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Bench-Scale Testing and Evaluation of the Direct Sulfur Recovery Process

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ABSTRACT

The Direct Sulfur Recovery Process (DSRP) is a two-stage catalytic reduction process for efficiently recovering up to 99% or higher amounts of elemental sulfur from SO_2-containing regeneration tail-gas produced in advanced integrated gasification combined cycle (IGCC) power systems by reacting the tail-gas with a small slipstream of coal gas. In this project, the DSRP was demonstrated with simulated gases at bench-scale with 3-in. diameter, 1-L size catalytic reactors. Fundamental kinetic and modeling studies were conducted to explain the significantly higher than thermodynamically expected sulfur recoveries in DSRP and to enable prediction of sulfur recovery in larger reactors. Technology transfer activities to promote the DSRP consisted of publications and discussions with architectural engineering firms and industrial parties especially IGCC system developers. Toward the end of the project, an agreement was signed with an IGCC system developer to scale up the DSRP and test it with actual gases in their 10-MW (thermal) coal gasification pilot-plant under a cooperative R&D agreement with the U.S. Department of Energy.

ACKNOWLEDGMENTS

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EXECUTIVE SUMMARY

Advanced integrated gasification combined cycle (IGCC) power plants employing hot-gas desulfurization are being developed with a projected efficiency (high heating value to electricity basis) as high as 47%. These plants employ air-regenerable metal oxides for sulfur removal. A dilute SO_2-containing tail-gas results on regeneration which needs to be properly treated and disposed. Elemental sulfur recovery from this tail-gas is the most desirable option. Elemental sulfur represents the lowest volume sulfur-containing product and it can be easily stored or sold.

The U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) is supporting the development of Direct Sulfur Recovery Process (DSRP) at Research Triangle Institute (RTI) since 1988. The DSRP is a two-stage catalytic process for reducing the SO_2 to elemental sulfur using a small slipstream of coal gas. The Stage I reaction stoichiometry is represented by:

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

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

$$H_2 + (1/n)\ S_n \rightarrow H_2S\ .$$

By adjusting the reducing gas to SO_2 ratio in the Stage 1 feed, a 2 to 1 H_2S to SO_2 ratio gas is provided to the Stage II reactor where the modified Claus reaction ($2H_2S + SO_2 \rightarrow 3/8\ S_8 + 2H_2O$) occurs. The overall sulfur recovery efficiency of DSRP was projected at over 99% based on results of a previous project (DE-AC21-86MC23260) which tested DSRP at lab-scale with 25 to 50 cc catalyst beds.

The objective of this project is to demonstrate the DSRP for up to 99% or higher sulfur recovery in a bench-scale unit scaled up by a factor of up to 40 over the previously tested lab-scale unit. Fundamental kinetic and modeling studies were conducted to shed light on the mechanism of DSRP reactions and to develop a model to allow the design of larger reactors. The ultimate goal of the project is to advance the DSRP technology to the point where industry is willing to support its further development.

A bench-scale unit with two integrated reaction stages was designed, constructed, and commissioned for demonstration of DSRP. The reactors were made of 4-in. schedule 160 pipe and each housed 1-L of catalyst. Some 50 parametric tests were conducted in the bench unit to evaluate the effect of pressure (1.7 to 25 atm), space velocity (1,000 to 14,000 scc/(cc·h), reducing gas to SO_2 ratio (1.6 to 2.2), SO_2 concentration (2 to 12%), Stage I temperature (500 to 700 °C), Stage II temperature (244 to 337 °C), and fixed or fluidized Stage I reactor. Improved sulfur condenser designs were also evaluated.

The bench-scale test results confirmed the previous highly promising results obtained at laboratory-scale. The primary conclusions of bench-scale testing are as follows:

- Increased pressure rapidly increased conversion to sulfur in Stage I up to 10 atm and then more slowly up to 24.8 atm. Up to 96% conversion was achieved in Stage I.
- Optimum reducing gas to SO_2 ratio was the stoichiometric value, 2.
- Efficient interstage sulfur removal is necessary to further increase sulfur conversion to 99% or higher in Stage II.
- The sulfur recovery in Stage I is governed by kinetics and selectivity rather than thermodynamics.
- The COS formed in the first reactor is completely removed, presumably via hydrolysis to H_2S which then further reacts with SO_2 to produce sulfur in the second reactor.

Kinetic and modeling studies were conducted using a quartz high-pressure microreactor system with 0.2 g of catalyst. These experiments firmly established the beneficial effect of pressure on kinetics of sulfur recovery. These studies further indicated that at high pressure the major reaction sequence for the H_2-SO_2 reaction system was $SO_2 \rightarrow S \rightarrow H_2S$ whereas for the CO-SO_2 reaction system it was $SO_2 \rightarrow COS \rightarrow S$. Best-fit rate equations were obtained from the kinetic data and equilibrium-modified kinetic models were developed to enable prediction of sulfur recovery for larger reactors. The model that fit the bench-scale reactor data well assumed that the water gas shift reaction was at equilibrium and the reduction reactions constrained by the kinetic equations.

Technology transfer activities were conducted to promote DSRP. These activities have resulted in several publications and independent economic evaluations of DSRP by Gilbert Commonwealth and Texaco. The results of these evaluations firmly establish DSRP as a leading contender for treatment of the SO_2 regeneration off-gas from hot-gas desulfurization processes. Very recently, an agreement has been reached with an IGCC system developer to test the DSRP with actual coal gas and actual regeneration off-gas at a scale that is six times larger than the present DSRP bench-scale unit. These tests are to be conducted under a Cooperative Research and Development Agreement (CRADA) between DOE/METC and the IGCC system developer. Prior to testing the larger DSRP unit, DOE/METC is also sponsoring slipstream tests using the existing DSRP skid-mounted unit at their 10 in. coal gasifier facility in Morgantown, West Virginia.

In summary, experimental results in a bench-scale unit demonstrate the effectiveness of the DSRP in obtaining near 96% conversion in one stage of reaction. Thermal degradation of the catalyst was not observed in the liter-size adiabatic reactors. Laboratory results reported earlier, which were largely restricted to gases containing 2% SO_2, were confirmed in the relatively large bench unit. In another series of tests, the potential of the DSRP was demonstrated on gases containing up to 12.4% SO_2. The effect of kinetic limitations on conversion became more apparent. At times, increased space velocity yielded higher conversions. Reversal of conversion can occur in the second stage of reaction if sulfur is not effectively removed in the interstage condensers. By removing additional sulfur with the water at the interstage level, sulfur conversion did increase to 98.5% to 99.1%. Further improvement in interstage sulfur condensation and its subsequent removal will be required to achieve higher than 99% conversion. DOE/METC and RTI are vigorously pursuing technology transfer activities. The goal of these activities is to find industrial partners who would be willing to participate in the continued development of the sorbent and DSRP technologies toward a commercial process.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 INTRODUCTION AND OBJECTIVES

Integrated gasification combined cycle (IGCC) power plants are being advanced worldwide to produce electricity from coal due to their potential for superior environmental performance, economics, and efficiency in comparison to conventional coal-based power plants. Conventional power plants rely on the thermally inefficient Rankine steam cycle and operate at near ambient pressure resulting in large flue-gas flow rates; treatment of these large flue gas volumes is relatively expensive. In contrast, in an IGCC system, coal is gasified at elevated pressure, typically 20 to 30 atmospheres (atm), to produce a relatively low volume fuel gas which is desulfurized prior to burning in a combustion turbine to produce electricity. In the first generation Cool Water IGCC plant demonstrated at Dagget, California, the fuel gas was cooled and sulfur was removed using a commercially available liquid-phase scrubbing process. Although this plant was a success in terms of emissions, its thermal efficiency of 32% was similar to conventional power plants due in large measure to the energy penalty imposed by cooling the gas.

Advanced IGCC plants (Figure 1) are being developed with a projected efficiency, high heating value basis to electricity, as high as 47%. A key component of these plants is a hot-gas desulfurization system employing efficient regenerable mixed-metal oxide sorbents. Leading sorbent candidates include Z-SORB III and zinc titanate. These sorbents can remove hydrogen sulfide (H_2S) in fuel gas down to very low levels (typically less than 20 parts per million by volume [ppmv]) at 500 to 750 °C and can be easily regenerated for multicycle operation using air. The desulfurization and regeneration reactions can be carried out using fixed-, moving-, or fluidized-bed reactors. Fluidized-bed reactors are perhaps most suited for hot-gas desulfurization due to their ability to control the temperature during the highly exothermic regeneration that is typically carried out using an air-diluent (typically nitrogen or

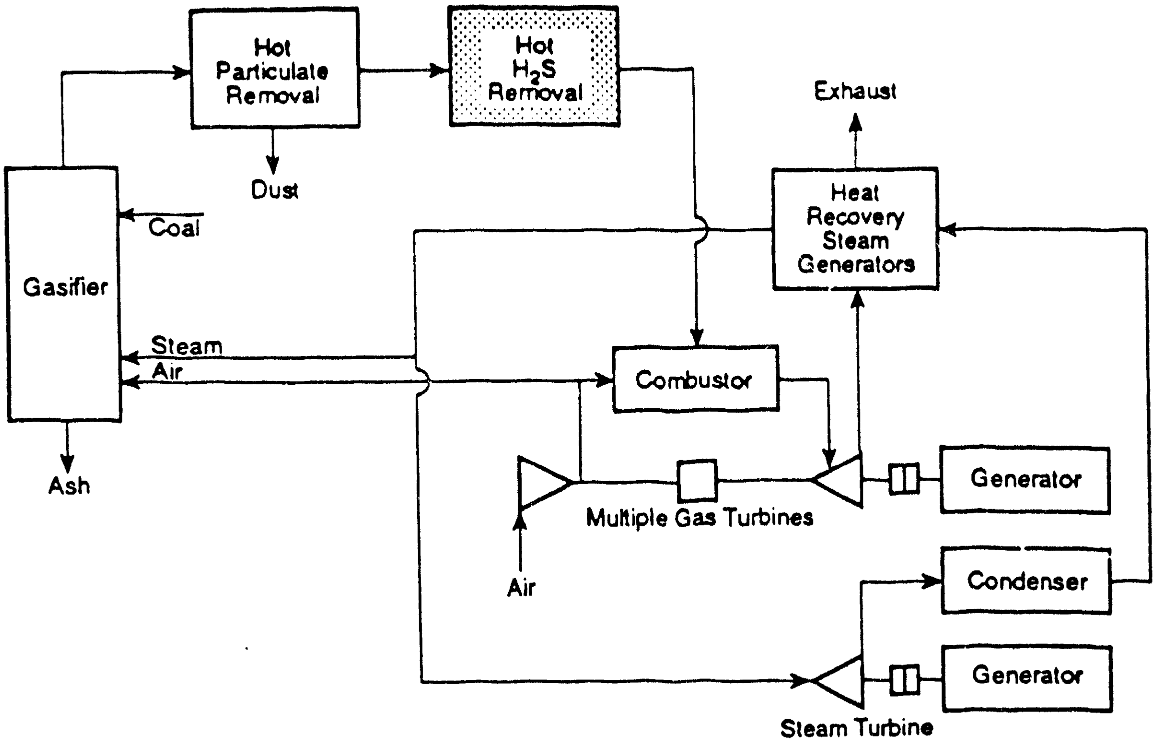


Figure 1. Schematic of a simplified IGCC system.

steam) mixture. The sorbent regeneration results in a dilute sulfur dioxide (SO_2)-containing off-gas which must be treated in an environmentally acceptable manner. Options for treating this gas include conversion to elemental sulfur or sulfuric acid or recycle to the gasifier in which an in-bed disposable sorbent such as limestone or dolomite is employed. Elemental sulfur recovery from the off-gas is believed to be the most desirable option because sulfur can be easily stored or sold—a preferable choice by most utilities.

Research Triangle Institute (RTI) with the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) sponsorship is developing highly efficient, attrition-resistant, zinc titanate sorbents for fluidized-bed reactors and the Direct Sulfur Recovery Process (DSRP) for catalytically reducing the SO_2-containing off-gas using a small slipstream of coal-gas to elemental sulfur.

The DSRP has been under development since 1988. In a previous project (Contract No. DE-AC21-86MC23260), the DSRP was demonstrated at laboratory scale by RTI using 25 to 50 cc of catalyst in a 1-in. diameter fixed-bed reactor (McMichael and Gangwal, 1990). Based on encouraging results, the DOE/METC contracted with RTI to scale up the DSRP by a factor of up to 40 to the bench-scale level.

The objective of this work is to demonstrate on a bench-scale the DSRP for up to 99% or higher recovery of sulfur (as elemental sulfur) from regeneration off-gases and coal-gas produced in IGCC power generating systems. Fundamental kinetic and thermodynamic studies were also conducted to enable development of a model to predict DSRP performance in large-scale reactors and to shed light on the mechanism of DSRP reactions. The ultimate goal of the project is to advance the DSRP technology to the point where industry is willing to support its further development.

2.0 BACKGROUND

Over the last 15 years or so under contracts with DOE/METC, a number of regenerable mixed-metal oxide sorbents have been prepared and tested. Zinc titanate (Zn_2TiO_4 and/or $ZnTiO_3$) is currently one of the leading regenerable sorbents. It is formed by a solid-state reaction of zinc oxide (ZnO) and titanium oxide (TiO_2). Overall chemical reactions with Zn_2TiO_4 during the desulfurization (sulfidation)-regeneration cycle are shown below:

Sulfidation: $Zn_2TiO_4 + 2H_2S \rightarrow 2ZnS + TIO_2 + 2H_2O$

Regeneration: $2ZnS + TiO_2 + 3O_2 \rightarrow Zn_2TiO_4 + 2SO_2$.

The sulfidation/regeneration cycle can be carried out in fixed-, moving-, and fluidized-bed reactor configurations. The regeneration reaction is highly exothermic, requiring the use of large volumes of diluent to control the temperature and results in a dilute SO_2-containing tail-gas that must be further treated. Under contracts with DOE/METC, many approaches have been evaluated for treatment of the tail-gas. These include adsorption of SO_2 using calcium-based sorbents followed by landfilling of calcium sulfate as well as conventional methods such as Wellman-Lord coupled with high-temperature syngas reduction and Augmented Claus for converting the SO_2 to elemental sulfur. There are two leading advanced approaches that DOE/METC is currently sponsoring to convert the SO_2 tail-gas to useful byproducts. These include the GE moving-bed process and the DSRP.

In the GE moving-bed process (Cook et al., 1992), the H_2S in coal gas is removed by moving a bed of sorbent countercurrent to the upward gas flow. The sorbent is typically zinc titanate, 3/8- to 1/2-in. in diameter, made by subjecting zinc titanate extrudates to a rounding process. The sulfided sorbent is transferred to a moving-bed regenerator below the moving-bed absorber using a lock-hopper arrangement. In the regenerator, SO_2-recycle is used to both control the exothermicity of the reaction of the sulfided sorbent with air as well as to produce an SO_2 tail-gas containing 10- to 13-vol% SO_2. The regenerated sorbent is lifted back to the absorber using a bucket elevator arrangement. The 10- to 13-vol% SO_2 is a suitable feed for a sulfuric acid plant. The General Electric (GE) moving-bed process has undergone a series of pilot-scale tests and has been selected for demonstration in two Clean Coal Technology projects.

In the DSRP (McMichael and Gangwal, 1990; Dorchak et al., 1991; Gangwal et al., 1993), the SO_2 tail-gas is reacted with a slipstream of coal gas over a fixed or fluidized bed of selective catalyst to directly produce elemental sulfur at the high-temperature, high-pressure (HTHP) conditions of the tail-gas and coal gas. As shown in Figure 2, the process is carried out in two reaction stages. In the first stage, approximately 95% of the sulfur gas in the inlet stream is converted to elemental sulfur. The stoichiometry of the first-stage reactions is shown below:

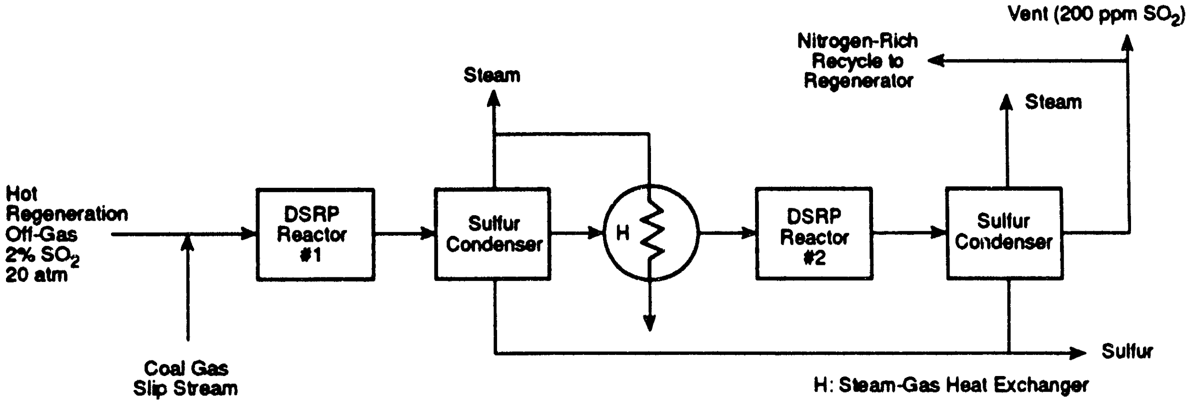


Figure 2. Simplified schematic of the DSRP.

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

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

$$H_2 + (1/n)\ S_n \rightarrow H_2S\ .$$

The outlet gas from the first DSRP reactor is cooled condensing out sulfur. By adjusting the proportion of coal gas to tail-gas, the effluent composition of the first reactor is controlled to produce an H_2S to SO_2 ratio of 2 to 1 at 95% sulfur conversion. The cooled gas stream is then passed to the second DSRP reactor where 80% to 90% of the remaining sulfur compounds are converted to elemental sulfur via the modified Claus reaction ($2H_2S + SO_2 \rightarrow 2H_2O + (3/8)\ S_8$). The combined efficiency of the two reactors for the conversion of sulfur compounds to elemental sulfur is projected to be over 99%. Elemental sulfur is the desired sulfur byproduct because it is easily stored, transported, or sold. It is also the preferred choice of utilities.

The DSRP integrates better with zinc titanate fluidized-bed desulfurization (ZTFBD) (Gupta et al., 1992), as shown in Figure 3, as opposed to fixed- or moving-bed, because of

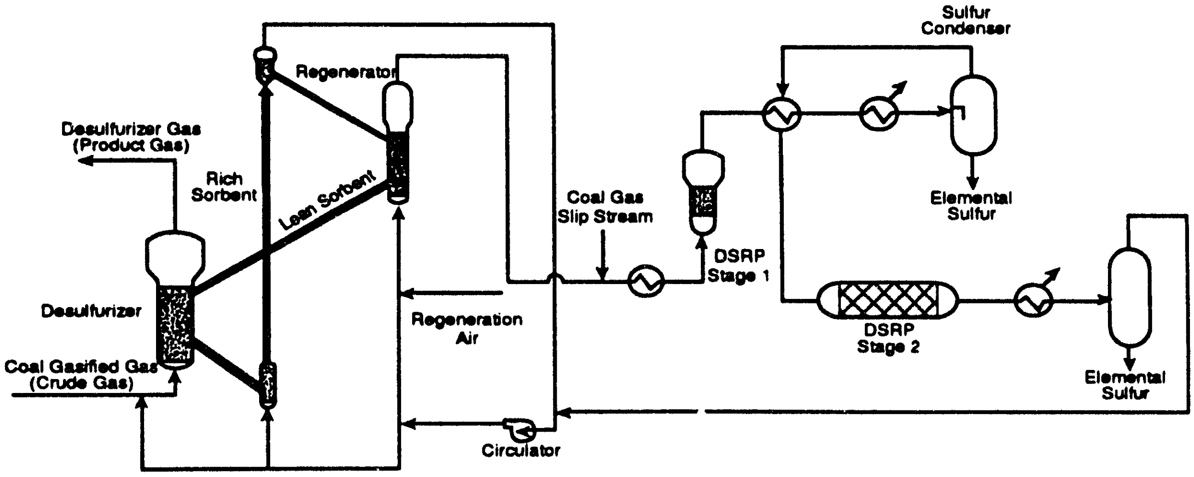


Figure 3. Simplified schematic of integrated fluidized-bed desulfurization/DSRP system.

the relative ease of achieving a constant concentration of SO_2 in the tail-gas using the fluidized-bed desulfurization-regeneration system. Recently, economic evaluations of the GE moving-bed process coupled to a sulfuric acid plant and fluidized-bed desulfurization coupled to DSRP have been conducted by Gilbert Commonwealth for DOE. These evaluations show the two approaches to be very closely competitive, with costs within 1% of each other. One aspect of the integrated fluidized-bed desulfurization DSRP that is advantageous to DSRP is that the nitrogen diluent associated with air input to the regenerator can be balanced in the recycle loop by purging the excess flow containing traces of sulfur compounds either through the desulfurizer to the turbine (as shown in Figure 3) when very high sulfur removal efficiencies are desired or directly to the turbine at slightly lower removal efficiencies. The extra diluent flow to the turbine provides added power. Preliminary economic evaluations of DSRP have also been conducted at RTI and have shown that DSRP can produce sulfur at a small fraction of the costs associated with conventional processes such as Wellman Lord-Syngas Reduction-Augmented Claus (McMichael and Gangwal, 1990).

3.0 HIGHLIGHTS OF PRIOR WORK

As stated earlier, in a previous project (Contract No. DE-AC21-86MC23260), the DSRP was demonstrated at laboratory scale using 25 to 50 cc of catalyst in a 1-in. diameter fixed-bed reactor (McMichael and Gangwal, 1990). Some 55 DSRP runs were conducted during the project. The most important results of this study are highlighted in this section.

Seven different catalysts were tested at a variety of conditions in a 1-in. HTHP lab-scale reactor as candidates for use in the DSRP. These are designated A, B, C, D, E, F, and G. The tests showed that up to 96% sulfur recovery can be achieved in a single stage. Furthermore, experiments simulating two reactors in series with an intermediate sulfur condensation step showed the potential of over 99% overall sulfur recovery.

Tests conducted in the bench-scale reactor system to simulate DSRP Stage I utilized a range of conditions and a variety of catalysts. Defining conversion as the percent of the inlet sulfur converted to elemental sulfur, the effects of the variables on conversion at 20 atm pressure (unless otherwise noted) were observed. These variables are listed below.

Catalyst: Catalyst A was found to give the highest conversion of the inlet SO_2 to sulfur. At a space velocity of up to 2,800 scc/(cc·h) with 36 vol% steam in the inlet gas, conversions to elemental sulfur were consistently greater than 96% at 500 to 650 °C. At a space velocity of around 1,800 scc/(cc·h), at 650 °C, all catalysts showed conversions greater than 90%. The approximate order of the activity of the catalyst was

$$A \approx B > C \approx D > E > F \approx G \ .$$

Space Velocity: Catalyst A showed conversions to sulfur as high as 93% at a space velocity of 5,500 scc/(cc·h) at 550 to 650 °C, but conversions were in the 40 to 60% range at 10,000 scc/(cc·h). Catalyst C was tested up to 20,000 scc/(cc·h). At 650 °C, conversions were 94%, 90%, 87%, and 56% at space velocities of 1,900, 5,500, 10,000, and 20,000 scc/(cc·h). respectively. Thus over 90% conversion was achievable at space velocities up to 5,500 scc/(cc·h).

Temperature: The conversion were somewhat insensitive to temperature above a threshold temperature which depended on the catalyst type.

Steam: The effect of steam concentration in the inlet gas was studied because steam and nitrogen are both likely diluents in hot tail-gas. Steam levels up to 36 vol% were studied and appeared to have no detrimental effect in the temperature range of interest.

Pressure: Pressure was by far the most important variable affecting conversion in the Stage I reactor. For example, a space velocity of 400 scc/(cc·h) at 1.5 atm and a space velocity of 5,000 scc/(cc·h) at 20 atm give nearly equivalent reactor residence time. Yet the conversion at 20 atm was nearly double that obtained at 1.5 atm, clearly demonstrating the importance of pressure.

Bench-scale reactor tests were carried out to simulate DSRP Stage II reactor. These tests were conducted with a gas simulating the effluent from DSRP Stage I reactor after sulfur condensation.

The H_2S to SO_2 mole ratio in the inlet gas was approximately 2.0. Conversions as high as 98% were achieved in the absence of steam. With up to 34% steam, conversions as high as 80% were achieved. Combined with a Stage I conversion of 96%, this translates into an overall conversion of 99.2% to 99.9%. A summary of Stage II results and the effects of various operating variables are given below.

Catalyst: Catalyst A, the best catalyst for Stage I, was not the best catalyst for Stage II. The order of catalyst activity was as follows:

$$B = C > A \ .$$

Temperature: As temperature was reduced, conversion increased. The higher conversion at lower temperature is desirable since it reduces the reheat requirement after the Stage I condenser.

Steam and Pressure: For Catalysts B and C, pressure had a significant effect on conversion in the presence of steam. Steam reduced the conversion significantly but a 2-stage conversion of 99% was achievable even at high steam levels.

A detailed thermodynamic analysis of the DSRP Stage II reactions was carried out. The results of the thermodynamic analysis are as follows:

- The conversion of sulfur gases to elemental sulfur is underestimated by thermodynamic calculation. The experimental conversion is always greater than calculated.
- In the DSRP Stage II simulation the effects of steam on conversion are greatly overestimated by thermodynamic calculations. Thermodynamics predict high losses in conversion due to small increases in inlet steam to the DSRP Stage II reactor.

A preliminary economic study of the DSRP was carried out in the third year of the project. This study compared the DSRP to two process designs that were based on conventional processes for converting dilute SO_2-containing streams to elemental sulfur. The conventional processes were the Partial Wellman-Lord/BSRP and the Wellman-Lord/ Augmented Claus. Preliminary designs and economic evaluations of these processes were sponsored by DOE. The preliminary engineering/economic comparison indicates that the DSRP can produce a ton of sulfur at costs about 10% to 13% of the conventional processes for recovery of sulfur from the regeneration tail-gas.

Based on the work performed, the DSRP appears to be able to recover over 99% of the SO_2 in the H_2S sorbent regeneration off-gas. The process is conceptually uncomplicated and the economics of the DSRP compared to more conventional processes for converting dilute SO_2 to elemental sulfur looks attractive.

Because of the highly promising results, DOE awarded this contract to RTI to scale up the DSRP by a factor of up to 40 to bench scale. This report briefly describes the work carried out in this follow-on contract (DE-AC21-90MC27224) in the following sections.

The objective, as stated in Section 1.0, is to demonstrate the DSRP on a bench-scale for up to 99% or higher recovery of sulfur (as elemental sulfur) from regeneration off-gas and coal-gas produced in IGCC power generating system. Fundamental kinetic and thermodynamic studies will also be conducted to explain the mechanism of DSRP reactions. The goal of the project is to advance the DSRP technology to the point where industry is willing to support its further development.

4.0 PROJECT DESCRIPTION

The work carried out in this project for development of DSRP can be divided into the following three categories:

- Bench-scale testing,
- Kinetic and modeling studies, and
- Technology transfer.

4.1 BENCH-SCALE TESTING

4.1.1 Test Equipment

A bench-scale unit was designed, constructed, and commissioned for demonstration of DSRP at a scale of up to 40 times larger than that used in the previous lab-scale study. The objectives included confirmation of the promising data obtained at lab-scale with 2% SO_2, integrated operation of Stage I and Stage II DSRP reactors, and evaluation of DSRP with larger concentration of SO_2 up to 12% typical of the GE moving-bed process.

A simplified flow sheet for the DSRP bench-scale unit commissioned in the first year of the project is shown in Figure 4. The bench-scale unit consists of four subunits. These are the Gas Delivery, Reactor #1, Reactor #2, and Gas Conditioning/Pressure Control subunits. The elements of the bench-scale unit are mounted on a transportable skid. For safety considerations, the liquid SO_2 and H_2S supply cylinders and positive displacement pumps are located away from the bulk of the equipment in a ventilated hood.

In addition to the major items shown in Figure 4, the bench-scale DSRP unit also includes a data acquisition system, which is used to monitor and record system temperatures, pressures, and flow rates, and a sampling/analytical system for measuring inlet and outlet gas compositions of each reactor.

The Gas Delivery Subsystem is shown on the left-hand side of Figure 4. The system has the capability of simulating mixtures of a regeneration off-gas containing up to 12% SO_2

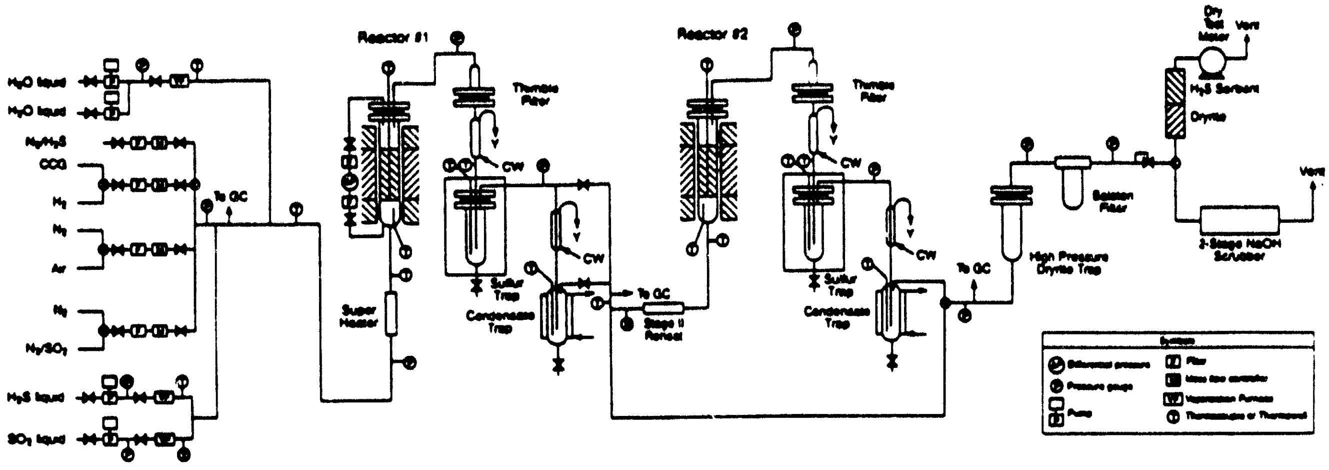


Figure 4. Simplified flow sheet for the DSRP bench-scale unit.

and typical air-blown (GE, KRW) and oxygen-blown (Texaco, Shell, Dow) gasifier gases. These gas mixtures are produced using a combination of bottled gases, and pressurization and vaporization of appropriate liquids. The gas delivery system provides capability for a space velocity of up to 10,000 scc/(cc·h) with 1 L of catalyst in either reactor.

The pressure shells for Reactors #1 and #2 are built from 4 in. schedule 160 316H stainless pipe and are rated at pressures to 400 psig at 750 °C. The pipes are approximately 24 in. in length. A cross-sectional view of Reactor #1 is shown in Figure 5. The DSRP catalyst bed is held within the pressure vessel in a removable catalyst cage constructed from a 3-1/4 in. tube with 0.120 in. walls made of 304 stainless steel. The cage has a porous ceramic gas distributor which also supports the catalyst bed. About 9 in. of bed height is occupied by 1 L of catalyst. The condenser systems for the two reactors are essentially identical. Ceramic thimble filters operating at temperatures above sulfur dew point are

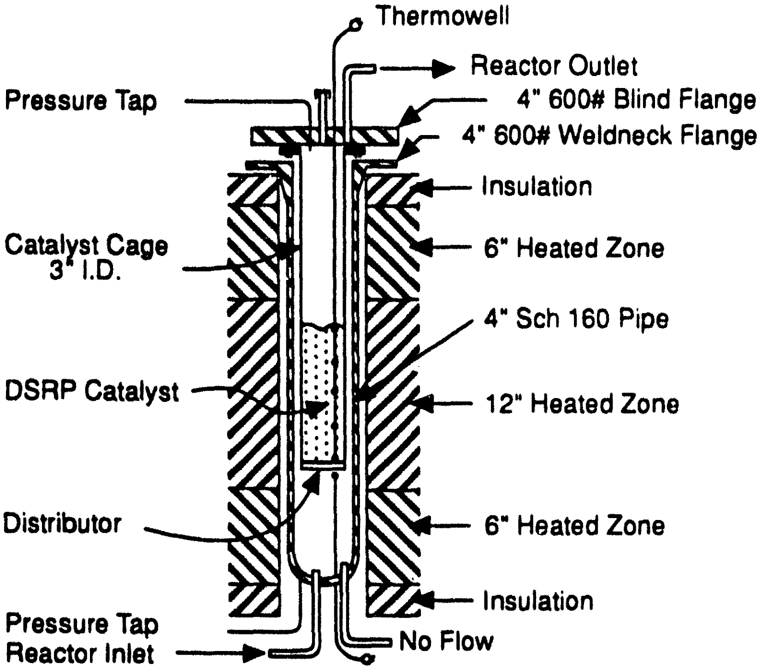


Figure 5. Cross-sectional view of Reactor #1 setup for fixed-bed DSRP operation.

installed between each reactor and elemental sulfur trap to catch particulate. The filtered gas is then cooled and its temperature is monitored and maintained slightly above the desired sulfur trap temperature. A high temperature ball valve is used to periodically drain the trap during a test.

In the condenser system associated with Reactor #1, provisions are made to feed the gases exiting the sulfur trap directly either to the second reactor through the reheat furnace or to a second condenser trap to further cool the gas. The gases leaving this trap are directed through the reheat furnace to Reactor #2 or passed to the Gas Conditioning Subsystem.

The gas cooling systems associated with Reactors #1 and #2 are essentially identical. The exception is that the cooling system following Reactor #2 does not have provision for bypassing the reactor gases around the second heat exchanger and the condensate trap, as can be done in the cooling system following Reactor #1.

The Gas Conditioning Subsystem is shown on the right-hand side of Figure 4. Cooled gases from either the gas cooling system of Reactor #1 or #2 are passed through a high pressure Dryrite trap to virtually eliminate water vapor from the gas stream. Particulates are removed from the product gas with a Balston filter before passing through the back pressure regulator for pressure reduction. As shown in Figure 4, system pressure is monitored by a pressure gauge just upstream of the back pressure regulator. The nearly atmosphere pressure product gas passes through a two-stage NaOH scrubber to remove H_2S/SO_2 prior to venting. Occasionally, the low pressure product gas is vented through the dry test meter for measurement of the dry product gas flow rate.

Selected temperatures and electronically controlled gas flow rates are monitored and recorded using a 32-channel data logger and computer. Gas composition is determined at three locations within the DSRP bench-scale unit as shown in Figure 4. The gas stream from any one of the three gas chromatograph (GC) sampling locations in the bench-scale unit is passed to two on-line GCs. One of the GCs is equipped with a flame photometric detector (FPD) and a thermal conductivity detector (TCD) for analysis of sulfur gases at low concentrations, and CO_2 and sulfur gases at high concentrations, respectively. Analysis time for H_2S, COS, CO_2, and SO_2 is less than 8 minutes. The other GC is used to analyze fixed gases (H_2, CO, CO_2, CH_4, and N_2).

The DSRP bench-scale unit has been designed to handle a fairly wide range of operating conditions in harsh H_2S-containing environments. The major equipment items shown in Figure 4 that are exposed to a high temperature sulfur containing environment are Alon processed to prevent corrosion.

4.1.2 Bench-Scale Test Results

Some 50 parametric DSRP tests have been conducted in the bench-scale unit at a range of pressures (1.7 to 25 atm), space velocity (1,000 to 14,000 scc/(cc·h)), coal-gas type (KRW, GE, Texaco), reducing gas to SO_2 ratio (1.6 to 2.2) and off-gas SO_2 concentration (2 to 12.4 vol%). The latest tests included tests of improved condenser designs and fluidized-bed Stage I reactor. The Stage I temperature typically ranges from 500 to 700 °C, whereas the Stage II temperature ranges from 250 to 350 °C.

4.1.2.1 Stage I Results

Sulfur conversion after Stage I with 2% SO_2 as a function of experimental parameters is shown in Table 1. As found in the previous laboratory-scale experiments (Dorchak et al., 1991; Dorchak and Gangwal, 1991), the conversions were insensitive to temperature and space velocity but were a strong function of pressure and reducing gas/SO_2 ratio. As seen from Table 1, pressure has a rather dramatic effect from 1.7 to about 10 atm. Between 10 and 21.4 atm, conversion increases slowly and as high as 96% conversion is achieved. Increase in space velocity from 1,250 to 7,500 scc/(cc·h) does not appear to reduce conversion. It may be possible that throughput and sulfur production can be increased significantly by operating at higher space velocities. The optimal reducing gas to SO_2 ratio is about 2 as anticipated. Conversions are lower both at a higher ratio of 2.17 as well as lower ratios of 1.79 to 1.84 as can be seen from Table 1. However, the conversions are relatively insensitive to the temperature between 524 and 660 °C. All of the results obtained in this bench-scale testing corroborate the data previously obtained in the laboratory-scale reactor.

Table 1. Parametric Study of Conversion to Elemental Sulfur in Stage I

Pressure (atm)	Temperature (°C)	Space velocity [scc/(cc·h)]	Stoichiometric ratio	Conversion to elemental S_x
21.4	627	3,750	2.00	95.8
21.4	552	7,500	2.00	94.9
21.4	524	3.750	2.00	94.5
21.4	608	2,500	1.84	92.1
21.4	660	1,250	2.17	91.1
21.4	660	1,250	1.79	89.6
14.6	610	2,500	1.84	89.3
14.6	656	1,250	1.79	88.5
9.8	662	1,250	1.79	86.4
9.8	610	2,500	1.84	84.1
1.7	659	1,250	1.90	18.1

Efforts were also directed at demonstrating the DSRP with higher concentration, up to 12%, of SO_2, typically obtained in the regeneration off-gas from the GE moving-bed regenerator (Cook et al., 1992). A series of experiments were carried out with gases containing 7.5% to 12.4% SO_2 using a dry GE/Lurgi coal-gas as the reductant. Runs were made at two pressures and varying hourly gas space velocity. The Stage II reactor was not operated in this series of experiments. In the GE moving-bed/DSRP concept, the Stage I effluent, after sulfur condensation, can be recycled back to the regenerator and/or the gas turbine depending on emission regulations.

The conversion data taken with the high SO_2 concentration in the regeneration off-gas are shown in Figure 6. As can be seen, the conversions are clearly limited by stoichiometry, i.e., the molar ratio of H_2S to SO_2. Problems with the liquid SO_2 pump led to problems in controlling the high SO_2 concentrations, making it difficult to control the stoichiometry. As

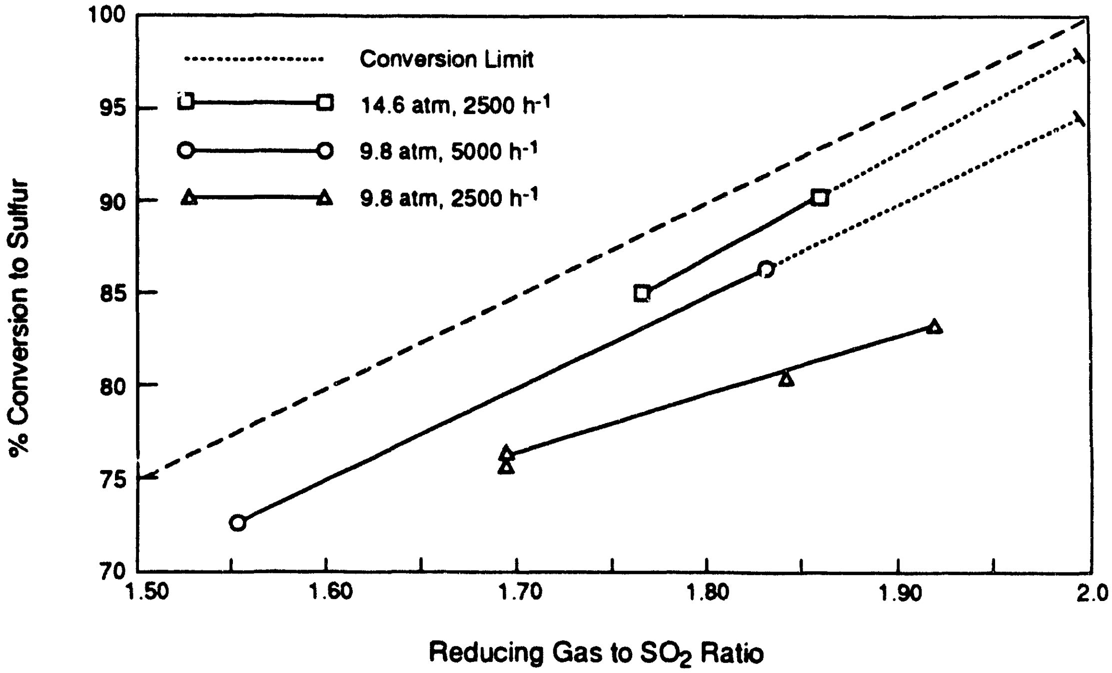


Figure 6. DSRP sulfur recovery from off-gases containing 7.5% to 12.4% SO_2.

presented in the figure, at each pressure level, the conversion correlates well with the stoichiometry. As expected, conversions are somewhat higher at 14.6 atm than at 9.8 atm. Extrapolating up to a stoichiometry of 2 results in conversions of over 95% at 14.6 atm. At 9.8 atm and an hourly gas space velocity of 5,000, conversion is still over 90%. Somewhat surprising, at the lower pressure, increasing space velocity results in higher conversion. This may be indicative of kinetic effects that limit the effect of Claus-type reactions that inhibit Stage II conversion as discussed next.

4.1.2.2 Stage II Results

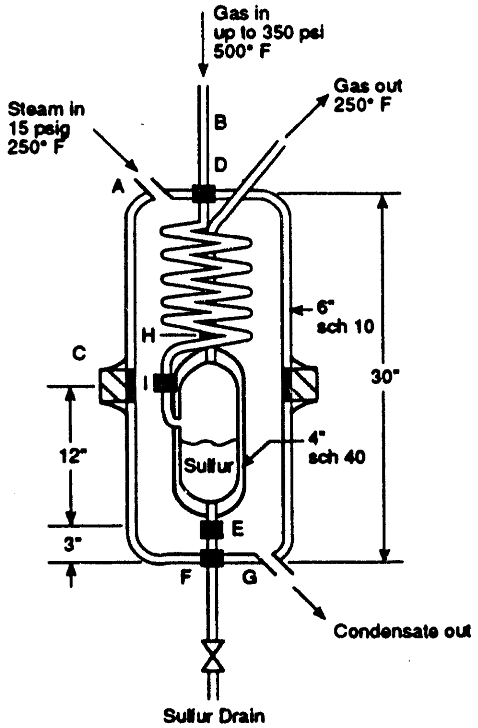
During the bench-scale testing, the Stage II reactor was operated in an integrated manner at temperatures from 244 to 337 °C. The results, however, show that the overall conversions to elemental sulfur after Stage II were lower than after Stage I as indicated by two sets of data in Table 2. Because sulfur condensation was not complete between the reactors, Claus reactions apparently produce H_2S and SO_2 from sulfur and H_2O. As a result, overall conversion from the integrated two-stage operation is lower.

Table 2. Conversion to Elemental Sulfur After Stages I and II

Pressure (atm)	Space velocity [scc/(cc·h)]	Reducing gas to SO_2 ratio	Conversion to sulfur	
			Stage I	Stage II
21.4	3,750	2.00	95.8	88.3
21.4	3,750	2.00	94.5	88.2

4.1.2.3 Tests with Improved Sulfur Condensers

Discussions with experts in sulfur recovery processes have indicated that the scale of equipment has a major impact on sulfur removal by condensation. As the scale increases to commercial, it becomes relatively easier to efficiently remove the sulfur using an interstage condenser as practiced commercially in the Claus process. For bench-scale equipment of the size used in this study, it is very difficult to design a highly efficient sulfur condenser. However, improvements to the sulfur condenser design were made at the suggestions of experts in sulfur recovery. The improved design consists of a steam-jacketed condenser with a turbulent-flow coil for condensing and coalescing the sulfur on the coil wall. A schematic diagram of the improved condenser is shown in Figure 7. The sulfur-laden gas is cooled by surrounding steam at 250 °F in a coil and then flashed into the sulfur collection pot for separation of gas and sulfur. A sulfur drain is included so that it is not necessary to dismantle the condenser after every run. The ability to drain the sulfur during a run allows extended runs to be carried out. Also fittings are provided in strategic locations to allow dismantling when cleanup becomes necessary. Using this new design, a number of two-stage tests were again conducted and the results are shown in Table 3.



A, G: 1/2" Female weld fitting
B: SS 3/8" Tubing, 0.035" Wall
C: Blind flange
D, F: 3/8" Weld fitting
E, H, I: 3/8" Bored-through union

Figure 7. Steam-jacketed sulfur condenser.

As shown in Table 3, additional conversion was obtained in the second reactor when low conversions were achieved in the first reactor presumably due to a less active catalyst. However, additional conversion in the second reactor was not achieved when conversions in the first reactor were high—around 95% to 96%.

Table 3. Bench-Scale Test Results with Improved Sulfur Condensers[a]

Test No.	Temperature (°C)		Reducing gas to SO_2 ratio	Overall SO_2 conversion to sulfur (%)	
	Reactor 1	Reactor 2		Reactor 1	Reactor 2
SS1[b]	525	300	2.14	78.4	92.4
SS2	633	306	1.93	79.6	94.0
SS3	641	298	2.00	81.5	97.4
SS4	620	288	2.00	84.1	NA[c]
SS5	623	286	2.00	84.3	97.3
SS6	623	260	2.00	96.0	96.0
SS7[d]	623	286	2.00	95.5	95.5
SS8	623	300	2.00	96.0	95.0
SS9[e]	623	300	2.00	96.0	98.5

[a] 21.4 atm, 2000 scc/cc·h, 3.2% SO_2 off-gas, Texaco coal gas, 10% steam in gas mixture.
[b] Space velocity was 4000 scc/cc·h.
[c] NA = Not available due to experimental problems.
[d] Pressure was 350 psig; test was run for 16 h.
[e] Water removed interstage, 350 psig, test was run for 8 h.

Note also that Test SS7 was a 16-h test which demonstrated a long-term plug- and leak-free operation at a pressure of 350 psig. This relatively long duration test, in addition to proving operability and reliability, also confirmed the high efficiency of the sulfur condensers.

Prior to Test SS8, the Stage II reactor was opened to replace the catalyst. It was found that the catalyst was agglomerated due to the deposition of sulfur in the bed allowing gas channeling. This may be the reason why no additional Stage II conversion (in either direction) was obtained in Tests SS6 and SS7. In Test SS8, a fresh batch of the catalyst was used. It was seen that the reverse Claus reaction slightly decreased the overall conversion after Stage II for this test. However, this decrease was nowhere near the decrease obtained in the Stage II reactor with the condensers previously used (Table 2). The results therefore indicate that even more efficient condensation will be required to achieve sufficient sulfur removal and allow additional conversion in Stage II. One important reaction that occurred in Stage II was COS conversion. COS formed in the first reactor was completely reacted in the second reactor.

Test SS9, in which the water was removed using an interstage cooler, was conducted to see if most of the sulfur could be removed with the water. This test showed that conversion in the second reactor could be increased to achieve an overall 98.5% conversion. Examination of the sulfur removed in the condensers after each reactor indicated that even after removing the water at interstage level, only about 80% of the sulfur produced in the first stage could be removed and about 20% still carried over to the second stage.

Thus, to increase the conversion further, i.e., beyond 99%, it appears that even more efficient interstage sulfur removal is necessary. However, as stated earlier, condensation should improve with increase in scale of equipment.

4.1.2.4 Tests with Fluidized-Bed Stage I Reactor

For a series of tests, the Stage I reactor was modified for fluidized-bed operation using catalysts cages of diameters ranging from 1.5- to 3-in. ID. Better temperature control of the exothermic SO_2 reduction reaction was expected to be achieved using fluidized beds. A number of tests were carried out with fluidized bed in Stage I and fixed bed in Stage II. The particle size of the catalyst used in the fluidized-bed reactor was 50 x 120 mesh.

The results of these tests are shown in Table 4. Runs S-10 to S-13 were conducted with a 1.5-in.-ID Stage I fluidized-bed reactor, whereas Run S-15 was conducted with a 3-in.-ID Stage I fluidized-bed reactor. All tests used a fixed-bed reactor in Stage II. Test S-15 used an 80 slpm total gas flow (the highest gas flow processed to date) which required better temperature control of the sulfur condenser. This was provided by designing and installing a boiling-water/steam siphon system around the condenser and sulfur catchpot.

Table 4. DSRP Test Results With Fluidized-Bed Stage I and Fixed-Bed Stage II Reactors[a]

	Stage I-Fluidized bed		Stage II-Fixed bed		Sulfur recovery (%)	
Run No.	Space velocity scc/(cc·h)	Temperature (°C)	Space velocity scc/(cc·h)	Temperature (°C)	Stage I	Overall
S-10-A	13,700	627	1,960	265	84.0	NM
S-10-B	9,570	653	1,370	263	85.0	98.7
S-11-A	9,560	650	1,370	260	92.2	97.3
S-11-B	6,810	649	980	253	93.1	97.4
S-12	9,570	650	1,370	265	89.5	99.1
S-13	8,940	650	1,280	270	93.9	98.5
S-15[b]	8,300	659	4,790	283	82.4	94.4

[a] Test Conditions: 300 psig, nominal reducing gas to SO_2 ratio = 2; 50 x 120 mesh Stage I catalyst, 1/8" Stage II catalyst, 2.5% SO_2 containing off-gas, medium-Btu reducing coal gas.

[b] All tests except S-15 conducted with 1.5-in.-ID Stage I fluidized-bed and interstage water removal. S-15 conducted without interstage water removal and with 3.0-in.-ID Stage I fluidized bed.

NM = Not measured.

The fluidized-bed tests ran smoothly for long durations and were quite successful because of the ease of temperature control in the Stage I reactor. As opposed to a 75 to 100 °C temperature rise in a fixed-bed reactor with about 2.5% SO_2, only a 15 °C rise in temperature occurred. Up to 99.1% sulfur recovery was obtained with interstage water removal. Complete sulfur condensation, however, was not achieved interstage, even after water was allowed to condense, thus limiting the Stage II conversion. In Test S-15, the second stage conversion was even lower due to a higher space velocity and no interstage water removal. Complete sulfur condensation was achieved in the Stage II sulfur condenser following the second reactor in Test S-15.

The primary conclusion of the fluidized-bed Stage I reactor test was that the fluidized-bed mode allowed processing a larger gas throughput with better temperature control in Stage

I (i.e., high space velocity) than the fixed-bed mode. The interstage sulfur condensation problem, however, persisted and was not completely resolved at the conclusion of the bench-scale test program. However, by removing water interstage, over 99% conversion was demonstrated. This result suggests that if sulfur could be nearly completely removed interstage, then overall conversion could also be increased above 99%. The >99% recovery was also suggested by earlier nonintegrated Stage I and Stage II tests in which even at 30% water in Stage II, an additional 80% conversion is obtained (McMichael and Gangwal, 1990).

The primary conclusions of bench-scale testing are as follows:

- Increased pressure rapidly increased conversion to sulfur in Stage I up to 10 atm and then more slowly up to 24.8 atm. Up to 96% conversion was achieved in Stage I.
- Optimum reducing gas to SO_2 ratio was the stoichiometric value, 2.
- Efficient interstage sulfur removal is necessary to further increase sulfur conversion to 99% or higher in Stage II.
- The sulfur recovery in Stage I is governed by kinetics and selectivity rather than thermodynamics.
- The COS formed in the first reactor is completely removed, presumably via hydrolysis to H_2S which then further reacts with SO_2 to produce sulfur in the second reactor.

4.2 KINETIC AND MODELING STUDIES

4.2.1 Experimental System for Kinetic Studies

A microcatalytic reactor system (Figure 8) was designed and constructed to study the kinetics of the DSRP reactions, with emphasis on the reduction of SO_2 using H_2 or CO at elevated pressure. In the system, the feed is prepared by blending the gases in desired proportion using electronic mass flow controllers. The reactor, designed for high-pressure operation, consists of a 3/8 in.-OD quartz-lined stainless-steel tube in which about 0.2 g of the DSRP catalyst is positioned at the center using two plugs of quartz wool on both sides. A single zone furnace controlled by a temperature controller was used to heat the reactor. The

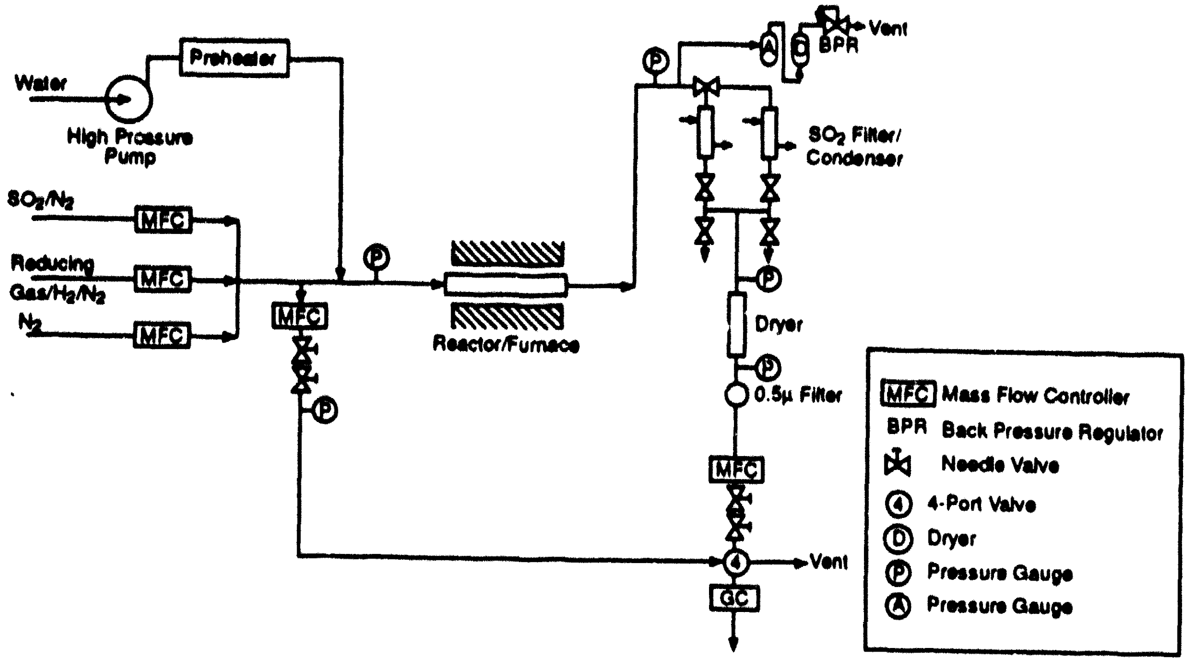


Figure 8. Schematic of reactor for DSRP kinetic studies.

effluent stream from the reactor is vented through a back pressure regulator after condensing sulfur. A small portion of the effluent stream is sent to the GC for product analysis. A four-port valve is used to analyze either the feed or the effluent stream without disturbing the gas flow to the reactor. The catalyst is crushed to 60/80 mesh size to minimize the presence of pore diffusion. The quartz-lined reactor minimizes gas-phase reactions. For example, the conversion of SO_2 was <2% in the quartz-lined reactor at temperatures as high as 650 °C. In contrast, the SO_2 conversion was 13% in a stainless-steel reactor under similar reaction conditions.

4.2.2 Thermodynamic Analysis of Bench-Scale Reactor Data

DSRP lab- and bench-scale experimental data to date were compared (Figure 9) with predictions of a conventional thermodynamic model consisting of the water gas shift (WGS)

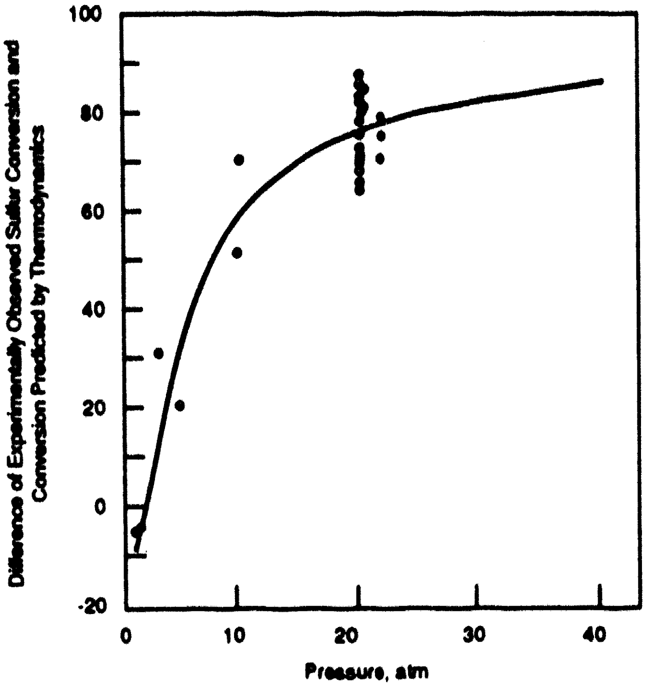


Figure 9. Comparison of experimentally observed and predicted sulfur conversions.

reaction ($CO + H_2O = CO_2 + H_2$), reduction of SO_2 with H_2 or CO to form the various forms of sulfur from S_1 to S_8 ($2H_2 + SO_2 = (1/x) S_x + 2H_2O$), and reduction of SO_2 with H_2 to form H_2S ($3H_2 + SO_2 \rightarrow H_2S + 2H_2O$). The data in Figure 9 were consistent at low pressure (~1.5 to 1.7 atm). However, as pressure was increased, experimental conversions to sulfur were found to be significantly higher than predicted conversions. Fundamental kinetic and thermodynamic studies have been undertaken to shed light on this discrepancy and to evaluate DSRP kinetic rate equations for application to large-scale reactor design.

4.2.3 Results of Kinetic Studies

H_2-SO_2 System

Kinetics of the catalytic reaction of SO_2 and H_2 or CO was studied in the microcatalytic reactor system (Figure 8) using a sulfur-selective catalyst. Of maximum interest in these experiments was the effect of total pressure, space velocity, and H_2/SO_2 ratio on percent SO_2 conversion (x) and percent H_2S selectivity (y). The percent SO_2 conversion to elemental sulfur can be estimated as x(1-y/100). Figure 10 shows the effect of changing total pressure with all other conditions including H_2/SO_2 ratio, SO_2 partial pressure, temperature, and residence time held constant. The total SO_2 conversion increased and the H_2S selectivity decreased with pressure. These results firmly establish the beneficial effect of total pressure. The pressure effect suggests that the kinetic rate constant depends on pressure and goes against the general observation with most kinetic reactions that the rate constant is a function of temperature but not of pressure. Laidler (1965) suggests reasons and rate constant equations to account for the pressure effect for very high pressure liquid phase reactions. These include a pressure term in the rate equation. The pressure effect is probably due to sulfur isomerization shifted toward higher members of S_x (x>4).

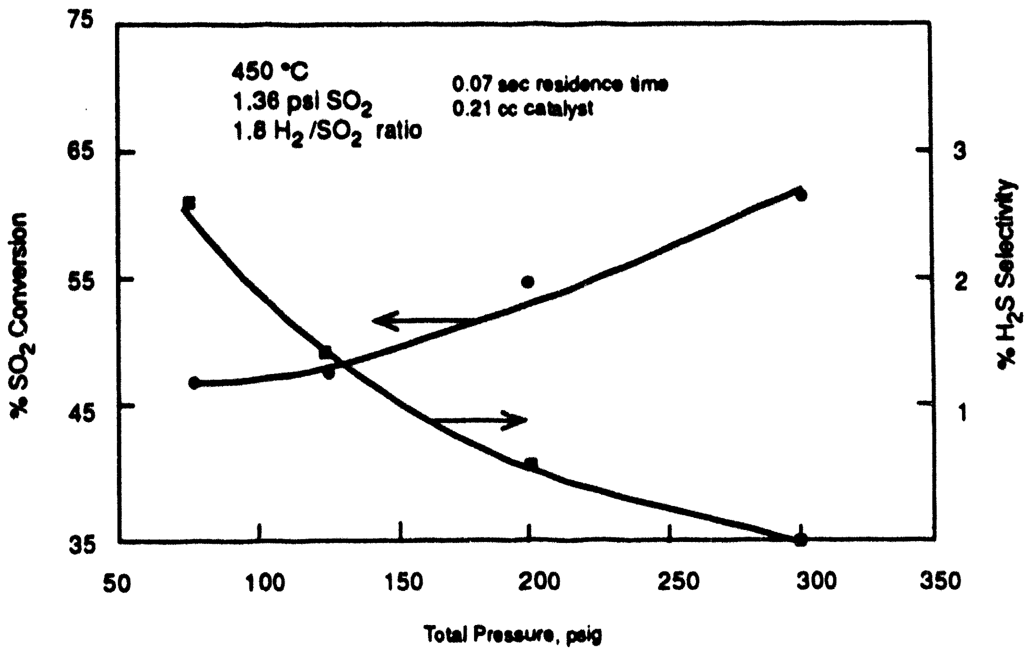


Figure 10. Effect of total pressure on SO_2 conversion and H_2S selectivity.

Figure 11 shows the effect of space velocity on SO_2 conversion and H_2S selectivity at 350 °C and 300 psig. A very high space velocity is used to obtain differential rates. As expected, SO_2 conversion decreases with an increase in space velocity. Interestingly, however, H_2S selectivity also decreases with space velocity and approximately levels off above 600,000 scc/h/g catalyst. This indicates that elemental sulfur (S) and not H_2S is the primary product of SO_2 reduction with H_2 at elevated pressure. The reactions to form S and H_2S are sequential or consecutive ($SO_2 \rightarrow S \rightarrow H_2S$).

In addition to pressure and space velocity, the effect of temperature and H_2/SO_2 ratio on the H_2-SO_2 reaction was also examined. The effect of temperature, studied in the low 250 to 380 °C temperature region (to keep conversions low), showed that the rate of reaction could be well represented by an Arrhenius equation with an activation energy of about 17 kcal/mol. The effect of variation of H_2/SO_2 ratio was studied at 450 °C, 1.1 vol% H_2, 300 psig total pressure, and 5.5×10^5 cc/h/g space velocity. SO_2 conversion increased from about 20% to about 75% as H_2/SO_2 ratio increased from 1 to 5.5. On the other hand, H_2S

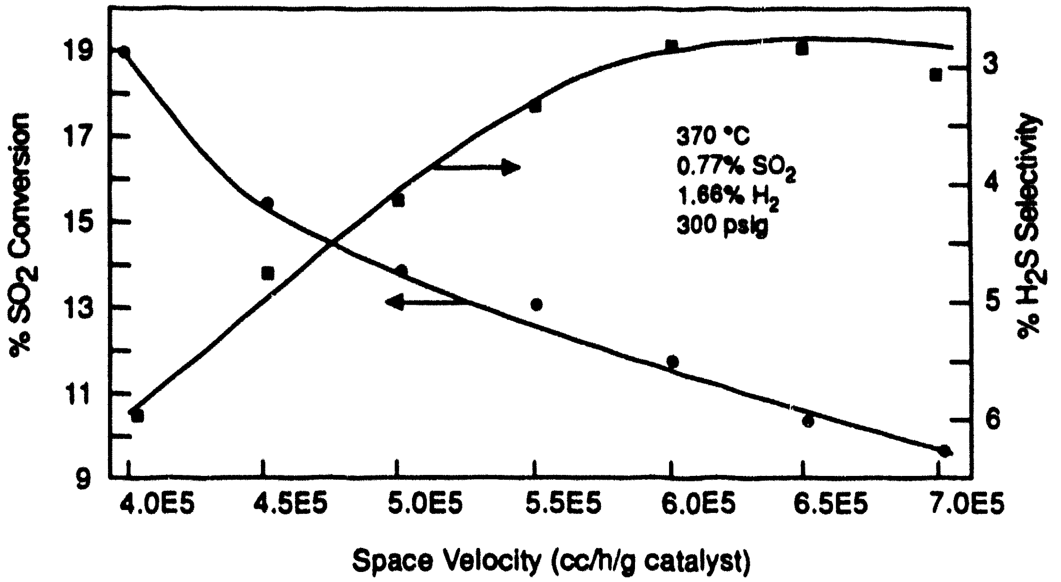


Figure 11. Effect of space velocity on SO_2 conversion and H_2S selectivity.

selectivity remained below 4% at H_2 to SO_2 ratio up to 3 and below 10% at H_2/SO_2 ratio of 5.5. At 425 °C, 0.61 vol% SO_2, 300 psig and 5.5×10^5 cc/h/g, SO_2 conversion increased from about 20% to 95% as H_2/SO_2 ratio increased from 0.6 to 3.4. Again, however, H_2S selectivity remained below 2% at H_2/SO_2 ratio up to 2.6 and below 12% at an H_2/SO_2 ratio of 3.4. These results show that most of the selectivity is toward sulfur at elevated pressure and H_2/SO_2 ratio can be increased at 425 to 450 °C above the stoichiometric 2 to achieve higher conversion without significant loss of sulfur selectivity.

CO-SO_2 System

In contrast to the H_2-SO_2 reaction system, COS was found to be the primary reaction product in the CO-SO_2 reaction system via $SO_2 + 3CO \rightarrow COS + 2CO_2$, with elemental sulfur being produced sequentially via reaction of COS and SO_2 ($SO_2 + 2COS \rightarrow (3/x)S_x + 2CO_2$). This conclusion is corroborated by the data in Figures 12 and 13. In Figure 12, COS selectivity decreases as space velocity decreases, indicating greater production of elemental sulfur at lower space velocities. This indicates the series reaction sequence $SO_2 \rightarrow COS \rightarrow S$. In Figure 13, the CO_2 to COS ratio in the product becomes a constant at 2 at higher space velocities, whereas it increases at lower space velocities. This again is in agreement with the stoichiometry and reaction sequence above.

4.2.4 Modeling

The lower selectivity toward sulfur with CO as opposed to H_2 is in contrast with the high sulfur recovery in the bench unit using coal gas as reductant. However, because the WGS reaction presumably proceeds rapidly, thus providing the hydrogen necessary for high elemental sulfur selectivity, a much smaller quantity of COS was present in the Stage I effluent in bench-scale reactor tests than would be predicted by the microreactor data for the CO-SO_2 system. Also COS conversion, presumably via hydrolysis, was seen to occur in the

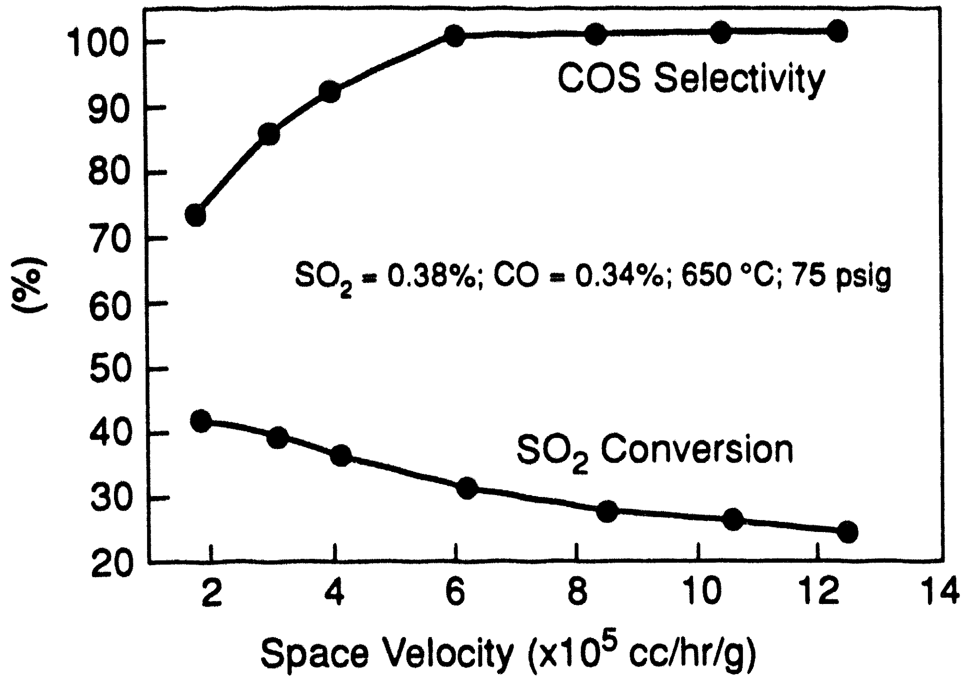


Figure 12. Effect of space velocity on SO_2 conversion and COS selectivity.

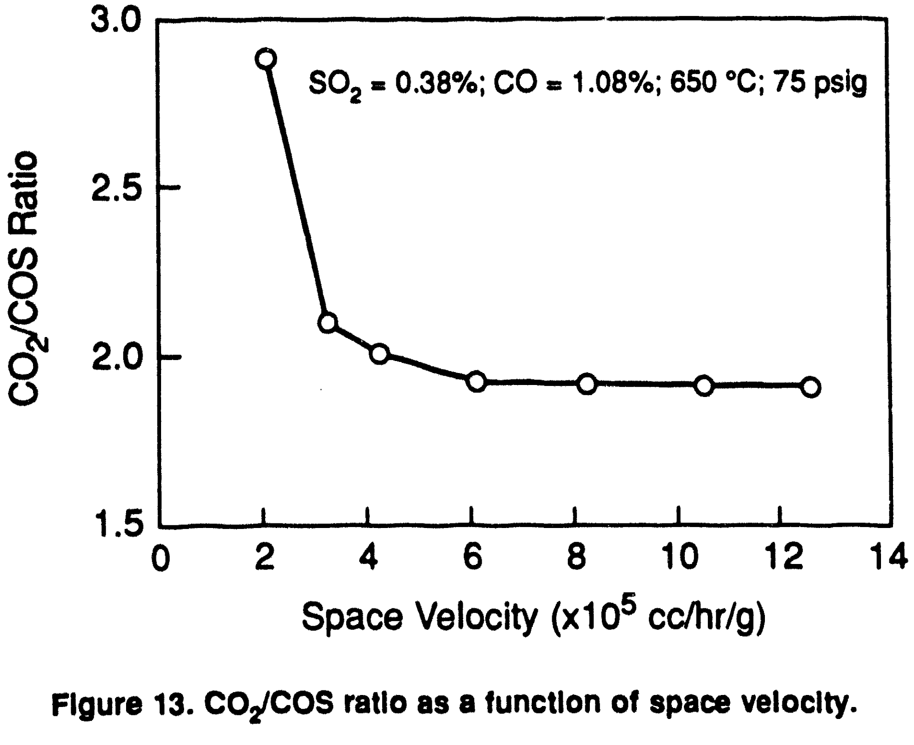


Figure 13. CO_2/COS ratio as a function of space velocity.

DSRP Stage II bench-scale reactor tests (Gangwal et al., 1992). Based on the kinetic experiments and bench-scale tests, Table 5 presents the most plausible DSRP reaction network.

Empirical best-fit equations were derived from the CO-SO_2 and H_2-SO_2 microreactor kinetic data for SO_2 conversion, H_2S selectivity, and COS selectivity. These equations were used to predict the results of the DSRP Stage I bench-scale tests. An equilibrium-modified kinetic model following the approach of Wen et al. (1987) was used for these predictions. In this approach, kinetics of a small number of reactions (about 4 or 5) are considered in the modeling, while other reactions are assumed to reach equilibrium.

For the DSRP Stage I reactions of Table 5, Reactions (1), (2), (4), and (5) were handled by kinetics. The empirical best-fit rate equations for SO_2 conversion, H_2S selectivity, and COS selectivity, modified using appropriate effectiveness factors to allow for larger particle size in the bench-scale reactor, were used to set constraints for SO_2, H_2S, and COS. Because no kinetic data were measured for WGS (Reaction 3 in Table 5), as a first approximation, two extreme models were considered. In the first model, the WGS reaction

Table 5. DSRP Reaction Network

Stage I

$$SO_2 + 2\ H_2 \rightarrow (1/x)S_x + 2\ H_2O \tag{1}$$
$$(1/x)S_x + H_2 \rightarrow H_2S \tag{2}$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{3}$$
$$SO_2 + 3\ CO \rightarrow COS + 2\ CO_2 \tag{4}$$
$$SO_2 + 2\ COS \rightleftharpoons (3/x)S_x + 2\ CO_2 \tag{5}$$

Stage II

$$SO_2 + 2\ H_2S \rightleftharpoons (3/x)S_x + 2\ H_2O \tag{6}$$
$$COS + H_2O \rightleftharpoons H_2S + CO_2 \tag{7}$$

was assumed to reach equilibrium instantaneously at the entrance to the reactor. In the second model, the WGS reaction was assumed not to affect DSRP kinetics. All other minor side reactions, e.g., those that could lead to formation of S_2O, SO, CS_2, SH, H_2S_2, and H_2S_3 were assumed to reach equilibrium in both cases. Gibbs free-energy minimization was carried out for the above-mentioned models with kinetic constraints for SO_2 conversion, H_2S selectivity, and COS selectivity. For comparison, a third model, which assumed all reactions to reach equilibrium, was also considered. No kinetic constraints were imposed in this third model.

The experimental fixed-bed bench-scale Stage I reactor data (McMichael and Gangwal, 1990) are compared to the three models described above in Figure 14. Figure 14 shows that the first model which assumes shift equilibrium predicts the data better than the second model

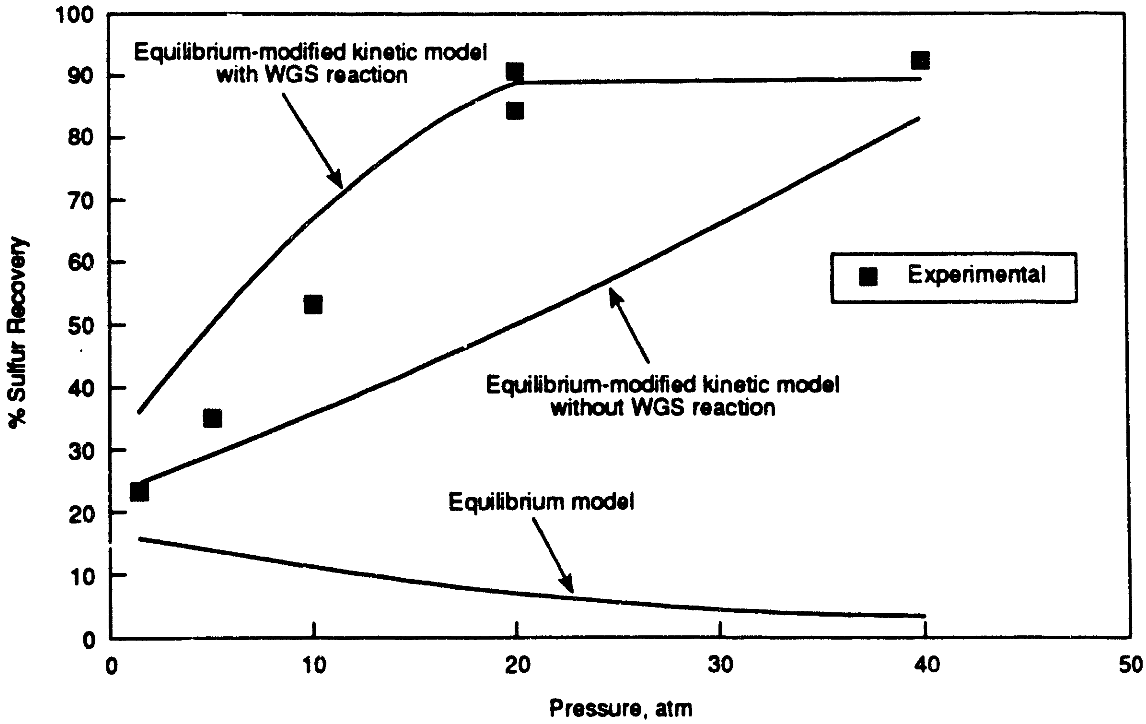


Figure 14. Comparison of model predictions and bench-scale reactor test data.

in which the shift reaction is assumed not to affect DSRP kinetics. The actual experimental data, as expected, lie in between the two extremes. This indicates that inclusion of shift kinetics should further improve model predictions over the first mode. The equilibrium model completely fails to predict the data and its trend with pressure, indicating that equilibrium is not reached in the Stage I reactor.

4.3 TECHNOLOGY TRANSFER ACTIVITIES

The technology transfer activities under the contract have included the following:

1. Making and maintaining contacts with industrial providers of sulfur recovery equipment, processes, and/or services;
2. Presenting detailed results of DSRP testing to selected companies that are developers of or are developing coal gasification, hot-gas cleanup and/or turbine systems for IGCC;
3. Negotiating with the types of companies listed in item (2) leading to potential license agreements;
4. Participating with other companies to independently carry out an economic evaluation of the DSRP; and
5. Presenting results obtained from the experimental investigation of the DSRP along with the engineering and economic evaluation of these results at national symposiums.

The technology transfer activities have resulted in several publications and independent economic evaluations of DSRP by Gilbert Commonwealth and Texaco. The results of these evaluations firmly establish DSRP as a leading contender for treatment of the SO_2 regeneration off-gas from hot-gas desulfurization processes. Very recently, an agreement has been reached with an IGCC system developer to test the DSRP with real coal gas and real regeneration off-gas at a scale that is six times larger than the present DSRP bench-scale unit. These tests are to be conducted under a Cooperative Research and Development Agreement (CRADA) between DOE/METC and the IGCC system developer.

Prior to testing the larger DSRP unit, DOE/METC is also sponsoring slipstream tests using the existing DSRP skid-mounted unit at their 10 in. coal gasifier facility in Morgantown, West Virginia.

5.0 CONCLUSIONS AND FUTURE WORK

Experimental results in a bench-scale unit demonstrate the effectiveness of the DSRP in obtaining near 96% conversion in one stage of reaction. Thermal degradation of the catalyst was not observed in the liter-size adiabatic reactors. Laboratory results reported earlier, which were largely restricted to gases containing 2% SO_2, were confirmed in the relatively large bench unit. In another series of tests, the potential of the DSRP was demonstrated on gases containing up to 12.4% SO_2. The effect of kinetic limitations on conversion became more apparent. At times, increased space velocity yielded higher conversions. Reversal of conversion can occur in the second stage of reaction if sulfur is not effectively removed in the interstage condensers. By removing additional sulfur with the water at the interstage level, sulfur conversion did increase to 98.5% to 99.1%. Further improvement in interstage sulfur condensation and its subsequent removal will be required to achieve higher than 99% conversion. DOE/METC and RTI are vigorously pursuing technology transfer activities. The goal of these activities is to find industrial partners who would be willing to participate in the continued development of the sorbent and DSRP technologies toward a commercial process.

Recently a new contract (No. 30010) was awarded to RTI by DOE/METC. The objectives of this contract are listed below:

- Design and commissioning of a mobile bench-scale reactor system for hot-gas desulfurization and DSRP;
- Bench-scale demonstration of DSRP in conjunction with hot-gas desulfurization using a slipstream of coal gas from a 10 in. fluidized-bed gasifier at DOE/METC;
- Development of a database for scale-up of the DSRP;
- Provision of a six times larger DSRP unit than the present bench-scale unit for testing with slipstreams of real coal gas and real regeneration off-gas at a coal gasification pilot plant.

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