the inlet gas flow and the heater.

(11) The collected adsorbent was analyzed by TGA and the total sulfur analyzer.

4. RESULTS AND DISCUSSION

4.1 Potential Catalysts and Related Experimental Materials

As described in the previous chapter, there was no established standard method for the preparation of the sulfide form of Co-Mo-alumina catalysts. A survey of the literature indicated that it was usually carried out by customized preparation methods that were highly dependent on actual experimental conditions. In most situations, an active metal sulfide catalyst was prepared by converting the corresponding oxide into the sulfide form. A test was performed by using the thermogravimetric analyzer (TGA) to set up a procedure that the sulfide catalyst could be prepared by first reducing, then sulfiding the oxide catalyst into the sulfided form. The method of preparation described in Chapter 3 was performed before they were used as a catalyst for the current experimental tests.

The chemicals used in this period of experiments were: hydrogen sulfide (C.P. grade liquid phase, 99.5%), carbon dioxide (Coleman Instrument grade, 99.99%), nitrogen (oxygen-free), and hydrogen (zero grade, impurities <1 ppm) purchased from Wright Brothers Inc., a distributor for the Matheson Gas Products. Carbon disulfide (purity, 99.95%) was obtained from Fisher Scientific Inc. Cobalt-molybdenum catalyst (CoO-MoO_3-alumina, Crosfield 465, 1/20" extrudate) was obtained without any charge, compliments of Crosfield Catalysts (4099 West 71st Street, Chicago, Illinois 60629). Alumina pellets were purchased from Engelhard Corporation (120 Pine Street, Elyria, Ohio 44035).

Three kinds of adsorbents were also selected for this period of investigation. Commercially manufactured activated carbon (100 mesh, product name: centaur powder carbon) was supplied by Galgon Carbon Corporation (P.O. Box 717, Pittsburgh, PA 15230-0717). Iron(II) sulfide (100 mesh, 999.9% purity) was purchased from Aldrich Chemical Company (P.O. Box 355, Milwaukee, WI 53201-9358). Sulfided Co-Mo-alumina powder was prepared in our laboratory by first sulfiding the commercial Crosfield catalyst then grinding it into 100 mesh powder under an inert environment.

4.2 Preparation of Analytical Techniques and Instruments

4.2.1 TGA

A thermogravimetric analyzer (Thermal Analyst 2000, Du Pont Instruments 951 TGA) was used during the preparation to monitor the sample weight as a function of temperature and time. The weight of solid particles was recorded against temperature or time when the gas passed through the sample catalyst. In this way, the TGA was used to investigate the kinetics of gas-solid reactions by measuring the weight of sample. The TGA was also used to test the thermal stability under different heating conditions. It was a valuable instrument in establishing the procedure of preparation for the sulfided catalyst from the oxide form. The catalyst oxide pellets were loaded into the TGA and determined what extent or the amount of time was needed to reduce or sulfide. Approximately 40 mg of sample was used in the TGA, which consisted of several oxide catalyst pellets.

4.2.2 Preparation and Calibration of Gas Chromatograph

A Gas Chromatographic (GC) analysis was utilized to obtain qualitative and quantitative determination of the products. A Perkin Elmer (Sigma 300 model) Gas Chromatograph equipped with a hot wire detector and two separate injectors was selected to conduct this analysis. Two new columns were installed in the same GC unit for detecting CO, CO_2, CH_4, H_2, H_2S, COS and CS_2. Column A was for sulfur containing substances such as H_2S, COS and CS_2, and column B was for CO, CH_4 and H_2. The operating temperature for the GC was programmed as follows:

Injector temperature:	315°C
Oven temperature:	75°C
Detector temperature:	325°C

Helium was used as a carrier gas. The GC was calibrated by using pure sample gases (CO, CO_2, CH_4, H_2, H_2S, COS and CS_2). The flow rate of the carrier gas was set at 26 cm^3/min for both column A and column B. Column A [Chromosil 310, 2.4 m/8 ft (1.83 m/6 ft packed) x 1/8 inch OD, Teflon (FEP)] and Column B (18 ft x 1/8 inch SS, packed with Silica Gel, 60/80) were obtained from SUPELCO (SUPELCO, Inc., Supelco Park, Bellefonte, PA 16823-0048) and Alltech (Alltech Associates, Inc., 2051 Waukegan Road, Deerfield, IL 60015-1899), respectively. The standard sample gases for calibration (CO, CO_2, CH_4, H_2, H_2S, COS and CS_2) were purchased from Wright Brother Inc. and CS_2 from Fisher Scientific Company.

4.3 Temperature Profile in the Quartz Reactor

Before the reactor modification (Figure 4), temperature profiles inside the reactor were measured by inserting type-K thermocouples at different positions of the reactor. The reactor was heated by a tubular Lindberg furnace. Three different operating temperatures, 550°C, 650°C and

750°C, were investigated in the empty bed and the bed packed with quartz wool for varying flow rates of N_2. The measured temperature curves are shown in Figures 12-14. The results showed that the temperature remained relatively uniform in the reaction zone (about 5 to 6 inches long in the middle of the reactor).

After the reactor modification (Figure 5), the temperature profile inside the reactor was measured by inserting type-K thermocouples at different positions of the reactor and the condenser. The corresponding positions at which the temperature was measured are shown in Figure 15. The reactor was heated by a horizontal tubular Lindberg furnace. The condenser was cooled by tap water. Several temperatures (500°C, 600°C, 700°C and 800°C) and flow rates of N_2 were chosen for the investigation of the empty bed and the bed packed with quartz wool. The measured temperature curves are shown in Figures 16-17. The result shows that the temperature remained relatively uniform in the proposed reaction zone (about 5 to 6 inches long in the middle of the reactor) (Figure 5) and the pattern of the temperature profile was not affected by the flow rate of inlet gas. When the exit gas reached about 3 to 4 inches in distance, its temperature almost reached the cooling water temperature around 10°C. The modified reactor was designed to quickly quench the exit gas so that the occurrence of re-equilibration of reaction products would be prohibited. The temperature profile is valuable data for the interpretation of future experimental results.

4.4 Thermal Stability of the Co-Mo Catalyst v.s. Its Specific Surface Area

Measurement of specific surface area was a part of the catalyst characterization procedure.

A Quanta Chrome Surface Area Analyzer was used in conjunction with the thermogravimetric analyzer (Thermal Analyst 2000, Du Pont Instruments 951 TGA). The purpose of using the TGA was to test the thermal stability under different heating conditions. Before the thermal stability test, the specific surface area of the vender-supplied catalyst was 96 m^2/gram. The thermal tests were carried out for two hours using two different gases, dry air and pre-purified nitrogen. Figure 18 shows the weight loss of the catalyst with dry air. Figure 19 shows the weight loss of the catalyst with nitrogen. The longer the test time of the catalyst, the more percentage of weight loss. After 2 hours of heating, the weight of the catalyst reached at a stable value for each experimental temperature. The higher temperature did not always result in the higher percentage of weight loss. Figure 20 shows the specific area changes under the different purge gases. Increasing the temperature resulted in reduction of the specific surface area of the catalyst. The purge-gas flow rate of both gases was set at 10 cm^3/sec during the thermal tests.

4.5 TGA Results of Catalyst Sulfidation

Catalyst sulfidation results from the TGA are shown in Figure 21. The method for catalyst preparation consists of three steps. The first step, as depicted in Figure 21(a), consisted of removing the moisture and other unreacted content of the oxide catalyst (approximately 8-9%) by purging for 1 hour under N_2 at 200°C.

Following the purge, the next step consisted of reducing the catalyst under H_2 at approximately 500°C. An indication that reduction was taking place was a color change from blue to dark black. Figure 21(b) showed that 80% reduction was achieved after 3 hours of reduction and 90% reduction after 24 hours. The percent reduction was calculated on a dry catalyst basis.

As shown in Figure 21 (c), the sulfidation step took place rapidly. Within the first five minutes, the catalyst was sulfided approximately 20% on the molar basis of reducible metal. The plateau reached after five minutes of sulfidation indicated that additional sulfidation required a longer time and might not be necessary. Since after 20% of the catalyst was sulfided, it was capable of acting as an effective catalyst for H_2S decomposition to produce elemental sulfur. This was confirmed by the observation of condensed elemental sulfur on the reactor walls at the exit of the furnace during the sulfidation experiment.

According to the material balance calculation, approximately 90% sulfidation was obtained within 20 minutes and the rest 10% sulfidation required another 60 minutes presumably due to the pore diffusion through the catalyst pellets. Based on these TGA experiments, sulfidation time was set at 45 to 50 minutes for packed-bed reactor experiments. During the screening study, visual observation was made to determine whether the sulfidation had been finished by inspecting the reactor cooling section. When trace amount of element sulfur was observed, it was assumed that the sulfidation was over and the catalytic reaction had started.

4.6 Decomposition of H_2S under Non-Catalytic Conditions

The purpose of these experiments was to record reference conditions for comparison with catalytic reactions. Non-catalytic decomposition of H_2S at these temperatures was expected to be both kinetically and thermodynamically unfavored.

Experiments were carried out under 1 atm with pure H_2S in order to obtain base-line decomposition data which would be used to compare with those of catalytic decomposition. The experimental apparatus was described in Chapter 3. The experimental temperatures were between 500 and 600°C in consideration of the catalyst which required a lowest possible temperature to avoid sintering of active site while maintaining high reaction rates. As the vaporization temperature of elemental sulfur was approximately 444.6°C (Perry et al., 1984), an operation below this temperature would result in deposition of elemental sulfur on the catalyst pellets as the reaction proceeds. In order to avoid both catalyst sintering and sulfur condensation on catalyst, the limits of experimental temperature were chosen to be 500 and 600°C.

Experiments were conducted in the reactor packed with the quartz wool and the blank alumina pellets. The reactor was first purged with pure nitrogen, 50 cm^3/min, at 200°C for one hour in order to remove moisture and other adsorbed species from the bed. Nitrogen was then switched to H_2S for 6 hours with the flow rate of 50 cm^3/min at the experimental temperature of 500°C or 600°C. The results indicated that only a trace amount of sulfur was condensed at the exit of the reactor even at 600°C.

4.7 Decomposition of H_2S under Catalytic Conditions

4.7.1 Pure H_2S Feed

To test that H_2S decomposition was kinetically favored by using the CoO-MoO_3-alumina catalyst, a number of experiments were performed in the reactor packed with catalyst pellets according to the procedures as described in the previous chapter:

(1) The catalyst bed was purged with N_2 (50 cm^3/min) at 200°C for 1 hour.

(2) The collected moisture was removed from the cooling zone of the reactor.

(3) The bed was heated to 500°C with N_2 (50 cm^3/min).

(4) The bed was reduced for 24 hours under H_2 (50 cm^3/min).

(5) The flow was switched to H_2S (50 cm^3/min) and the bed was sulfided for 30 minutes.

(6) The decomposition reaction was carried out for about 6 hours under pure H_2S flow (50 cm^3/min) at a set temperature (500, 550 or 600°C).

(7) The reactor was cooled down under N_2 (50 cm^3/min).

(8) The produced sulfur was collected.

The experimental results from the quartz tube reactor were summarized in Table 1. The amount of sulfur in the feed stream was calculated from the total volume of H_2S that was introduced into the reactor.

The H_2S conversion to sulfur is defined as:

$$Conversion\,of\ H_2S\ \% = \frac{2(Moles\ of\ S_2\ produced)}{Initial\ moles\ of\ H_2S}\ x\ 100$$

The conversions were within a reasonable range from the thermodynamic equilibrium value which was about 1% at 500°C.

4.7.2 H_2S - CO_2 Feed

Since H_2S also reacts with CO_2, the H_2S decomposition reaction could be shifted to the product side and more sulfur could be produced as shown by the thermodynamic analyses in

Chapter 5. Experiments were performed with the feed mixture of H_2S and CO_2 at various ratios for 6 hours. The catalyst used was the commercially available CoO-MoO_3-alumina. The experiments were carried out in the reactor following the similar procedure as described before. The key differences were that CO_2 was added into the feed and the flow rates were adjusted accordingly.

The purpose of this test was to find out the effect of CO_2 on H_2S conversion and to compare the H_2S conversion with the equilibrium value. The secondary purpose of this test was to test the reaction mechanism proposed by Liptak (1974). Our experiments were performed within the medium temperature range from 500 to 600°C. No methane (CH_4) was detected at 550°C using the GC, indicating that the CH_4 concentration was probably below the detectable level of 100 ppm.

A summary of the experimental results are listed in Table 1. Although some H_2 and CO were detected (3.24% and 0.98%, respectively), no SO_2, COS and CS_2 were present. As one can see in Table 1, the conversion of H_2S to elemental sulfur increased significantly with the introduction of a catalyst. Therefore, it was experimentally demonstrated that the Co-Mo sulfided catalyst was a good candidate for the decomposition of H_2S to elemental sulfur. The equilibrium conversion for the inlet ratio of H_2S to CO_2 of 4 was 5.62% at 550°C. The difference between the equilibrium and the experiment values was due to the fact that the reaction inside the reactor did not reach equilibrium. The experimental values were reasonably close to the thermodynamic equilibrium value. This level was still too low to be considered for a large scale industrial application using the present mode of operation.

4.8 Adsorbability of Elemental Sulfur on Solid Adsorbents

The investigation was performed on two experimental systems. The first experimental system for adsorption of sulfur vapor on selected materials was schematically shown in Figure 7. (The experimental procedure was discussed in Chapter 3.) The results of the experiments are tabulated in Tables 2 and 3. Four different types of adsorbents were tested during the investigation. They were alumina (with two different shapes), CoO-MoO_3-alumina and activated carbon.

The experimental results are also plotted in Figure 22. The results indicate that activated carbon was the best adsorbent among the four adsorbents tested. The amount of sulfur adsorbed on the activated carbon did shown an increase with time, though equilibrium values were not reached within the duration of the experiments. Capillary condensation occurring in the pores might be responsible for this behavior. In the case of alumina pellets (both spherical and cylindrical types, size of 1/8"), adsorption of sulfur almost remained constant for 3 hours. At higher temperatures above 420°C, oxidation of activated carbon was observed because of leakage of air in the tube even though the purge step was performed prior to the experiment. For the equal period of experiment, the amount of sulfur adsorbed on activated carbon at lower temperature (e.g. 220°C) was smaller than that of at high temperature (e.g. 290°C). It was due to the fact that the lower the system temperature, the less vaporized sulfur (Perry et al. 1984, Hultgren et al. 1973 and Barin et al. 1977) was available for adsorption (low partial pressure of sulfur). The results proved that this adsorption process may be capable of removing sulfur vapor from high-temperature gas mixtures, such as H_2S and CO_2, and promoting the conversion of H_2S.

The first experimental system, shown in Figure 7, was not equipped to control the sulfur vapor mole fraction quantitatively with respect to the experimental temperature. It did not provide an oxygen free environment for the investigation. Therefore, the second experimental system, shown in Figure 8, was built incorporating numerous improvements on the experimental system. The experimental results proved that the second system for sulfur vapor adsorption could be operated at higher experimental temperatures to investigate the condensation and adsorption effect of sulfur vapor on activated carbon without oxidizing it. The second system could control the sulfur vapor pressure effectively through its two sulfur vapor generators and extend the range of experimental temperature. Using the second system, it was expected to find at what temperature sulfur vapor could be effectively condensed or adsorbed by activated carbon. However, due to the fact that the stainless tubing which linked between the sulfur tanks and the adsorption bed was frequently blocked by condensing sulfur, the experiment could not run as smoothly as originally planned. Another fact was that the corrosive nature of sulfur vapor on the adsorption bed at a high temperature caused difficulty in making the material balance of activated carbon samples before and after adsorption, even though the adsorption bed was made of stainless steel. Due to these problems, useful experimental data could not be generated from the second system.

4.9 Simultaneous Sulfur Adsorption and Catalytic Reaction in a Packed-Bed Reactor

Based on the above experimental results of adsorption of sulfur vapor on activated carbon, a new experimental design shown in Figure 10 was set up. Inclusion of activated carbon in the H_2S decomposition reaction was carried out at temperatures between 450 and 550°C. The process combined with two unit operations: catalysis and adsorption. The motivation of this phase of experiment was based on the experimentally measured adsorption of elemental sulfur on various adsorbents near the reaction temperature. In order to find out whether it was applicable to the H_2S decomposition reaction system, experiments were performed using various adsorbents flowing through the reactor along with the reactant gas. Three kinds of adsorbents were selected: activated carbon, iron sulfide (FeS) and sulfided Co-Mo-alumina catalyst. They were all prepared in the size of 100^+ mesh fine powders.

Various designs of adsorbent feed system were tested including a small scale jet pump, a screw feeder and a vibrating and rolling feeder. The experimental tests proved that the vibrating and rolling feeder system performed best for the current experimental setup. All adsorbents could easily pass through the packed-bed with vibration.

The collected adsorbents were analyzed by Thermogravimetric Analysis (TGA) (Thermal Analyst 2000, Du Pont Instruments 951 TGA) to determine the amount of adsorbed sulfur on the adsorbent. Each analysis consisted of two steps: (1) heating approximately 30 mg of the sample under ultra high purity helium over the temperature range of 25 to 700°C at a heating rate of 10°C/min; (2) keeping at 700°C for a period of time until no significant weight loss was detected to insure no volatile contents remaining on the adsorbent.

The experimental results from TGA are tabulated in Table 4. For the activated carbon and sulfided Co-Mo-alumina catalyst powders, the TGA analyses showed that around the sulfur boiling point of 444.6°C (Perry and Green, 1984) the weight loss of the adsorbents was between 4 to 6%. For the iron sulfide powders, no significant percentage of weight loss was observed. All three types of adsorbents had additional weight loss between three to four, when the TGA temperature reached 700°C.

Besides the TGA analyses, desorption tests were also performed. The collected samples of the adsorbents were placed into a horizontal quartz tube and purged by a flow of oxygen-free nitrogen gas at 20 cm^3/min. The quartz tube was heated by a tubular furnace gradually raising the temperature from the room temperature (~21°C) to 700°C in order to observe whether there was any elemental sulfur condensed at the exit of the quartz tube. Only trace amounts of elemental sulfur were observed and were below the amount required for quantitative measurement.

Total Sulfur Analyser (TSA) (Leco Corporation, 3000 Lakeview Ave., St. Joseph, MI 49085) was used for the additional analyses of sulfur from activated carbon. As tabulated in Table 5, the tests results showed that activated carbon adsorbed up to 9 weight percent of sulfur. Probably, there was some portion of the sulfur chemisorbed on carbon (Walker, 1970) although physical adsorption was expected from the experiments.

Even though the adsorption of pure sulfur vapor was shown to be effective utilizing activated carbon, the current experimental results showed that it might not be applicable to the H_2S decomposition system due to the fact that sulfur could be chemisorbed on activated carbon and some carbon might be participating in the H_2S decomposition reaction. The idea of combining two unit operations of catalytic decomposition and selective adsorption should be further developed to overcome the problems of chemisorption and short contact times of adsorbents in the reactor.

5. THERMODYNAMIC ANALYSIS AND SIMULATION

5.1 Reaction System and Assumptions

A part of the project was to study the feasibility of producing methane from hydrogen sulfide (H_2S) and carbon dioxide (CO_2) in addition to elemental sulfur. Thermodynamic simulations were carried out in order to understand the thermodynamic limits and reaction mechanisms within the reaction system. The proposed overall reaction was as follows (Paushkin, 1988):

$$4\ H_2S + CO_2 \rightleftharpoons 2\ S_2 + CH_4 + 2\ H_2O \qquad (5\text{-}1)$$

The basic idea of the reaction was that a rich gas stream of H_2S and CO_2 passed through a high temperature catalyst bed to form elemental sulfur, methane and water vapor. Although the reaction had been described to be effective, detailed thermodynamic analyses could not be found in the open literature.

In the simulation, the feed ratios of H_2S and CO_2 were changed depending on the interest of analysis. The reaction temperatures ranged from 100°C to 1100°C, and the pressure was kept at 1 atm for the most calculations. Gas components in the reaction system were CH_4, CO, COS, CO_2, CS_2, H_2, H_2O, H_2S, SO_2 and S_2. Although the sulfur actually consisted of various allotropes (Kaloidas et al, 1987 and Rau et al, 1973), only S_2 was considered in the simulation due to the fact that this approximation proved to be very close to the sum of all allotropes.

5.2 Background of the Simulation Software and Data

Computer simulations for the reaction of H_2S and CO_2 were performed using the Stanjan program (Reynolds, 1987) and the JANAF Thermochemical Tables (Stull et al., 1971 and Chase et al., 1985) as the source of original thermochemical data. The software package, created at Stanford University, minimizes the Gibbs free energy function to predict the equilibrium composition of a mixture of compounds. Based on the input stream composition and given set of temperature and pressure, the program calculates the equilibrium mole fractions of the system.

5.3 Enthalpy and Gibbs Free Energy

Reaction (5-1) could be divided into the following possible sub-reactions:

$$H_2S = H_2 + 0.5\ S_2 \qquad (5\text{-}2)$$

$$CO_2 + H_2 = CO + H_2O \qquad (5\text{-}3)$$

$$CO_2 + 4\ H_2 = CH_4 + 2\ H_2O \qquad (5\text{-}4)$$

$$CO + 3\ H_2 = CH_4 + H_2O \qquad (5\text{-}5)$$

At 500°C and 1 atm, the Gibbs free energies, the heats of reaction and the corresponding equilibrium constants are:

Reaction (5-2)	$\Delta G = 55.48$	kJ/mol,	$K=4.5\text{x}10^{-14}$
	$\Delta H = 88.58$	kJ/mol	Endothermic
Reaction (5-3)	$\Delta G = 10.15$	kJ/mol,	$K=3.6\text{x}10^{-3}$
	$\Delta H = 37.13$	kJ/mol	Endothermic
Reaction (5-4)	$\Delta G = -50.21$	kJ/mol,	$K=1.2\text{x}10^{12}$
	$\Delta H = -230.14$	kJ/mol	Exothermic
Reaction (5-5)	$\Delta G = -32.24$	kJ/mol,	$K=5.6\text{x}10^{7}$

$\Delta H = -185.21$ kJ/mol Exothermic

The values of ΔH and ΔG as a function of temperature are shown in Figures 23-26. The rate limiting step is the decomposition of H_2S (reaction 5-2). An increase in temperature would shift reactions (5-2) and (5-3) to the product sides, and shift reactions (5-4) and (5-5) to the reactant sides. Furthermore, an increase in pressure would shift reactions (5-4) and (5-5) to the product sides.

5.4 Simulation Results

Since experiments were performed within a specific range of temperatures at atmospheric pressure and with only a couple of specified ratios of H_2S to CO_2, testing a wide range of values of each parameter were desirable and carried out in simulation to determine the effects of parameters. Equilibrium calculations for the decomposition of H_2S with CO_2 were made using the Stanjan method (Reynolds, 1987) with the JANAF thermochemical tables (Chase et al., 1985).

5.4.1 Equilibrium Distribution of H_2S and S_2

Figures 27-28 show the equilibrium mole fraction of H_2S as a function of temperature and pressure with the inlet ratios of H_2S to CO_2 between one and nine. Because both the H_2S decomposition reaction and the water-gas shift reaction were endothermic, the H_2S mole fraction decreased as the system temperature increased. The H_2S mole fraction increased as the system pressure increased enabling the H_2S decomposition reaction to shift to the left. Figures 29-30 show the equilibrium mole fraction of S_2 as a function of temperature and pressure.

5.4.2 Conversions of H_2S

Figures 31-32 show the equilibrium conversions of H_2S as a function of the ratio of H_2S to CO_2 (from 0.001 to ∞) and temperature (from 100 to 1000°C). The highest conversion is obtained at the highest temperature and at the lowest ratio of H_2S to CO_2. When the temperature drops below 500°C with the H_2S/CO_2 ratio of 4 (80% of initial H_2S in H_2S and CO_2 mixture), the conversion of H_2S becomes almost the same level as the case without CO_2 present. Figures 33-34 show the effect of increasing the initial percentage of H_2S in the H_2S and CO_2 mixture on the equilibrium conversion of H_2S at several specific temperatures (500, 550, 600, 700, 800, 900 and 1000°C). The equilibrium conversion decreases with increasing initial percentage of H_2S. Figures 35-36 show the effect of temperature on the equilibrium conversions of H_2S when the initial percentage of H_2S was 11% and 80%, respectively. The equilibrium conversion increases with increasing temperature.

5.4.3 Yields of S_2

Figures 37-38 show the equilibrium yields of S_2 as a function of temperature and the initial ratio of H_2S to CO_2. The highest yield is obtained at the highest temperature and at the ratio of H_2S to CO_2 around 8.09 (11% of H_2S in the H_2S and CO_2 mixture). When the ratio of H_2S to CO_2 equals 4 and the temperature drops below 500°C, the yield of S_2 becomes almost the same level as the case without any CO_2 present. Figures 39-40 show the effect of increasing the initial percentage of H_2S on the equilibrium yield of S_2 at several specific temperatures. The equilibrium yield first increased with increasing initial percentage of H_2S then it decreased as the initial percentage of H_2S reached higher values. Figures 41-42 show the effects of temperature on the equilibrium yields of S_2 when the initial percentage of H_2S was set at 11% and 80%, respectively. The figures indicated that equilibrium yield increased with temperature.

5.4.4 Selectivity of S_2

Figures 43-44 show the equilibrium selectivity of S_2 as a function of temperature and the ratio of H_2S to CO_2. The highest selectivity is obtained at the highest temperature and at the highest initial ratio of H_2S to CO_2. But there were some exceptions, for example, when the system temperature went below 700°C, there was a small peak at low percentages of H_2S (between 0.1-6% depending on the temperature). When the temperature droped below 500°C with an H_2S/CO_2 ratio of 4, the selectivity of S_2 became less than 20.0%. Figures 45-46 show the effect of increasing the initial percentage of H_2S on the selectivity of S_2 at several specific temperatures. The values of selectivity were not sensitive to the initial H_2S percentage ranging from 10% to 80% at all temperatures investigated. Figures 47-48 show the effect of temperature on the selectivity of S_2 when the value of the initial percentage of H S_2 was 11% and 80%, respectively. The selectivity increased with temperature.

5.4.5 Continuous Removal of Sulfur

This part of the thermodynamic simulation was to study the feasibility of producing CH_4 from H_2S and CO_2 in addition to elemental sulfur. The basic idea of this reaction was that a rich gas stream of H_2S and CO_2 passed through a high temperature catalyst bed to form elemental sulfur, methane and water vapor. A stoichiometric feed ratio was chosen first for the simulation (80 mole % of H_2S and 20 mole % of CO_2). The reaction temperature ranged from 450°C to 1100°C, and the pressure was kept at 1 atm. Possible gas components after the reaction were CH_4, CO, COS, CO_2, CS_2, H_2, H_2O, H_2S, SO_2 and S_2.

As previously mentioned, recycle and multiple reaction zones are necessary for reaction (5-1) to progress to any appreciable extent. The thermodynamic limiting step of the overall reaction is the decomposition of H_2S (reaction 5-2). The initial ratio of H_2S to CO_2 is set to 4 which matches the stoichiometric ratio of reaction (5-1). The H_2S decomposition reaction and the water-gas shift reaction were endothermic, therefore the H_2S mole fraction decreased as the system temperature increased causing greater formation of sulfur and CO. However, the methanation reaction is exothermic, therefore the mole fractions of CO and CO_2 decrease as the system temperature decreased producing more CH_4. These two opposing facts require that the system must be divided into at least two reaction zones and at least one product should be removed from the system to prevent re-equilibrium to occur as the system temperature was lowered. We propose that the sulfur be continuously extracted from the reaction zone by means of condensation or adsorption/absorption. At the end of the reaction, the system would eventually cool down to room temperature at 25°C.

An example is listed in Table 6, where the reaction temperature was 900°C in zone one and gradually cooled down to 25°C in zone two. The results strongly support the concept of continuous removal of sulfur from the reaction zone and clearly demonstrate the feasibility of reaction (5-1). The significance of this simulation was that sulfur was removed from each equilibrium stage. After the sulfur was removed, the residues were fed into the next stage to react. This process continued until the efficiency of sulfur removal became very low. The thermodynamic limitation was controlled by the sulfur vapor pressure of the condensed phase. The equilibrium mole fractions of the species at the first stage before sulfur extraction are listed in Table 7. The final product distributions at various reaction temperatures are listed in Table 8. Table 9 shows the product distribution after the temperature decreased to 25°C. The H_2 mole fraction became lower in the presence of CO_2 since CO_2 and reacted with H_2 to form H_2O and CO. The equilibrium was shifted to favor the formation of elemental sulfur. Now, CO, CO_2 and H_2 could form CH_4 while the system cools down to room temperature.

(1) Production of CH_4:

Figure 49 shows the equilibrium mole fraction of CH_4 as a function of temperature from 450 to 1100°C. The high mole fraction of CH_4 was obtained at low reaction temperatures since the methanation reaction is exothermic. When the reaction temperature was around 500°C, the mole fraction of CH_4 was 1.5%. As shown in Figure 50, when the reaction temperature in zone one was maintained at 950°C and the outlet gas from zone one gradually cooled down to 25°C in zone two (this step favors the formation of CH_4), the mole fraction of CH_4 in zone two reached 32%. Higher reaction temperatures promoted greater H_2S decomposition into H_2 and S_2. Since sulfur was removed at each equilibrium stage, there was less chance for regeneration of H_2S to occur. High mole fractions of H_2 in the system favored the methanation reaction to form CH_4.

Figure 51 shows the effects of reaction temperature and the number of theoretical stages on the equilibrium mole fraction of CH_4 in zone one. Low temperature in zone two and a large number of stages favored the methanation reaction. The majority of CH_4 was formed in zone two which acted as a methanation reactor.

(2) Production of H_2:

Figure 52 illustrated the equilibrium mole fraction of H_2 as a function of temperature when the system reached its final equilibrium stage where no more sulfur could be extracted from zone one. Between 450 and 1100°C, higher reaction temperatures promoted higher mole fractions of H_2. When the reaction temperature was around 900°C, the mole fraction of H_2 levels off at 62%. Above 900°C the H_2 mole fraction did not increase significantly. The system was allowed to cool down gradually to 25°C (Figure 53) without the need of quenching because virtually no re-equilibration occurred. Most of the H_2 reacted with CO and CO_2 to form CH_4 which depleted its mole fraction down to 2.9% for the first zone temperature above 900°C, and down to almost 0.0% below 900°C. The effects of the reaction temperature and the number of theoretical stages are shown in Figure 54. This study has indicated that high temperatures coupled with the requirement for many stages favored the production of H_2 in the first reaction zone.

(3) Production of CO:

Figure 55 shows the relationship of the equilibrium mole fraction of CO with reaction temperature when the system reached the final equilibrium stage. Because the water-shift reaction was endothermic, the higher mole fraction of CO was achieved at a high reaction temperature. At 700°C, the mole fraction of CO reached 11.4% and thereafter monotonically increased, reaching 17.3% at 1100°C. Considering that the initial concentration of CO_2 was 20%, the conversion of CO_2 was high. When the system cooled down to 25°C (Figure 56) the mole fraction of CO dropped down to less than 1 ppm. Figure 57 shows the effect of reaction temperature on the equilibrium mole fraction of CO. Results from this study indicate that high temperatures coupled with the requirement for many stages favored the production of CO in the first zone.

(4) Consumption of H_2S:

Figure 58 shows the final equilibrium mole fraction of H_2S as a function of temperature. The initial concentration of H_2S was set at 80% to match the stoichiometric ratio in reaction (5-1). The mole fraction of H_2S continually went down as the reaction temperature went up. At 900°C, the mole fraction of H_2S was only about 3.3%. There was only a small amount of re-equilibrium occurring after cooling down to 25°C. (See Figures 58 and 59.) Figure 60 shows that high temperatures coupled with the requirement for many stages favored the H_2S decomposition reaction in the first reaction zone.

(5) Consumption of CO_2:

The pattern of the CO_2 mole fraction change was similar to that of H_2S. Figure 61 shows the final mole fraction of CO_2 continually decreasing with the increasing reaction temperature due to the fact that the water-shift reaction was endothermic. When the reaction temperature reached

900°C, the mole fraction of CO_2 was only about 3.1%. As the system cooled down to 25°C (Figure 62), most of the CO and CO_2 reacted with H_2 to form CH_4. Figure 63 also indicated that high temperatures coupled with many stages favored the water-shift reaction.

(6) Production of H_2O:

Figures 64 and 65 show the equilibrium mole fraction of H_2O as a function of temperature when the system reached the final equilibrium. The high mole fraction was obtained at high reaction temperature.

(7) Production of COS and CS_2:

Within the temperature range being investigated, the equilibrium mole fractions of COS and CS_2 were very small (Figures 66 and 67) when the system reached its final equilibrium stage.

(8) Production of SO_2:

Between the reaction temperatures of 450 to 1000°C, the equilibrium mole fraction of SO_2 was always less than 1 ppm (Figures 68-70) when the system reached its final equilibrium stage.

(9) Production of S_2:

Figures 71 and 72 show the final equilibrium mole fractions of S_2. The highest number of stages up to 10,000 was used in order to find the final extraction equilibrium point. However, when the number of stages increased over 3000, the calculation reached beyond the significant figures of the computer. All the results of equilibrium calculations in the report were based on the first 1,000 stages.

Sulfur vapor pressure affected the condensation efficiency of sulfur which defined the limit for extraction of sulfur from the reaction system. The temperature of the condensed phase is between the sulfur melting point at 112.8°C and the boiling point at 444.6°C (Perry et al, 1984) at 1 atm. The relationship of sulfur vapor pressure with temperature determines the optimum value of reaction temperature in the first and second zones. It also determines the number of stages needed to reach a practical equilibrium limit in a bench scale experiment.

Figure 9 illustrates the relationship of sulfur vapor pressure with temperature at 1 atm from three independent sources (Perry et al, 1984, Hultgren et al, 1973 and Barin et al, 1977). Sulfur vapor pressure increased exponentially with the temperature. This feature made the operating temperature of condensed sulfur very sensitive to the sulfur removal efficiency. High sulfur vapor pressure in the system would inhibit sulfur condensation although high temperature would favor the main reaction to decompose H_2S and save the total cost of energy usage. Therefore, there was determined to be a set of optimum values for each system configuration.

During the simulation, the effect of sulfur vapor pressure was taken into account and the condensed sulfur temperature was arbitrarily set as 150°C. This temperature was not yet an optimum temperature but it would help us to demonstrate the changes in H_2S conversion and sulfur yield as functions of the operating temperature and the number of stages under the influence of sulfur vapor pressure. From Figure 9, the sulfur vapor pressure at 150°C is estimated to be $2x10^{-4}$ atm. After repeating the calculations with this sulfur pressure, the maximum number of stages was dropped to 220 from 10,000.

Figure 73 shows the effects of reaction temperature (from 450 to 1100°C) and the number of theoretical stages (form 1 to 220 stages) on the equilibrium conversion of H_2S. In general, a high conversion was obtained at a high temperature and a large number of stages. The increase in temperature had a greater positive effect on the conversion due to the endothermic nature of H_2S decomposition reaction. When N equaled to 1, the curve represents a single stage or a once-through flow reactor. As the number of N increased, H_2S conversion did not increase proportionally with N values. If the reaction temperature was fixed, the relationship of the conversion versus the number of stages N could be summarized by the following approximate equation:

$$\text{Conversion of } H_2S = a(T) + b(T) \bullet LOG_2(N) \quad (650 < T < 1000°C) \qquad (5\text{-}6)$$

where a(T) and b(T) are the functions of reaction temperature shown in Figure 74. It was true that the higher the number of N, the higher the H_2S conversion, however, this also meant the larger the dimension of the reaction system. Another feature illustrated in Figure 73 was that a multiple stage system had more positive effects on the H_2S conversion at higher reaction temperatures.

Figure 75 shows the effects of reaction temperature and the number of theoretical stages on the equilibrium yield of sulfur. The behavior shown in Figure 75 was similar to that in Figure 73. The reason was that sulfur produced at each theoretical stage was almost completely recovered by the system. There was very little by-product formed, such as COS and CS_2. Therefore, almost all the sulfur decomposed from H_2S was recovered as elemental sulfur. The yield of sulfur could be approximated similar to Equation (5-6):

$$\text{Yield of Sulfur} = c(T) + d(T)\bullet \text{LOG}_2(N) \quad (650 < T < 1000°\text{C}) \qquad (5\text{-}7)$$

where c(T) and d(T) are the functions of reaction temperature shown in Figure 76.

5.4.6 Possible Side Reactions

The chemistry of the process inevitably involves multiple intermediary reactions at or near the surface of the catalyst. Although neglected in the main mechanism, the possibility of the formation of side-products, including some that contain sulfur, does exist. The sulfur containing side-products that are most likely to form are COS and CS_2 (Table 10). At 550°C and 1 atm, the possible side reactions which might be expected to occur are shown in Table 10.

For each of these reactions, the Gibbs free energy was calculated to determine which of these reactions were most likely to take place at 550°C. This temperature was chosen since the experiments were carried out at the same temperature. The results showed that the following side reactions were most likely to occur since they had negative Gibbs free energy at 550°C.

$$2\,CO + S_2 \rightleftharpoons 2\,COS \qquad \Delta G = -44.644 \text{ kJ/mol} \qquad K=6.817\times10^2 \qquad (5\text{-}8)$$

$$4\,H_2 + CS_2 \rightleftharpoons 2\,H_2S + CH_4 \qquad \Delta G = -78.776 \text{ kJ/mol} \qquad K=1.000\times10^5 \qquad (5\text{-}9)$$

$$3H_2 + CO \rightleftharpoons CH_4 + H_2O \qquad \Delta G = -17.350 \text{ kJ/mol} \qquad K=12.624 \qquad (5\text{-}10)$$

These results did not strongly support the compounds listed in Table 11, indicating that these were probably the results of other side-reactions that were not taken into account in the above reactions. The results shown in Table 11 are probably more accurate, however, a conclusion could only be made after actual experiments.

6. CONCLUSIONS

It was experimentally proved that the Co-Mo sulfided catalyst was a good candidate for the decomposition of H_2S to elemental sulfur. In the presence of CO_2, the conversion of H_2S to elemental sulfur increased significantly. It was experimentally demonstrated that the present catalytic process produced a significant amount of sulfur, CO and H_2 and that the experimental values were reasonably close to the thermodynamic equilibrium limits. However, the H_2S conversion level of about 4.3% was still lower than the industrial interest at the present experimental temperature of 550°C, requiring a recycle and/or a hybrid system of catalysis and adsorption.

The results of the TGA experiments were very useful in determining the experimental procedures for operating the reaction system. This method was then extended to study other sulfided catalyst preparations.

Even though the adsorption of sulfur vapor was significant on activated carbon and Co-Mo-alumina catalyst powders which could adsorb up to 9 percent of sulfur in weight as demonstrated by the adsorption experiments, the experimental results of H_2S decomposition indicated that there were only trace amount of elemental sulfur produced using these adsorbents. Therefore, these adsorbents might not be applicable to the H_2S decomposition system at this point of developmental stage for the purpose of elemental sulfur recovery. The idea of combining two unit operations of catalytic decomposition and elemental sulfur adsorption should be further developed to overcome the problems of chemisorption and the short contact time of adsorbents in the reactor.

Thermodynamic simulations were performed on the main scheme of passing a concentrated gas stream of H_2S and CO_2 through a high temperature catalyst bed to form elemental sulfur, methane and water vapor. A simulation was based on the removal of sulfur from the system by condensation when the reaction reached an equilibrium. The residues were fed into the next stage, a new equilibrium was reached and sulfur was removed again. The results in Tables 8 and 9 strongly support the concept of continuous removal of sulfur, and clearly demonstrate the feasibility of the stoichiometric reaction between H_2S and CO_2. The results also indicated that the number of stages needed to reach the final equilibrium stage for recovering sulfur could be greatly affected by the sulfur vapor pressure. The H_2S conversion and sulfur yield did not increase proportionally with the number of stages. The simulation indicated that a multiple stage system was more effective at a higher reaction temperature in raising the H_2S conversion and the sulfur yield.

7. RECOMMENDATIONS FOR FUTURE WORK

(1) More studies on the catalytic reaction and selective separation through adsorption should be made in order to obtain a higher sulfur yield through decomposition of H_2S around 550°C.

(2) Durability and regeneration studies of catalyst and adsorbent should be made for the long-term application.

(3) In order to increase the production yield of CH_4, a dual step catalytic process should be explored involving the decomposition of H_2S and the methanation of the

decomposition products.

(4) To optimize the use of thermal energy, a combined equipment of reactor and heat exchanger should be considered, where the temperature of the outlet stream could be maintained near ambient temperature.

8. REFERENCES

Al-Shamma, L. M. and S. A. Naman, "Kinetic Study for Thermal Production of Hydrogen from H_2S by Heterogeneous Catalysis of Vanadium Sulfide in a Flow System." *Int. J. Hydrogen Energy*, vol. 14, no. 3, 173-179 (1989).

Al-Shamma, L. M. and S. A. Naman, "The Production and Separation of Hydrogen and Sulfur from Thermal Decomposition of Hydrogen Sulfide over Vanadium Oxide/Sulfide Catalysts." *Int. J. Hydrogen Energy*, vol. 15, no. 1, 1-5 (1990).

Andson, J. R. and K. C. Pratt, "Introduction to Characterization and Testing of Catalysis." Academic Press Australia (1985).

Bagajewicz, M. J., S. S. Tamhankar, M. F. Stephanopoulos and G. R. Gavalas, "Hydrogen Sulfide Removal by Supported Vanadium Oxide." *Environ. Sci. Technol.*, vol. 22, no. 4, 467-470 (1988).

Bagautdinov, A. Z., V. K. Zhivotov, I. A. Kalachev, S. Yu, Musinov, A. M. Pampushka, V.D. Rusanov, V. M. Tsoller and P. Ya. Épp, "Dissociation of Hydrogen Sulfide in a Mixture with Carbon Dioxide Gas in a High-Power Microwave Discharge." *Soviet Physics. Technical Physics.*, vol. 36, no. 4, 488-490 (1991).

Bandermann, F. and K.-B. Harder, "Production of H_2 via Thermal Decomposition of H_2S and Separation of H_2 and H_2S by Pressure Swing Adsorption." *Int. J. Hydrogen Energy*, vol. 7, no. 6, 471-475 (1982).

Barbeni, M., E. Pelizzetti, E. Borgarello, N. Serpone, M. Grätzel, L. Balducci and M. Visca, "Hydrogen from Hydrogen Sulfide Cleavage. Improved Efficiencies via Modification of Semiconductor Particulates." *Int. J. Hydrogen Energy*, vol. 10, no. 4, 249-253 (1985).

Barin, Ihsan, Ottmar Knacke and Oswald Kubaschewski, “Thermochemical Properties of Inorganic Substances.” Supplement, SpringerVerlag Berlin Heidelberg New York (1977).

Bartholomew, C. H., and R. W. Fowler Jr, "Activity and Sulfur Tolerance Studies of Molybdenum Base Methanation Catalysts." *Proceedings of the Third International Conference, (Sponsored by Chmex Molybdenum Company), Chemistry and Uses of Molybdenum*, Ann Arbor, Michigan, 213-218 (1979).

Beck, D. D., J. M. White and C. T. Ratcliffe, "Catalytic Reduction of CO with Hydrogen Sulfide. 2. Adsorption of H_2O and H_2S on Anatase and Rutile." *J. Phys. Chem.*, vol. 90, no. 14, 3123-3131 (1986).

Berk, D., R. A. Heidemann, W. Y. Svrcek and L. A. Behie, "Themodynamic Analysis of the Thermochemical Decomposition of H_2S in the Presence of Iron Sulphide." *The Canadian Journal of Chemical Engineering*, vol. 69, August, 944-952 (1991).

Bhambhani, Y, R. Burnham, G. Snydmiller, I. MacLean and T. Martin, "Comparative Physiological Responses of Exercising Men and Women to 5 ppm Hydrogen Sulfide Exposure." *Am. Ind. Hyg. Assoc. J.*, vol. 55, no. 11, 1030-1035 (1994).

Bixby, D. W., H. L. Fike, J. E. Shelton, T. K. Wiewiorowski, "Sulfur." *Kiri-Othmer Encyclopedia of Chemical Technology*, 3rd edition, Wiley, New York, vol. 22, 78-106 (1984). Bowman, Melvin G., "Thermochemical Cycle for Recovery of Hydrogen and Sulfur by Splitting Hydrogen Sulfide." *US Patent 4,999,178*, March 12 (1991).

Boublik, T., V. Fried and E. Hala, “The Vapour Pressure of Pure Substances; Selected Values of the Temperature Dependence of the Vapour Pressures of Some Pure Substances in the Normal and Low Pressure Region.” Amsterdam, New York, Elsevier Scientific Pub. Co. (1973).

Bowman, Melvin G., "Thermochemical Cycle for Recovery of Hydrogen and Sulfur by Splitting Hydrogen Sulfide." *US Patent 4,999,178*, March 12, (1991)

Calahorro, C. V., A. M. Garcia, A. B. Carcia and V. G. Serrano, "Study of Sulfur Introduction in Activated Carbon." *Carbon*, vol. 28, no. 2/3, 321-335 (1990).

Caruana, C. M., "Process Aim to Improve Sulfur Recovery from Gases." *Chemical Engineering Progress*, February, 11-17 (1996).

Chemical and Engineering News, June 29, 37 (1992).

Chemical Engineering, June, 30-35 (1994).

Chemical Rubber Company, "CRC handbook of chemistry and physics." Cleveland, Ohio, CRC Press (1996).

Chen, Q., L. Li and L. G. Hepler, "Kinetics of Desulfurization of Hydrogen Sulfide Using Metallic Copper as Desulfurizer." *The Canadian Journal of Chemical Engineering*, vol. 6915, October, 1160-1165 (1991).

Chivers, T., J. B. Hyne and C. Lau, "The Thermal Decomposition of Hydrogen sulfide over Transition Metal Sulfides." *Int. J. Hydrogen Energy*, vol. 5, 499-506 (1980).

Chivers, T. and C. Lau, "The Thermal Decomposition of Hydrogen sulfide over Alkali Metal Sulfides and Polysulfides." *Int. J. Hydrogen Energy*, vol. 10, no. 1, 21-25 (1985).

Chivers, T. and C. Lau, "The Thermal Decomposition of Hydrogen sulfide over Vanadium and Molybdenum Sulfides Catalysts in Quartz and Thermal Diffusion Column Reactors." *Int. J. Hydrogen Energy*, vol. 12, no. 4, 235-243 (1987).

Chowdury, A. I. and Eric L. Tollefson, "Catalyst Modification and Process Design Considerations for the Oxidation of Low Concentrations of Hydrogen Sulfide in the Natural Gas." *The Canadian Journal of Chemical Engineering*, vol 68, June, 449-454 (1990).

Coskun, I. and E. L. Tollefson, "Oxidation of Low Concentrations of Hydrogen Sulfide over Activated Carbon." *The Canadian Journal of Chemical Engineering*, vol 58, February, 72-76 (1980).

Dalai, Ajay K., Amitabha Majumdar, Aminul Chowdury and Eric L. Tollefson, "The Effects of Pressure and Temperature on the Catalytic Oxidation of Hydrogen Sulfide in Natural Gas and Regeneration of the Catalyst to Recover the Sulfur Produced." *Canadian Journal of Chemical Engineering*, vol. 71, February, 75-82 (1993).

Datta, A. and R. G. Cavell, "Claus Catalysis. 2. An FTIR Study of the Adsorption of H_2S on the Alumina Catalyst." *J. Phys. Chem.*, vol. 89, no. 3, 450-454 (1985).

de Beer, V. H. J., T. H. M. van Sint Fiet, G. H. A. M. van der Steen, A. C. Zwaga and G. C. A. Schuit, "The $CoO\text{-}MoO_3\text{-}\gamma\text{-}Al_2O_3$ Catalyst, V. Sulfide Catalysts Promoted by Cobalt, Nickel and Zinc." *Journal of Catalysis*, vol. 35, 297-306 (1974).

de Beer, V. H. J., C. Bevelander, T. H. M. van Sint Fiet, P. G. A. J. Werter and C. H. Amberg, "The $CoO\text{-}MoO_3\text{-}\gamma\text{-}Al_2O_3$ Catalyst, VI. Sulfur Content Analysis and Hydrodesulfurization Activities." *Journal of Catalysis*, vol. 43, 68-77 (1976).

de Beer, V. H. J., M. J. M. van der Aalst, C. J. Machiels and G. C. A. Schuit, "The $CoO\text{-}MoO_3\text{-}\gamma\text{-}Al_2O_3$ Catalyst, VII. Influence of the Support." *Journal of Catalysis*, vol. 43, 78-89 (1976).

Diver, R. B. and E. A. Fletcher, "Hydrogen and Sulfur from H_2S." *Energy (Oxford, England)*, vol. 10, July, 831-842 (1985).

DOW Chemical Company, Thermal Research Laboratory, "JANAF Thermochemical Tables." U.S. National Bureau of Standards, Washington (1971).

Dowling, N. I., J. B. Hyne and D. M. Brown, "Kinetics of the Reaction between Hydrogen and Sulfur under High-Temperature Claus Furnace Conditions." *Ind. Eng. Chem. Res.*, vol. 29, no. 12, 2327-2332 (1990).

Fellmuth, P., W. Lutz and M. Bülow, "Influence of Weekly Coordinated Cations and Basic Sites upon the Reaction of H_2S and CO_2 on Zeolites." *Zeilotes*, vol. 7, July, 367-371 (1987).

Fire, F. L., "Chemical Data Notebook Series #62: Hydrogen Sulfide." *Fire Engineering*, July, 91-95 (1991).

Fukuda, K, M. Doklya, T. Kameyama and Y. Kotera, "Catalytic Decomposition of Hydrogen Sulfide." *Ind. Eng. Chem. Fundam.*, vol. 17, no. 4, 243-248 (1978).

Gai, P. L., "In Situ Studies of Metal Oxide Catalysts." *Proceedings of the Third International Conference, (Sponsored by Chmex Molybdenum Company), Chemistry and Uses of Molybdenum*, Ann Arbor, Michigan, 143-156 (1979).

Gamson, B. W. and R. H. Elkins, "Sulfur from Hydrogen Sulfide." *Chemical Engineering Progress*, vol. 49, no. 4, 203-215 (1953).

Gangwal, S. K., W. J. McMichael and T. P. Dorchak, "The Direct Sulfur Recovery Process." *Environmental Progress*, vol. 10, no. 3, 186-191 (1991).

Gangwal, S. K., R. Gupta and W. J. McMichael, "Hot-Gas Cleanup -- Sulfur Recovery Technical, Environmental, and Economic Issues." *Heat Recovery System & CHP*, vol. 15, no. 2, 205-214 (1995).

George, Z. M., "Kinetics of Cobalt-Molybdate-Catalyzed Reactions of SO_2 with H_2S and COS and the Hydrolysis of COS." *Journal of Catalysis*, vol. 32, 261-271 (1974).

Ghosh, T. K. and E. L. Tollefson, "A Continuous Process for Recovery of Sulfur from Natural Gas Containing Low Concentrations of Hydrogen Sulfide." *The Canadian Journal of Chemical Engineering*, vol. 64, December, 960-968 (1986).

Ghosh, T. K. and E. L. Tollefson, "Kinetics and Reaction Mechanism of Hydrogen Sulfide Oxidation over Activated Carbon in the Temperature Range of 125-200°C." *The Canadian Journal of Chemical Engineering*, vol. 64, December, 969-976 (1986).

Goar, B. G., Goar, Allison & Associates Inc., "Sulfur Recovery Technology." *Energy Progress*, vol. 6, no. 2, 71-75 (1986).

Gong, SungYong, Xueyu Jiang and SoonJai Khang, "Production of Elemental Sulfur and Methane from H_2S and CO_2 Derived from a Coal Desulfurization Process." DOE Quarterly Technical Progress Report, January 1, 1996 March 31, 1996. DEPS2293PC20110.

Hardison, L. C., "Catalytic Gas-Sweetening Process Selectively Converts H_2S to Sulfur, Treats Aids Gas." *Oil & Gas Journal*, June 4, 60-62 (1984).

Hardison, L. C., "Treating Hydrogen Sulfide: An Alternative to Claus." *Chemical Engineering*, vol. 64, January, 62-63 (1985).

Hardison, L. C., "Go from H_2S to S in One Unit." *Hydrocarbon Processing*, vol. 64, April, 70-71 (1985).

Hardison, L. C., "H_2S to S: Process Improved." *Hydrocarbon Processing*, vol. 71, January, 89-90 (1992).

Harkness, J. B. L., A. J. Gorski and E. J. Daniels, "Hydrogen Sulfide Waste Treatment by Microwave Plasma Dissociation." *Proceedings of the Intersociety Energy Conversion Engineering Conference, published by IEEE, IEEE service center, Piscatawy, NJ, USA*, vol. 6, 197-202 (1990).

Helfritch, D. J., "Pulsed Corona Discharge for Hydrogen Sulfide Decomposition." *IEEE Transactions on Industry Applications*, vol. 29, no. 5, 882-886 (1993).

Hultgren, Ralph, Pramod D. Desai, Donald T. Hawkins, Molly Gleiser, Kenneth K. Kelley (University of California, Berkeley) and Donald D. Wagman (U.S. National Bureau of Standards), "Selected Values of the Thermodynamic Properties of the Elements." American Society for Metals (1973).

Ingrid, W. and V. Meyn, "An Experimental Study on the Kinetics of the Formation and Decomposition of Sulfanes in the Sulfur/H_2S System." *Ind. Eng. Chem. Res.*, vol. 35, no. 4, 1257-1262 (1996).

Kaliva, A. N. and J. W. Smith, "Oxidation of Low Concentration of Hydrogen Sulfide by Air on a Fixed Activated Carbon Bed." *The Canadian Journal of Chemical Engineering*, vol 61, April, 208-212 (1983).

Kaloidas, V. E. and N. G. Papayannakos, "Hydrogen Production from the Decompostition of Hydrogen Sulphide. Equilibrium Studies on the System $H_2S/H_2/S_i$, (I=1,...,8) in the Gas Phase." *Int. J. Hydrogen Energy*, vol 12, no. 6, 403-409 (1987).

Kaloidas, V. E. and N. G. Papayannakos, "Kinetics of Thermal, Non-Catalytic Decomposition of Hydrogen Sulfide." *Chemical Engineering Science*, vol 44, no. 11, 2493-2500 (1989).

Kaloidas, V. E. and N. G. Papayannakos, "Kinetic Studies on the Catalytic Decomposition of Hydrogen Sulfide in a Tubular Reactor." *Ind. Eng. Chem. Res.*, vol. 30, no. 2, 345-351 (1991).

Kameyama, T., M. Dokiya, K. Fukuda and Y. Kotera, "Differential Permeation of Hydrogen Sulfide through a Microporous Vycor-Type Glass Membrane in the Separation System of Hydrogen and Hydrogen Sulfide." *Separation Science and Technology*, vol. 14, no. 10, 953-957 (1979).

Kameyama, T., M. Dokiya, M. Fujishige, H. Yokokawa, K. Fukuda and Shih-Ger Chang, "Possibility for Effect Production of Hydrogen from Hydrogen Sulfide by Means of a Porous Vycor Glass Membrane." *Ind. Eng. Chem. Fund.*, vol. 20, 97-99 (1981).

Kameyama, T., K. Fukuda, M. Fujishige, H. Yokokawa and M. Dokiya, "Production of Hydrogen from Hydrogen Sulfide by means of Selective Diffusion Membranes." *Adv. Hydrogen Energy (Hydrogen Energy Prog. 2)*, no. 2, 569-579 (1981).

Kameyama, T., M. Dokiya, M. Fujishige, H. Yokokawa and K. Fukuda, "Production of Hydrogen from Hydrogen Sulfide by means of Selective Diffusion Membranes." *Int. J. Hydrogen Energy*, vol. 8, no. 1, 5-13 (1983).

Katsumoto, Masayuki, Kazuo Fueki and Takashi Mukaibo, "An Investigation of the Gas-solid Interface Reaction." *Bulletin of the Chemical Society of Japan*, vol. 46, 3641-3644 (1973).

Khudenko, B. M., G. M. Gitman and T. E. P. Wechsler, "Oxygen Based Claus Process for Recovery of Sulfur from H_2S Gases." *Journal of Environmental Engineering*, vol. 119, no. 6, November/December, 1233-1251 (1993).

Kiuchi, H., T. Nakamura, K. Funaki and T. Tanaka, "Recovery of Hydrogen from Hydrogen Sulfide with Metals of Metal Sulfides." *Int. J. Hydrogen Energy*, vol. 7, no. 6, 477-482 (1982).

Knaebel, K. S., "For Your Next Separation." *Chemical Engineering*, November (1995).

Kodama, Tatsuya, Hiroyasu Kato, Masamichi Tyji and Yutaka Tamaura, "Methanation of CO_2 with Activated Ni(II)-, or Co(II)-Bearing Ferrites." Emerging Technologies For Environment Protection - preparing for the 21st Century, Proceedings of Word Congress II on Engineering and Environment, Oct. 12-14, Beijing, China, 518-523 (1993).

Kotera, Y., "The Thermochemical Hydrogen Program at N.C.L.I." *Int. J. Hydrogen Energy*, vol. 1, 219-220 (1976).

Kutsovskaya, M. L., M. T. Hepworth and J. R. McGaa, "Recovery of Lime, Sulfur, and Iron from Gypsum and Pyrite Wastes." *American Chemical Society*, vol. 35, no. 5, 1736-1746 (1996).

Kwong, V. and R. E. Meissner, "Rounding up Sulfur - As the Noose Tightens on Plant Emissions, Demand Increases for Better Removal and Recovery Processes." *Chemical Engineering*, February, 74-83 (1995).

Lee, Bryan, "Highlight of the Clean Air Act Amendments of 1990." *Journal of A&WMA*, vol. 41, no. 1, (1991).

Li, K. T., M. Y. Huang and W. D. Cheng, "Vanadium-Based Mixed-Oxide Catalysts for Selective Oxidation of Hydrogen Sulfide to Sulfur." *Ind. Eng. Chem. Res.*, vol. 35, no. 2, 621-626 (1996).

Linkous, C. A., T. E. Mingo and N. Z. Muradov, "Aspect of Solar Hydrogen Production from Hydrogen Sulfide Using Semiconductor Particulates." *Int. J. Hydrogen Energy*, vol. 19, no. 3, 203-208 (1994).

Liptak, B. G., "Environmental Engineer's Handbook, Vol. II: Air Pollution." Chilton Book .Company, Radner, PA, 998 (1974).

Marshneva, V. I. and V. V. Mokrinskii, "Catalytic Activity of Metal Oxides in Hydrogen Sulfide Oxidation by Oxygen and Sulfur Dioxide." *Kinetics and Catalysis*, vol. 29, no. 4, February, 854-861 (1989).

Massoth, F. E. and P. Zeuthen, "Sulfur Exchange Studies on a Mo/Al_2O_3 Catalyst." *Journal of Catalysis*, vol. 145, 216-222 (1994).

Megalofonos, S. K. and N. G. Papayannakos, "Hydrogen Production from Natural Gas and Hydrogen Sulfide." *Int. J. Hydrogen Energy*, vol. 16, no. 5, 319-327 (1991).

Mitchell, P. C. H., "Sulphide Catalysts: Characterization and Reactions Including Hydrodesulphurization." Catalysis Volume 4, The Royal Society of Chemistry, London, 176 (1981).

Mizuta, S., W. Kondo, K. Fujii, H. Iida, S. Isshiki, H. Noguchi, T. Kikuchi, H. Sue and K. Sakai, "Hydrogen Production from Hydrogen Sulfide by the Fe-Cl Hybrid Process." *Ind. Eng. Chem. Res.*, vol. 30, 1601-1608 (1991).

Monnery, W. D., W. Y. Svrcek and L. A. Behie, "Modelling the Modified Claus Process Reaction Furnace and the Implications on Plant Design and Recovery." *The Canadian Journal of Chemical Engineering*, vol. 71, October, 711-724 (1993).

Nesmeianov, A. N., “Vapor Pressure of the Chemical Elements.” Edited by Robert Gary, Amsterdam, New York, Elsevier Pub. Co. (1963).

Nigara, Y. and B. Cales, "Production of Carbon Monoxide by Direct Thermal Splitting of Carbon Dioxide at High Temperature." *Bull. Chem. Soc. Jpn.*, vol. 59, no. 6, June, 1997-2002 (1986).

Niu, Y., "The Corrosion of Ni-Nb Alloys in H_2-H_2S Mixtures at 600-800°C." *Corrosion Science*, vol. 36, May, 883-900 (1994).

Oil & Gas Journal, “Sulfur Recovery Reaches All-Time High in 1991." February 1, 45-46 (1993).

Okamoto, Y., M. Oh-Hara and A. Maezawa, "H_2S Adsorption on Al_2O_3, Modified Al_2O_3, and MoO_3/Al_2O_3." *The Journal of Physical Chemistry*, vol. 90, May 22, 2396-2407 (1986).

Oosawa, Y., R. Takahashi, M. Yonemura and T. Sekine, "Proposal of a New H_2S Decomposition Process Using Solar Energy." *Solar Energy*, vol. 39, no. 5, 429-431 (1987).

Patrick, V. and G. R. Gavalas, "Reduction, Sulfidation, and Regeneration of Mixed Iron-Aluminum Oxide Sorbents." *American Chemical Society*, vol. 32, no. 3, 519-532 (1993).

Paushkin, Ya. M., "Synthesis of Organic Compounds on the Basis of the Inorganic Compounds CO_2, H_2O, and H_2S." *Doklady Chemical Technology*, January-June, 61-66 (1988).

Perry, Robert H. and Don Green, “Perry's Chemical Engineers' Handbook.” 6th edition, McGraw Hill Book Company, New York (1984).

Petrov, K. and S. Srinivasan, "Low Temperature Removal of Hydrogen Sulfide from Sour Gas and Its Utilization for Hydrogen and Sulfur Production." *Int. J. Hydrogen Energy*, vol. 21, no. 3, 163-169 (1996).

Plummer, M. A., "Sulfur and Hydrogen from H_2S." *Hydrocarbon Processing*, April, 38-40 (1987).

Prange, F., "High Sulfur Content Causes Stainless Steel Corrosion." *Materials Performace*, vol. 31, May, 69 (1992).

Rapaport, D., "Warning: Hydrogen Sulfide." *Water/Engineering & Management*, January, 36 (1990).

Rau, Hans, T. R. N. Kutty and J. R. F. Guedes De Carvalho, "Thermodynamics of Sulphur Vapor." *J. Chem. Thermodynamics*, no. 5, 833-844 (1973).

Raymont, M. E. D., “The Thermal Decomposition of Hydrogen Sulfide.” Doctoral dissertation, University of Calgary, Alberta, (1974).

Raymont, M. E. D., "Make Hydrogen from Hydrogen Sulfide." *Hydrocarbon Processing*, vol. 54, no. 7, 139-142 (1975).

Reid, Robert C., John M. Prausnitz and Bruce E. Poling, *The Properties of Gases & Liquids.* McGraw-Hill Book Company, New York (1987).

Rendall, W. A., M. E. Moir and J. Szarka, "Process for Removing Hydrogen Sulfide from a Gaseous Mixture and Producing Sulfur Therefrom." *British UK Patent GB 2,248,444 A*, April 8, (1992).

Reynold, Wm. C., “Stanjan Chemical Equilibrium Solver.” Department of Mechanical Engineering, Stanford University (1987).

Rice J., G. Hoffmann and C. Wittig, "Photoinitiated H + $CO_2 \rightarrow$ OH + CO Reactions: OH Distributions and Three-Body Interactions in CO_2H_2S Complexes." *J. Chem. Phys.*, vol. 88, no. 4, 2841-2843 (1988).

Ross, A. and M. R. Jeanes, "Oxidation of Hydrogen Sulfide over Cobalt Molybdate and Related Catalysts." *Ind. Eng. Chem. Prod. Res. Develop.*, vol. 13, no. 2, 102-105 (1974).

Roth, P, R. Löhr and U. Barner, "Thermal Decomposition of Hydrogen Sulfide at Low Concentrations." *Combustion and Flame*, vol. 45, 273-285 (1982).

Rothstein, J., "Short Communication: Hydrogen, Methane and Carbon Dioxide." *Int. J. Hydrogen Energy*, vol. 21, no. 5, 423-424 (1996).

Shiina, H., M. Oya, K. Yamashita, A. Miyoshi and H. Matsui, "Kinetic Studies on the Pyrolysis of H_2S." *J. Phys Chem.*, vol. 100, no. 6, 2136-2140 (1996).

Shuai, X. and A. Meisen, "New Correlations Predict Physical Properties of Elemental Sulfur." *Oil and Gas Journal*, October 16, (1995).

Sivasanker, S., A. V. Ramaswamy and P. Ratnasamy, "Nature of the Acid Sites in Sulfided Co-Mo-Al_2O_3 Hydrodesulfurisation Catalysts." *Proceedings of the Third International Conference, (Sponsored by Chmex Molybdenum Company), Chemistry and Uses of Molybdenum*, Ann Arbor, Michigan, 98-104 (1979).

Smith, J. M. and H. C. Van Ness, “Introduction to Chemical Engineering Thermodynamics.” McGraw-Hill, New York (1975).

Soriano, D., T. C. Keener and S. J. Khang, "Catalystic Production of Elemental Sulfur from the Thermal Decomposition of H_2S in the Presence of CO_2." *Chem. Eng. Comm.*, vol. 143, 73-89 (1996).

Sreeramamurthy, R. and P. G. Menon, "Oxidation of H_2S on Active Carbon Catalyst.", *Journal of Catalysis*, vol. 37, 287-296 (1975).

Steijns, M. and P. Mars, "The Role of Sulfur Trapped in Micropores in the Catalytic Partial Oxidation of Hydrogen Sulfide with Oxygen.", *Journal of Catalysis*, vol. 35, 11-17 (1974).

Steijns, M., F. Derks, A. Verloop and P. Mars, "The Mechanism of the Catalytic Oxidation of Hydrogen Sulfide II. Kinetics and Mechanism of Hydrogen Sulfide Oxidation Catalyzed by Sulfur.", *Journal of Catalysis*, vol. 42, 87-95 (1976).

Stull, D. R. and H. Prophet et al., “JANAF Thermochemical Tables.” Second Edition, Office of Standard Reference Data, National Bureau of Standards, Washington, D. C., June (1971).

Sugioka, M. and K. Aomura, "A Possible Mechanism for Catalytic Decomposition of Hydrogen Sulfide over Molybdenum Disulfide." *Int. J. Hydrogen Energy*, vol. 9, no. 11, 891-894 (1984).

Swain, E. J., "Coke, Sulfur Recovery from U.S. Refineries Continues to Increase." *Oil & Gas Journal*, January 2, 33-39 (1995).

Tamaura, Yutaka, Kazuhiro Akanuma, Takayuki Togawa, Takashi Yoshida and Masamichi Tsuji, "CO_2-CH_4 Recycling System Using Activated Magnetite." Emerging Technologies for Environment Protection-preparing for the 21st Century, Proceedings of Word Congress II on Engineering and Environment, Oct. 12-14, Beijing, China, 642-647 (1993).

Terorde, R. J. A. M., P. J. van den Brink, L. M. Visser, A. J. van Dillen and J. W. Geus, "Selective Oxidation of Hydrogen Sulfide to Elemental Sulfur Using Iron Oxide Catalysis on Various Supports." *Catalysis Today*, vol 17, no.1/2, 217-224 (1993).

Towler, G. P. and S. Lynn, "Development of a Zero-Emission Sulfur-Recovery Process. 1. Thermochemistry and Reaction Kinetics of Mixtures of H_2S and CO_2 at High Temperature." *Ind. Eng. Chem. Res.*, vol 32, 2800-2811 (1993).

Towler, G. P. and S. Lynn, "Development of a Zero-Emission Sulfur-Recovery Process. 2. Sulfur-Recovery Process Based on the Reaction of H_2S and CO_2 at High Temperature." *Ind. Eng. Chem. Res.*, vol 32, 2812-2819 (1993).

Traus, I. and H. Suhr, "Hydrogen Sulfide Dissociation in Ozonizer Discharges and Operation of Ozonizers at Elevated Temperatures." *Plasma Chemistry and Plasma Processing*, vol. 12, no. 3, 275-285 (1992).

Traus, I., H. Suhr, J. E. Harry and D. R. Evans, "Application of a Rotating High-Pressure Glow Discharge for the Dissociation of Hydrogen Sulfide." *Plasma Chemistry and Plasma Processing*, vol. 13, no. 1, 77-91 (1993).

True, Warren R., "World Gas Processing, Sulfur-Recovery Capacities Still Growing." *Oil & Gas Journal,* July 12, 41-46 (1993).

Tsuchiya, K., K. Yokoyama, H. Matsui, M. Oya and G. Dupre, "Reaction Mechanism of Atomic Oxygen with Hydrogen Sulfide at High Temperature." *The Journal of Physical Chemistry*, vol. 98, no. 34, 8419-8423 (1994).

Twigg, M. V., “Catalyst Handbook.” 2nd edition, Wolfe Publishing Ltd., London (1989).

Walker, Philip L. Jr., Editor, "Chemistry and Physics of Carbon - A Series of Advances." Volume 6, Marcel Dekker, Inc., New York (1970).

Weil, E. D., "Sulfur Compounds, Inorganic."*Kiri-Othmer Encyclopedia of Chemical Technology*, 3rd edition, vol. 22, John Wiley, New York, 387-398 (1983).

Weisser, Otto and Stanislav Landa, *Sulphide Catalysts, Their Properties and Applications*. Academia-Publishing House of the Czechoslovak Academy of Sciences, Prague, 23-26 (1973).

Wender, I., "Catalysis in the Conversion of Synthesis Gas to Chemicals." *Chemicals from Coal: New Processes, Critical Reports in Applied Chemistry*, vol. 14, Society of Chemical Industry, John Wiley & Sons, Chichester, Great Britain (1987).

West, J. R., "Sulfur Recovery."*Kiri-Othmer Encyclopedia of Chemical Technology*, 3rd edition, Editor: Martin Grayson et al., vol. 22, John Wiley, New York, 276-289 (1984).

Winter, I. and V. Meyn, "An Experimental Study on the Kinetics of the Formation and Decomposition of Sulfanes in the Sulfur/H_2S System." *Ind. Eng. Chem. Res.*, vol. 35, no. 4, 1257-1262 (1996).

Woiki, D. and P. Roth, "Kinetics of the High-Temperature H_2S Decomposition." *J. Phys. Chem.*, vol. 98, no. 49, 12958-12963 (1994).

Xu, L., R. A. Keogh, C. Huang, R. L. Spicer, D. E. Sparks, S. Lambert, G. A. Thomas and B. H. Davis, "Catalytic Hydrotreatment of Coal-Derived Naphtha." *American Chemical Society, Division of Fuel Chemistry*, vol. 36, no. 4, 1909-1911 (1991).

Xueyu Jiang and SoonJai Khang, “Production of Elemental Sulfur and Methane from H_2S and CO_2 Derived from a Coal Desulfurization Process.” DOE Technical Progress Report, October 1, 1995 September 30, 1996. DEFG2293PC22012.

Yang, Ralph T., “Gas Separation by Adsorption Processes.” Butterworth Publishers, Boston (1987).

Yang, B. L. and H. H. Kung, "Hydrogen Recovery from Hydrogen Sulfide by Oxidation and by Decomposition." *Ind. Eng. Chem. Res.*, vol. 33, no. 5, 1090-1097 (1994).

Zaman, J and A. Chakma, "Production of Hydrogen and Sulfur from Hydrogen Sulfide." *Fuel Processing Technology*, vol. 41, 159-198 (1995).

Zhenglu, P., H. Weng, F. Han-Yu and J. M. Smith, "Kinetics of the Self-Fouling Oxidation of Hydrogen Sulfide on Activated Carbon." *AIChE Journal*, vol. 30, no. 6, November, 1021-1024 (1984).

9. LIST OF FIGURES

10. LIST OF TABLES