

DIRECT SULFUR RECOVERY PROCESS FOR ELEMENTAL SULFUR RECOVERY FROM GAS

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ABSTRACT

Research Triangle Institute, under contract to the U.S. Department of Energy, has investigated several processes for recovering elemental sulfur from tail-gas that contains SO₂. The work focuses on a dilute tail-gas that is produced by the oxidative regeneration of mixed metal oxide sorbents. The sorbents have been proposed for hot gas cleanup of raw coal gas, upstream of a gas turbine in an integrated, gasification/combined-cycle system. Initially, SO₂ in the tail gas was absorbed on a specially prepared sodium alumina sorbent, followed by reductive regeneration, to produce a concentrated stream of hydrogen sulfide (H₂S), which is a suitable feed for a Claus plant to recover elemental sulfur. It was found that elemental sulfur could be continuously recovered from the tail-gas, thereby eliminating the Claus processing. In a single stage, over 90% of the SO₂ was converted to elemental sulfur using the new direct sulfur recovery process (DSRP). In a two-staged system, overall recoveries of over 99.5% are expected. The effectiveness of the new catalytic process on gases that contain H₂S has also been demonstrated. Tests were conducted to evaluate the effects of pressure, temperature, stoichiometry, space velocity, and steam content.

INTRODUCTION

In the U.S., elemental sulfur is recovered by steam injection from underground deposits using the thermally inefficient Frasch process. Concern is growing that this source may dwindle in capacity and productivity by the year 2000 (Joseph 1988). Natural gas and petroleum processing is another large source. Dwindling production of natural gas and petroleum in the U.S. will further limit the supply of sulfur. Sulfur is mostly used to produce sulfuric acid, the largest single chemical produced in the U.S. The U.S. consumed over 11 million long tons of sulfur in 1988 (U.S. Bureau of Mines 1988). Elemental sulfur production offers an alternative to flue gas and other gas treatment processes, which produce large volumes of throwaway waste that must be disposed of in an environmentally safe manner.

Increasingly stringent environmental emission standards here and in Europe are another driving force for the high efficiency 99%-recovery of sulfur. The U.S. Environmental Protection Agency standards of October 1, 1985 (40 CFR, Part 60, Subpart LLL), limit natural gas processing plants to sulfur emissions of less than 2 long tons per day. Petroleum refineries are limited to emissions of less than 90 ppm. These limitations require sulfur removal of 99% efficiency, above the conversions achieved in simple, multi-stage Claus plants of 95 to 97%. The European Economic Community will require a minimum of 98.5% recovery rates from Claus plants by 1992. Currently, Federal Republic of Germany regulations require up to 99.5% recovery. Environmental concerns and improved process economics have engendered the commercialization of a number of modified Claus processes enhanced with tail-gas treatment processes (Goar 1986).

The U.S. Department of Energy's (DOE's) Morgantown Energy Technology Center has developed and advanced a hot, coal-gas desulfurization concept that is based on a regenerable zinc ferrite sorbent (Grindley 1988). The potential benefit of hot gas cleanup is most significant when the clean coal gas is used to fuel a gas turbine in

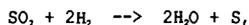
an integrated, gasification/combined-cycle system. In the zinc ferrite process, H₂S reacts with zinc ferrite, which is then regenerated by a dilute air stream. This produces a hot regeneration off-gas containing 1 to 3% SO₂, which must be disposed of in an environmentally acceptable manner. Other desulfurization sorbents can be used in a similar manner that produce an off-gas that contains SO₂. Alternative throwaway processes, such as the hot lime bed developed by the Esso Research Centre (Kowszun 1979), lead to the generation of a large amount of waste, which must be disposed of under an increasingly stringent regulatory burden.

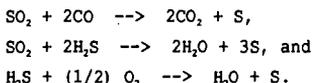
Among the options for the ultimate disposal of off-gas containing SO₂, production of elemental sulfur is attractive. The Ralph M. Parsons Company, under contract to DOE, has evaluated the technical and economic feasibility of candidate processes that can recover sulfur from hot coal gas desulfurization processes (O'Hara et al. 1987). Elemental sulfur, an essential commodity for industrial and military use, is easily stored and transported. Research Triangle Institute, under contract to DOE, has investigated several processes that can recover elemental sulfur from the off-gases that contain SO₂ (Harkins and Gangwal 1988). The initial work focused on absorption of SO₂ on a novel sorbent (Gangwal et al. 1988), followed by reductive regeneration, to produce a concentrated stream of H₂S that would be a suitable feed for recovery of elemental sulfur at a Claus plant. During these investigations, it was found that elemental sulfur could be continuously recovered from the off-gas, thereby eliminating the need for Claus processing. In a single stage, over 90% of the SO₂ was converted to elemental sulfur. In a two-staged system, overall recoveries of over 99.5% are expected. The effectiveness of the new catalytic process on gases containing H₂S has also been demonstrated.

PROCESS PRINCIPLES

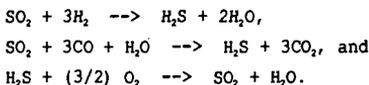
The new direct sulfur recovery process (DSRP) is capable of converting over 90% of the sulfur in gas streams that contain reduced or oxidized gaseous sulfur compounds to elemental sulfur in a direct continuous process. No preconcentrating, oxidation, or reduction is necessary. The residual sulfur in the effluent can be obtained either as essentially all H₂S or as all SO₂ by controlling the inlet gas composition. The DSRP can also reversibly convert oxidized gaseous sulfur compounds such as SO₂ to reduced sulfur compounds such as H₂S and vice versa. Conversion of H₂S and carbonyl sulfide to elemental sulfur has also been demonstrated, confirming the reversible nature of the DSRP. However, the work has focused largely on conversion of SO₂ to elemental sulfur.

The primary gas stream to be treated is mixed with a small flow of a secondary gas stream, and is contacted with a catalyst at temperatures from about 400 to 700 °C and at pressures up to 20 atmospheres. If the primary gas stream to be treated contains mainly oxidized sulfur gases, then the secondary gas stream should be reducing in nature. Near stoichiometric quantities are desirable to promote the conversion to elemental sulfur and to reduce reaction with other components in the gas stream. It is possible to have oxidizing gases such as steam and CO₂ in the secondary gas stream as long as the gas is overall reducing. If the primary gas stream already has close to the desired stoichiometry, then a secondary gas stream is not required. On the other hand, if the primary gas stream contains mainly reduced sulfur gases, then the secondary gas stream should be oxidizing in nature (e.g., containing oxygen or other oxidants). In all cases, if elemental sulfur is the desired product, the mixture of the primary and secondary gas streams should have close to such stoichiometry that the sulfur gases can be completely converted to elemental sulfur. Simple examples of these stoichiometries are



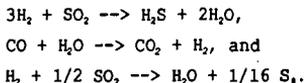


It is also possible to convert oxidized sulfur gases to reducing sulfur gases and vice versa by shifting the stoichiometry of the inlet mixture toward the desired gas and by choosing the proper temperature and pressure. Simple examples of the stoichiometries are



The chemistry of the process invariably involves multiple intermediary reactions at or near the surface of the catalyst. When SO_2 and reducing gases are simultaneously contacted with the catalyst, steady state is quickly reached, and SO_2 is continuously converted to elemental sulfur. When H_2S and oxidizing gases are simultaneously contacted with the catalyst, H_2S is continuously converted to elemental sulfur as steady state is reached. The yield of elemental sulfur increases with increasing temperature between 400 and 700 °C and with increasing pressures from above atmospheric to 20 atmospheres.

These observed results have been verified by thermodynamic equilibrium analysis of the seven compounds: H_2 , CO_2 , CO , H_2S , SO_2 , H_2O , and S_x (or S_2). Since the number of compounds is seven and the number of atoms is four (H, C, O, S), only 7 - 4 or three reactions between these compounds were needed to completely describe the system from the standpoint of thermodynamic equilibrium. The following reactions were selected (others are possible) to completely define the system from a thermodynamic standpoint:



The state of the catalyst is constant and was not incorporated into the analysis.

Starting with a mixture containing about 2% SO_2 , 4% $\text{CO} + \text{H}_2$, 4% $\text{CO}_2 + \text{H}_2\text{O}$, and the balance N_2 , the predicted yield of elemental sulfur as S_2 is about 60% of the inlet sulfur at 20 atmospheres and 700 °C. Since more than 90% yield was observed experimentally, it is postulated that the elemental sulfur products obtained may be combinations of S_2 , S_4 , S_6 , and S_8 or higher polysulfides. It is known that S_2 , S_4 , and S_8 are not stable at 700 °C at 1 atmosphere. However, data are not available at 20 atmospheres. The thermodynamic analysis, in any event, lends credence to the results obtained in the laboratory.

EXPERIMENTAL APPARATUS

Tests were performed using the fixed-bed reactor system shown in Figure 1. The system consists of a 1-in. O.D., 0.87-in. I.D., Alon-processed 316 stainless steel reactor, a gas feed system, and a filter/condenser for the removal of elemental sulfur and water. Premixed gases flow from pressure regulated gas bottles, controlled by mass flow controllers. A high pressure, positive displacement pump injects water into the gases before an electric heater prior to entering the bottom of

the reactor. After exiting the reactor, the gas is cooled to 160 °C to condense sulfur on the filter. Water is removed in a condenser and then the dry gas flows through a back pressure regulator, which controls the bed pressure. A sample of gas is continuously withdrawn before the back pressure valve. The gas is analyzed for H₂S and SO₂ by gas chromatography and a continuous SO₂ analyzer. The outlet gas flow rate is measured periodically using a soap bubble meter.

EXPERIMENTAL RESULTS

Tests were conducted to evaluate the effects of pressure, temperature, space velocity, and steam content on sulfur recovery in the DSRP. These tests were conducted over a wide range of pressures up to 40 atmospheres and at temperatures from about 390 to 700 °C. Space velocities ranging up to 5500 standard cubic centimeters per cubic centimeter hour, scc/(cc).hr were evaluated. Steam content ranged up to 25% by volume. The work focused on the reduction of SO₂ to elemental sulfur with simulated coal gas; however, a number of runs demonstrated the oxidation of H₂S and the reversibility of the reactions. A large database was generated that deals with the conversion of SO₂ to elemental sulfur over the range of conditions and inlet gas compositions shown in Table 1.

All experimental runs were carried out in a single-stage fixed-bed reactor with either 25 or 50 cm of catalyst. The two sizes allowed investigation of a range of space velocities within the capacity of the gas delivery system. Blank runs without the catalyst showed the reactor walls to be essentially inactive. Experimental results are summarized in Figures 2 through 6.

The initial investigations focused on the effects of pressure, space velocity, and temperature on the conversion rate of SO₂ to elemental sulfur. By far the greatest effect was observed by varying the pressure at a near constant temperature of 650 °C. (See Figure 2.) Beginning slightly above atmospheric pressure, conversion to elemental sulfur was about 20%, which quickly rose to near 60% at 10 atmospheres and then to over 90% near 20 atmospheres. Doubling the pressure to 40 atmospheres increased the conversion to 95%. In comparison, one stage of a Claus reactor may result in a 60 to 70% conversion, resulting in the typical commercial practice of using three stages of Claus reactors with intercooling between each stage to obtain 90% conversion. In addition, the hourly gas space velocity in a Claus ranges near 1000 scc/(cc).hr, while the results shown in Figure 2 were obtained at a space velocity near 1800 scc/(cc).hr. The higher pressure of the DSRP permits higher space velocities and therefore smaller size reactors, or higher through-put with a fixed size of reactor. Even space velocities higher than 1800 scc/(cc).hr can be used in the DSRP as shown in Figure 3.

Data presented in the upper band of Figure 3 were obtained at a constant pressure of 20 atmospheres and at temperatures from 550 to 650 °C. Up to a maximum space velocity of 5500 scc/(cc).hr, conversion was impacted to a small degree, essentially remaining above 90% at the extreme flow rate. Space velocities ranging from 1800 to 5500 scc/(cc).hr resulted in conversion rates varying between 90 and 95% near 550 °C. The variation was less pronounced at temperatures near 650 °C, remaining closer to 95%. In contrast, the impact of space velocity at the lowest pressure of near 1.5 atmospheres was dramatic.

The lower line in Figure 3 illustrates the impact. A variation in space velocity from 400 to 1800 scc/(cc).hr cuts the conversion rate in half, i.e., from about 46% to near 20%. As a result, the slope of the lower line is much steeper than the upper band obtained at 20 atmospheres pressure. We can also compare the results at varying pressures but at a fixed space velocity of 1800 scc/(cc).hr and a temper-

ature of 650 °C (i.e., point A at 1.5 atmospheres to point B at 20 atmospheres). At the lower pressure, the conversion is near 20% while at the higher pressure, the conversion is well over 90%. This shows that pressure plays an important role in the DSRP.

The data in Figure 3 also confirm the much higher throughput possible at higher pressure. At the lowest space velocity while at the lower pressure, conversion does not even approach the 90% achieved at higher pressure, which prevents an exact comparison. At the higher pressure, the conversion is hardly affected at the highest space velocity, which was at the limits of the laboratory gas supply system. Therefore, high conversion rates can be achieved using the DSRP even at extreme flow rates, provided the pressure is sufficiently high.

Somewhat analogous to the effect of pressure is the effect of temperature, but to a much lesser degree as shown in Figure 4. At 440 °C and above, conversion to elemental sulfur remains well above 90% and is essentially unaffected by any increase in temperature. These results obtained at a constant pressure of 40 atmospheres are significant because the insensitivity of both conversion rate and catalyst to temperature rise and thermal degradation is demonstrated. The catalyst has yet to show any sign of deactivation over hundreds of hours of testing, including repetitive testing of a single catalyst material and even with an accidental excursion to 760 °C. The possible effects of thermal degradation may become more evident as the DSRP is scaled-up to pilot-scale and larger size.

The effect of the steam content of the gas on conversion of SO₂ to elemental sulfur was evaluated. The Claus equilibrium is limited by the water content of the gas, which must be removed in the intercooling step between stages. However, this disadvantage is not experienced with the DSRP at high temperature and pressure. Figure 5 shows results at 20 atmospheres of pressure and at temperatures varying from 600 and 700 °C. Steam content in the inlet gas ranged from about 1 to 25% and produced virtually no impact on the conversion rate above 5% steam. The effect below 5% may be questionable since data from some early runs are included that may not have been at optimal conditions. However, the insensitivity to steam indicates that the conversion is not limited by the Claus equilibrium, at least at first. As the overall sulfur content in the gas drops to the ppm level and as H₂S and SO₂ levels become comparable, an equilibrium may be established that is not affected by steam content at high temperature and pressure. In contrast, the equilibrium and conversion rate are definitely dependent on stoichiometry.

Figure 6 presents the concentration of SO₂ and the reduced sulfur compounds COS and H₂S that are found in the outlet as the molar ratio of reducing gases was varied. The molar ratio was varied closely, at about a stoichiometric ratio of two moles of reducing gas, either as H₂ or CO, to one mole of SO₂ in the inlet. As the reducing content in the gas increased, the residual content of SO₂ in the gas decreased and the reduced compounds of sulfur increased. This confirms the equilibrium nature of the DSRP and demonstrates that the components in the outlet can be controlled. Figure 6 also shows that sulfur conversion is optimized as the stoichiometric ratio of 2.0 is approached, demonstrating the importance of controlling molar ratios. The data also suggest that H₂S in a gas stream could be efficiently converted to elemental sulfur.

The direct conversion of hydrogen sulfide to elemental sulfur was confirmed in a short series of experiments. In one preliminary experiment, an 88.2% conversion rate was observed when 2.5% H₂S and 0.6% COS in nitrogen were reacted over a catalyst with a stoichiometric amount of oxygen at a one-to-one molar ratio. In a more carefully controlled experiment, over 95% conversion to elemental sulfur was ob-

tained. These initial experimental results require further confirmation. It can be significant that the DSRP removes reduced sulfur species either as H_2S or COS from a gas stream. This introduces the possibility of treating a variety of industrial gas streams.

CONCLUSIONS

Experimental results indicate that the Direct Sulfur Recovery Process, DSRP, can convert SO_2 , COS and H_2S directly to elemental sulfur at conversion rates near 95% in a single stage, and above 99.5% after two stages.

Pressure has the most significant effects in terms of increased conversion to elemental sulfur and increased throughput with the DSRP. Gas hourly space velocities over 5500 scc/(cc).hr and above can increase the throughput.

Above a threshold temperature and depending on pressure, conversion rates remain above 90% with little impact caused by further increases in temperature.

The DSRP is insensitive to the steam content of the gas, which distinguishes it from other processes that rely on Claus equilibrium reactions.

Gas streams containing concentrations of sulfur compounds as low as 0.85%, possibly even lower, can be treated using the DSRP to efficiently recover elemental sulfur.

Gas phase equilibria are established in the DSRP (space velocity over a wide range has little impact on the products of reaction) that can control the composition of the outlet gas for SO_2 content or reduced sulfur compounds by controlling the stoichiometric ratio at the inlet of the reactor.

The conversion to elemental sulfur can be optimized by controlling the stoichiometric balance of gaseous components at the inlet of the reactor.

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Table 1. Inlet Gas Composition

COMPONENT	% by Volume
SO ₂	0.85 - 1.9
H ₂ O	1.0 - 25.0
H ₂	0.65 - 1.6
CO	0.85 - 2.1
CO ₂	0.25 - 0.6
N ₂	Balance

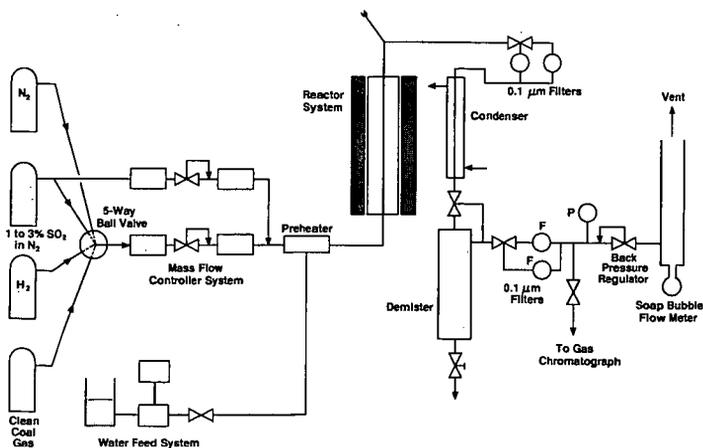


Figure 1. High-Pressure Fixed-Bed Test Apparatus

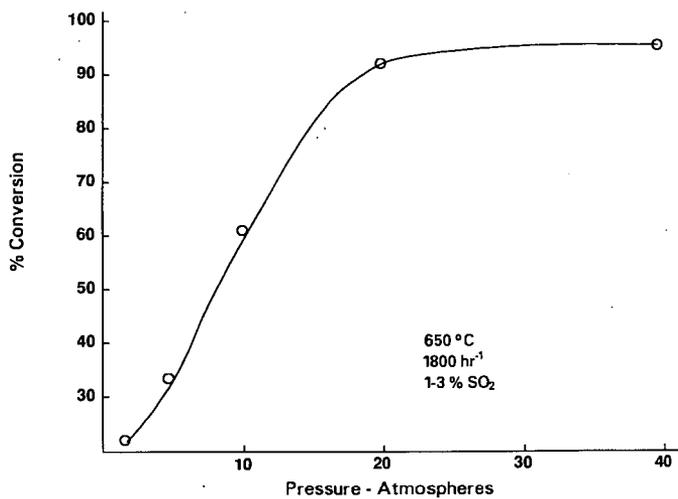


Figure 2. Effect of Pressure on the DSRP

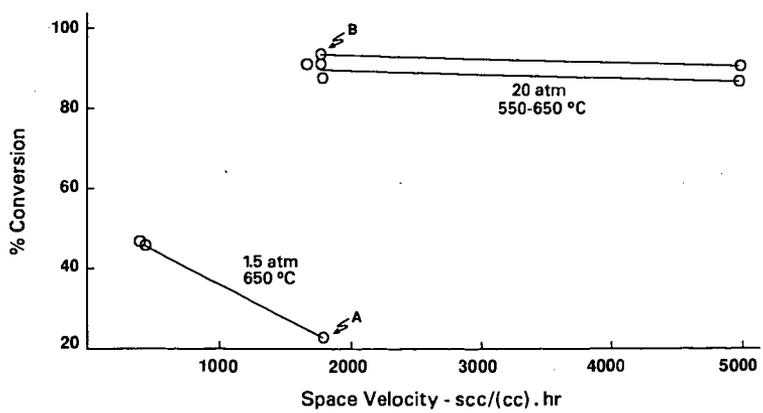


Figure 3. Effect of Space Velocity and Pressure on the DSRP

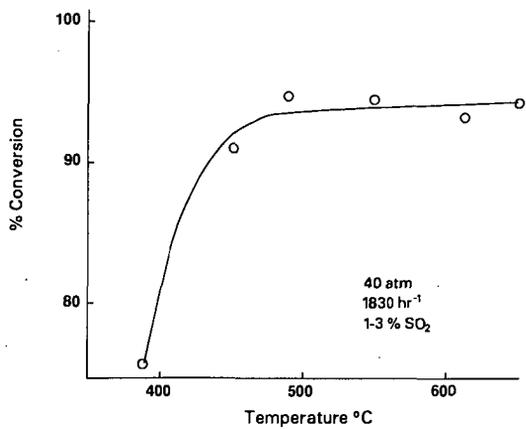


Figure 4. Effect of Temperature on the DSRP

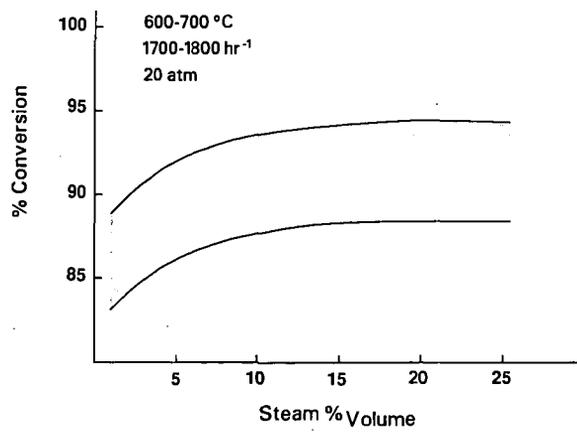


Figure 5. Effect of Steam Content on the DSRP

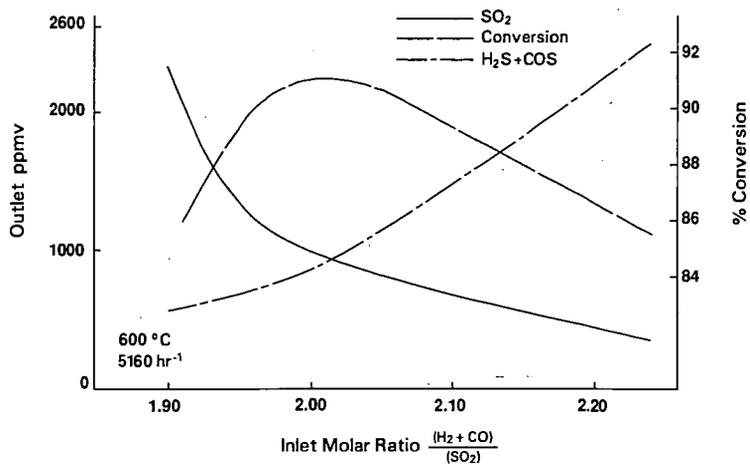


Figure 6. Effect of Stoichiometry on the DSRP