PLASMA-CHEMICAL TREATMENT
OF HYDROGEN SULFIDE
IN NATURAL GAS PROCESSING

FINAL REPORT
(May 1991 - December 1992)

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<p>A new process for the treatment of hydrogen sulfide waste that uses microwave plasma-chemical technology has been under development in Russia and the United States. Whereas the present waste-treatment technology, at best, only recovers sulfur, this novel process recovers both hydrogen and sulfur by dissociating hydrogen sulfide in a plasma by means of a microwave or radio-frequency reactor. A research project has been undertaken to determine the suitability of the plasma process in natural gas processing applications. The experiments tested acid-gas compositions with 30-65% carbon dioxide, 0-7% water, and 0-0.2% of a standard mixture of pipeline gas. The balance gas in all cases was hydrogen sulfide. The reactor pressure for the experiments was 50 torr, and the microwave power was 1.0 kW. Conversions of hydrogen sulfide ranged from 80 to 100%, while 35-50% of the carbon dioxide was converted to carbon monoxide. This conversion of carbon dioxide resulted in a loss of hydrogen production and an energy loss from a hydrogen sulfide waste-treatment perspective. Tests of a direct natural gas treatment concept showed that hydrocarbon losses were unacceptably high; consequently, the concept would not be economically viable.</p>			
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Research Summary

Title	Plasma-Chemical Treatment of Hydrogen Sulfide in Natural Gas Processing
Contractor	Argonne National Laboratory
	GRI Contract Number: 5090-260-2088
Principal Investigator	J.B.L. Harkness
Report Period	May 1991 - November 1992 Final Report
Objective	The technical objectives of this experimental program were to (1) determine the feasibility of operating the plasma reactor at atmospheric pressures, (2) test acid-gas compositions typical of natural gas processing, and (3) determine the feasibility of the concept of a direct process for the treatment of natural gas.
Technical Perspective	The natural gas industry uses a wide variety of waste-treatment technologies to process hydrogen sulfide at natural gas purification plants. The typical large-scale plant uses the Claus technology to recover the sulfur value contained in hydrogen sulfide, but such a plant requires a tail-gas cleanup unit to meet emission standards. The plasma-chemical process, being developed in Russia and studied in Canada and in a U.S. Department of Energy (DOE) project at Argonne National Laboratory (ANL), offers a unique opportunity for recovering the hydrogen value in hydrogen sulfide, as well as a sulfur product, at both large-scale and small-scale facilities. The emissions from plasma-chemical technology may also be lower than those from current processes.
Results	During the experiments, a plasma operating pressure of 200 torr was attained, but the plasma was unstable at this pressure. Therefore, the remaining experiments were conducted at 50 torr, and the plasma was sufficiently stable at this pressure to ensure the extended run times required to complete an experiment. The acid-gas experiments yielded conversions of hydrogen sulfide between 80 and 100%, but they appeared to use excessive energy to achieve these conversions. The experiments for the direct treatment of natural gas destroyed too high a percentage of the hydrocarbons for this concept to be commercially viable.

Technical Approach

A new microwave applicator was installed, and the feed system was upgraded to operate at pressures of up to 2 atm. Acid-gas compositions were prepared by mixing hydrogen sulfide, carbon dioxide, water, and a standard mixture of pipeline gas on-line in the laboratory. These experiments used a three-factorial statistical design with carbon dioxide, water, and pipeline gas to yield a range of gas compositions (hydrogen sulfide was the balance gas). The mixtures passed through a microwave-generated plasma operating at 50 torr, after which the sulfur product was condensed. The noncondensable gases were compressed to atmospheric pressure and collected for mass-spectrometric analysis. In the experiments conducted to study the direct treatment of natural gas, a two-factorial design was used, whereby low concentrations of carbon dioxide and hydrogen sulfide were mixed with a standard mixture of pipeline gas.

Project Implications

The purpose of this research project was to expand upon DOE studies of a hydrogen sulfide dissociation process by means of a microwave plasma reactor and to determine the applicability of this process in natural gas processing. Specific objectives of this research included increasing the operating pressure of the reactor and obtaining heat and material balances for both acid-gas and direct natural gas treatment applications. If successful, the research would generate data that would be used in a techno-economic study, performed by the M.W. Kellogg Company, that would quantify the benefits of the process.

The project was funded as part of GRI's Exploratory Research Program. To be selected for Exploratory Research funding, a proposal must include a well-defined work scope and specific performance criteria. If these criteria are met during the course of the research, the project will be transferred to an applied research program for further development. The criteria for success for this research project are given below:

- Achieve a sustainable reaction pressure between 500 and 760 torr.
- Achieve a hydrogen sulfide dissociation energy of less than 0.7 eV/molecule of hydrogen sulfide dissociated, while producing no unwanted by-products and achieving conversions of 45% or greater.

These performance criteria were not reached. The maximum sustained reactor pressure was 200 torr, but the plasma was not stable at this pressure. Although conversions of 45% were substantially exceeded, the dissociation energy required for this conversion at elevated pressures significantly exceeded the target of 0.7 eV/molecule. Furthermore, the reactions produced undesirable by-products — carbonyl sulfide and

carbon disulfide. These by-products may be treatable by the internal purification step included in the ANL-proposed process for the treatment of hydrogen sulfide waste. The direct natural gas treatment experiments resulted in the degradation of the hydrocarbon species. Because of these results, GRI's plans for a techno-economic evaluation of this technology have been suspended indefinitely. GRI may, however, serve as part of an industry working group that directs future ANL research in this area in order to continue monitoring this technology. GRI will reevaluate its position in this research area if future developments show that this technology has applications in the gas industry.

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Executive Summary

A new process for the treatment of hydrogen sulfide waste that uses microwave plasma-chemical technology is currently under development. Whereas present waste-treatment processes, at best, recover only sulfur, this novel process recovers both hydrogen and sulfur. The plasma process involves dissociating hydrogen sulfide in a plasma by means of a microwave or radio-frequency reactor. After the dissociation process, sulfur can be condensed and sold, just as is currently done. The remaining gases would be purified and separated into streams containing the product hydrogen, the hydrogen sulfide to be recycled to the plasma reactor, and the process purge containing carbon dioxide and water. Previous work has shown that this process could be particularly important to the petroleum refining industry, which has a growing demand for hydrogen; moreover, the hydrogen needed by industry must be produced from increasingly scarce hydrocarbon resources.

The research presented here was designed to determine how the plasma process might be applied to acid-gas streams in the natural gas industry, which may have higher concentrations of carbon dioxide than those previously studied for refining applications. Laboratory-scale experiments with pure hydrogen sulfide and mixtures of hydrogen sulfide, carbon dioxide, and water indicated that conversions exceeding 90% are possible with an appropriate reactor design.

Research at Argonne Sponsored by Gas Research Institute

Experimental work for the Gas Research Institute (GRI) built upon, and was coordinated with, continuing research sponsored by the U.S. Department of Energy (DOE) at Argonne National Laboratory (ANL). The experimental program included the following activities: (1) determining the technical feasibility of dissociating hydrogen sulfide at atmospheric (or higher) pressures, (2) testing acid-gas compositions typical of natural gas sweetening plants, and (3) evaluating the concept of direct plasma treatment of crude natural gas. The main feature of the program was the extension of the acid-gas composition database to compositions of interest to the natural gas industry.

The laboratory program was organized into five tasks. The first task was to change the existing experimental apparatus from a waveguide microwave applicator to a resonant-cavity reactor and to modify the system so that it could be operated at higher pressures. These modifications were successfully completed in November 1991, after which the following experimental tasks were carried out:

1. Increase the plasma operating pressure,
2. Test acid-gas compositions of interest to the natural gas industry, and

3. Explore the feasibility of the direct treatment of crude gas.

The final task was the preparation of this report which describes the laboratory results and conclusions.

Increased Operating Pressures

In addition to the planned modifications of the Argonne apparatus, a new gas injector was designed to improve the flow distribution in the reactor. The modified apparatus has operated at pressures of up to 200 torr. The objective of operating the system between 500 and 760 torr (atmospheric pressure) was not achieved in these experiments because the plasma was still impinging on the reactor wall and melting it when the microwave power was increased to maintain the plasma. Atmospheric operations are, nevertheless, technically feasible, as has been shown by the Hydrogen Energy and Plasma Technology Institute in Moscow. Recently, Canadian researchers have also successfully operated a system at atmospheric pressure.* They concluded that "operating at or near atmospheric pressure is possible. This will save compression energy, but will cause some decrease in reaction efficiency." Our discussions with Russian and Canadian researchers suggest that it will not be feasible to raise the operating pressure with the current nozzle configuration of the system and power source unless there is a concomitant increase in gas flow rate. A minimum gas flow rate is needed to develop and maintain the desired reactor hydrodynamics.

Experimental Results for Acid-Gas Compositions

Eleven experiments for the treatment of hydrogen sulfide were carried out at nine different acid-gas compositions by using the microwave system with a resonant-cavity applicator. The experiments employed a statistical design in three variables and were run in a random order. The experimental variables were the concentrations of carbon dioxide (30.0-65.0%), water (0.0-7.0%), and natural gas (0-0.2%). For all experiments, the gas-feed rate was 6 SLPM (standard liters per minute), the target plasma reactor pressure target was 50 torr (to maintain a stable plasma and to avoid melting the quartz tube), and the target microwave power level was 1,000 W. The natural gas mixture used for these tests was obtained from the Institute of Gas Technology (IGT). The resonant-cavity microwave applicator was tuned to minimize reflected power for each of the experiments. Several conclusions can be drawn from these experiments:

- The plasma-chemical process is technically capable of processing acid-gas compositions of interest to the natural gas industry.

* Personal communication from E. Luinstra and M.T. Craw-Ivanco, October 8, 1992.

- High concentrations of carbon dioxide will favor the formation of water at the expense of hydrogen. At the same time, high concentrations of carbon dioxide will impose an energy penalty on the process.
- Minor amounts of carbonyl sulfide (0.1-0.8%), carbon disulfide (0.04-0.70%), and sulfur dioxide (0.0-2.1%) were formed in these experiments, but these compounds appear to be treatable by the proposed process.
- Carbon dioxide inhibited the formation of carbon disulfide.
- The reaction mechanism of the water-gas shift is important to understanding the chemistry of this system; it inhibits both the conversion of carbon dioxide and the production of carbonyl sulfide, but it increases energy consumption.
- At trace levels, methane is a significant reagent in the system. It inhibits the conversion of carbon dioxide and the formation of sulfur dioxide.
- Methane's effect alone, and in combination with water, balances out to no net impact for the formation of carbonyl sulfide and carbon disulfide, although hydrocarbons probably were the starting material for the formation of carbon disulfide.

Experimental Results for the Direct Treatment of Crude Gas

The tests of the direct treatment of crude gas incorporated two different levels of hydrogen sulfide that were either 50 ppm or 100 ppm and carbon dioxide contents that ranged from 1% to 3%. The IGT natural gas mixture was used as the balance gas. The system flow rate was 4 L/min through a 0.12-in. nozzle, and the pressure of the plasma reactor pressure was held at 50 torr. The microwave power level was 1.0 kW.

The principal conclusions from these tests are listed below.

- This plasma-chemical application does not appear to be economically feasible, because hydrocarbon losses ranged from ~2% for ethane up to 50% for C₄⁺ species.
- Hydrogen was the major plasma product (0.56-1.2%), and most of the hydrogen was produced as a result of the destruction of hydrocarbons, which also caused coking.
- Carbon monoxide was the next major product of the plasma (0.04-0.6%).

- Hydrocarbons were preferentially destroyed in the order $C_{4+} > C_3 > C_2 > C_1$.
- Methane losses averaged 1.6%.

Process Design

A proposed flow sheet for a process to treat hydrogen sulfide waste based on plasma-chemical dissociation is shown in Figure S.1. Acid gas from an amine-purification system, which would contain carbon dioxide and water, is combined with recycled hydrogen sulfide and fed to the plasma reactor, which is connected to a microwave generator with wave guides. The process stream leaving the reactor would contain hydrogen, sulfur vapor, sulfur liquid, unconverted hydrogen sulfide, water, and, possibly, some impurities (such as carbonyl sulfide or carbon disulfide). The product sulfur would be cooled and collected in a scrubber. Available process energy might be recoverable at this point. The scrubbing step would remove the bulk of the sulfur and some of the sulfur-containing impurities. Remaining traces of the undesirable compounds would be removed in an internal catalytic reducing unit (i.e., no Tail-Gas Cleanup Unit [TGCU]). Sulfur compounds would be converted to hydrogen sulfide, which would be recycled to the plasma reactor. The operation of this unit would consume a small, but negligible, fraction of the hydrogen product. The purified gas phase would be compressed and sent to a separations step to recover the hydrogen product, recycle the unconverted hydrogen sulfide, and purge water and carbon dioxide.

Most of the operating costs are for the energy needed to generate the microwaves, although some additional energy would be needed to operate pumps and compressors. The capital costs of the Argonne version of the process have been estimated to be less than half those of a Claus Sulfur Recovery Unit (CSRU) with a TGCU.* For a refinery application, the annual operating costs of the plasma-chemical technology are estimated to be $\$2.0\text{--}4.0 \times 10^6/\text{yr}$ less than the current CSRU/TGCU technology (assuming a sulfur production of 157 long ton/day). This difference is insensitive to the price of sulfur because both processes generate essentially the same amount of sulfur. Because the plasma-chemical technology saves energy, this technology becomes more competitive as the cost of energy increases.

A similar cost comparison for a natural gas purification application has not been performed. For a natural gas application to accrue the principal economic benefits of the plasma-chemical technology, a market or use for the hydrogen would need to be identified.

* Daniels, E.J., J.B.L. Harkness, and R.D. Doctor, 1992, *Economics of Microwave Plasma Dissociation of H_2S* , 56b, American Institute of Chemical Engineers, 1992 Spring National Meeting, Houston, Texas, March 29-April 2.

FIGURE S.1 Proposed Process Design for the Treatment of Hydrogen Sulfide Waste

Acknowledgments

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Plasma-Chemical Treatment of Hydrogen Sulfide in Natural Gas Processing

by

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1 Introduction

Hydrogen sulfide is an extremely toxic gas that must be removed from natural gas before the natural gas can be distributed to customers. The natural gas industry has developed a wide range of technologies for removing and destroying hydrogen sulfide. When either the production rates of natural gas or the concentrations of hydrogen sulfide are relatively low, the "sweetening" technology may be as simple as adsorption by iron sponge, a process whereby hydrogen sulfide is first converted to iron sulfide and then to elemental sulfur when the iron is regenerated. Typically, larger production facilities use separate processes to purify and treat hydrogen sulfide waste. The larger facilities normally recover and sell by-product sulfur, a process that enables such facilities to offset their capital and operating costs. Although the sorption-type technologies have relatively lower capital and operating costs, they rarely receive any credits for sulfur.

The direct dissociation of hydrogen sulfide into hydrogen and sulfur by means of microwave-generated plasmas offers unique process alternatives for the treatment of hydrogen sulfide waste. At a larger scale facility, the credits earned from the hydrogen by-product could substantially lower the cost of waste treatment.

1.1 Previous Research

Previous research on the microwave (or radio-frequency) processing of hydrogen sulfide includes experimental and theoretical studies reported in Soviet technical literature (Balebanov et al. 1985; Rusanov et al. 1985) and a brief study sponsored by the Gas Research Institute (GRI) at Cottrell Environmental Sciences (Helfrich et al. 1989). Other related research includes reports of small-scale laboratory experiments carried out at the I.V. Kurchatov Institute of Atomic Energy* (now reorganized as the Russian Research Centre/Kurchatov Institute [RRC/KI]) in Moscow that were very similar to several theses prepared at the Massachusetts Institute of Technology in the 1960s about the dissociation of various gases (Brockmeier 1966; Bell 1968; Cooper 1967).

* The division conducting this effort became the Hydrogen Energy and Plasma Technology Institute (HEPTI) in 1992.

The Cottrell experiments (Helfrich et al. 1989) were focused on evaluating the concept of a one-step process for the simultaneous desulfurization and methanation of synthesis gas from coal gasification. The investigators' original plans called for using both microwave and radio-frequency experiments, but the microwave experiments were abandoned in favor of radio-frequency experiments because of equipment limitations. Because the plasma synthesis and dissociation mechanisms are essentially identical for these two energy sources, Cottrell's conclusion should also apply to microwave-generated plasmas. Cottrell reported that the methane yield was insufficient for commercial applications when energy consumption was taken into account. In addition, the investigators concluded that only moderate energy consumption was needed to remove hydrogen sulfide from the gas phase, and they recommended that microwave desulfurization be explored further. As was the case in the Soviet and the Argonne National Laboratory (ANL) work reported below, elemental sulfur was reported to be the end product.

1.1.1 Research at Kurchatov Institute

Research programs in the United States and Canada are currently studying the microwave dissociation of hydrogen sulfide, building upon research findings presented in Russian scientific literature describing research at the Kurchatov Institute. The Russian hydrogen sulfide research is part of a substantial, continuing program to develop new hydrogen-production technologies.

The Russians proposed that a microwave (or a radio-frequency) discharge be used to generate a "cold" nonequilibrium plasma that dissociates hydrogen sulfide into hydrogen and sulfur. One key feature of the plasma-chemical reactor proposed by the Russians (Balebanov et al. 1985) is that the feed gases should be injected into the plasma zone tangentially and at very high velocities. The Russian reactor, as shown in Figure 1, produces an isolated plasma zone, followed by a rapid separation and cooling of the dissociation products that "freezes" the product composition at its plasma condition, which is characterized by significantly higher temperatures than would be expected from the bulk-gas temperatures. The electronic temperatures of a plasma are on the order of 10-50,000 K (Brockmeier 1966), whereas the bulk-gas temperatures may only be a few hundreds of degrees centigrade. The reactor body is essentially a short section of circular waveguide with one, or more, ports for injecting the microwave energy. Figure 1 shows the four-port configuration used at Orenburg, the location of the Russians' primary experimental facility, where four separate 250-kW magnetron microwave generators have been combined to yield up to 1.0 MW. The end of the reactor volume is defined by the sulfur condenser, which brings the temperature of the reactor effluent to between 130 and 135°C.

The Russians also had a smaller (50-kW) experimental facility at a refinery near L'vov in the Ukraine. This facility used a feed stream rich in hydrogen sulfide, whereas the Orenburg acid gas is typically 40% CO₂ from a natural gas purification plant. The Orenburg experimental facility (Figure 2) has been used to test various components of the Russians' hydrogen sulfide plasma-chemical process concept, including different plasma-chemical reactor designs, gas-feed configurations, and membrane-separation technology. The Orenburg experimental facility has been operated at microwave power levels of up to 1.0 MW and at pressures of up to about 1.3 atm.

FIGURE 1 Orenburg 1.0-MW Plasma-Chemical Reactor

The concept for a commercial process designed to treat hydrogen sulfide waste proposed by the Russians (I in Figure 3) first removes water and particulate matter and then uses membrane technology (membrane unit 1) to concentrate the hydrogen sulfide feed to the plasmatron and produce a carbon dioxide product from the typical acid-gas stream from an amine-purification unit. An alternative approach (II in Figure 3) is to use membrane technology to remove the carbon dioxide and hydrogen sulfide from the crude natural gas. The carbon dioxide/hydrogen sulfide product stream would then go to membrane unit 1. Commercial quantities of helium could be recovered from the methane product in a subsequent membrane unit (membrane unit 4). Traces of hydrogen sulfide in the carbon dioxide product from membrane unit 1 could be removed by an ultraviolet- (UV-) treatment/filtration step, wherein the hydrogen sulfide is dissociated and the solid sulfur particles are removed mechanically. The hydrogen sulfide stream would pass through the plasmatron (plasma-chemical reactor), then the bulk of the sulfur would be condensed, and residual sulfur aerosols would be removed by an electrostatic precipitator. The gaseous stream — hydrogen, hydrogen sulfide, and carbon dioxide — would go to membrane unit 2, in which the product hydrogen would be separated. The stream, which is rich in hydrogen sulfide, would be recycled to membrane unit 1 and then to the plasmatron. If needed, any traces of hydrogen sulfide in the hydrogen product could be removed with the UV-treatment/filtration technology.

FIGURE 2 Flow Sheet for the Orenburg Experimental Facility

1.1.2 Canadian Research

The Canadian research effort, like the Argonne work, was modeled after the original laboratory apparatus described in the Russian literature. This effort was sponsored by Shell of Canada and conducted at Atomic Energy Canada/Chalk River. The Canadian experiments were run with hydrogen sulfide over a wide range of pressures (up to 1 atm) and flow rates (up to 50 SLPM [standard liters per minute]), with microwave power levels of about 1 kW.* The results were similar to those of Russian and Argonne researchers, except that the Canadians reported obtaining plasmas over the entire pressure range studied and that the conversions of hydrogen sulfide were somewhat lower. Furthermore, at the higher pressures, the conversions of

* Personal communication from E. Luihstra and M.T. Craw-Ivanco, October 8, 1992.

FIGURE 3 Commercial Version of the Russian Concept

hydrogen sulfide decreased following a maximum conversion at about one-third of an atmosphere. Comparisons between the experimental procedures used by the Canadians with those used by Argonne researchers strongly suggest that flow rate is an important variable for isolating a plasma from the reactor wall and obtaining plasmas at atmospheric pressures. Actually, these two events are closely related, because a plasma that is not isolated will lose excessive energy to the reactor wall and, thereby, be quenched (or burn through the wall if one attempts to maintain the plasma simply by increasing the microwave input power.)

1.1.3 Argonne Research

The claims in the Russian literature for the dissociation of hydrogen sulfide suggested that the process had a high potential for industrial success because hydrogen sulfide appeared to be a relatively easy gas to dissociate. Furthermore, the opportunities for energy savings with hydrogen sulfide appeared to be substantial in situations where the hydrogen produced could displace the hydrogen generated from primary hydrocarbon resources (Harkness et al. 1990).

The plasma-chemistry research program, "Recovery of Hydrogen and Sulfur from Hydrogen Sulfide Wastes," was established at ANL in September 1987 by the present-day Office of Industrial Technologies, Industrial Waste Reduction Programs (U.S. Department of Energy [DOE], Assistant Secretary for Energy Efficiency and Renewable Energy). Support for the development of a process for the dissociation of hydrogen sulfide was justified by the potential for

The plasma-chemistry research program, "Recovery of Hydrogen and Sulfur from Hydrogen Sulfide Wastes," was established at ANL in September 1987 by the present-day Office of Industrial Technologies, Industrial Waste Reduction Programs (U.S. Department of Energy [DOE], Assistant Secretary for Energy Efficiency and Renewable Energy). Support for the development of a process for the dissociation of hydrogen sulfide was justified by the potential for substantial energy savings that would accrue from the recovery and recycling of hydrogen in the refining industry. The results of preliminary research indicate that the energy savings may be greater than originally calculated (Daniels et al. 1992).

1.1.4 Argonne Feasibility Demonstration

The objective of the DOE program has been to experimentally determine the technical and economic feasibility of dissociating hydrogen sulfide in a microwave-induced plasma. The first series of experiments was designed to duplicate the results of Russian laboratory studies, and the earliest Argonne laboratory findings were very encouraging (Gorski et al. 1990). The energies of dissociation appeared to be in the same range as those reported by the Russians, while the single-pass yields were generally greater. Argonne was able to show that conversions of hydrogen sulfide in excess of 90% were relatively easy to attain; however, duplicating the Russians' low specific energies of dissociation was more difficult.

Detailed energy balances on the ANL apparatus indicated that the dissociation energies were within the range reported by the Russians, but the energy losses to the experimental apparatus were substantially larger than the dissociation energies. The losses were the result of interactions between the plasma and the reactor wall (the plasma was not completely isolated as in the Russian work). To isolate the plasma, better control was needed to match the maximum of the electric field in the waveguide and the plasma zone within the quartz tube. Several modifications to the tubular reactor decreased the external energy losses slightly and yielded incremental improvements in the measurements of the dissociation energies.

In addition to the dissociation energy experiments, the ANL program investigated the effects of gas compositions commonly found in petroleum-refinery acid-gas streams (carbon dioxide, 16.1%; water, 6.3%; and methane, 0.1%) on the process to dissociate hydrogen sulfide. The experiments were designed to determine how these species would behave in the presence of hydrogen sulfide and how they would affect the process to dissociate hydrogen sulfide. The two primary objectives of the screening experiments were to (1) determine the overall effect of carbon dioxide and water on the plasma processes and (2) identify the major stable by-products generated by dissociating mixed gases. With respect to the first objective, changes in the conversion of hydrogen sulfide and the microwave power required to maintain the dissociation process were monitored. The second objective arose from a concern that the plasma process might produce significant amounts of refractory by-products, which would then either interfere with hydrogen purification or accumulate in the recycle stream to a point at which they would have to be purged from the process, thereby creating a new waste-treatment problem. In this case, the product sulfur and gas compositions were analyzed by using mass spectrometry to obtain a qualitative measure of the by-product spectrum.

The results of the first series of experiments showed that, at relatively low pressures (20 torr), hydrogen sulfide can be efficiently dissociated into hydrogen and sulfur by means of a cold, nonequilibrium plasma with gas-feed compositions ranging from pure hydrogen sulfide to acid gases typical of the refining industry. The major findings of that research are summarized as follows:

- The specific energy of hydrogen sulfide dissociation is low enough for the plasma process to save energy when compared with the technology currently being used in the domestic petroleum-refining industry.
- The specific energies of hydrogen sulfide dissociation were found to be 0.47-0.77 eV/molecule, values that are obtainable with 52-82% conversion per pass.
- The energy losses to the experimental apparatus were significantly greater than the specific energies of hydrogen sulfide dissociation.
- Typical acid-gas components are compatible with microwave plasma dissociation.
- The major by-products of the reaction are carbon monoxide and sulfur dioxide, and the minor by-products of the reaction are carbon disulfide and carbonyl sulfide.

1.1.5 Argonne Cyclonic Flow Demonstration

The second series of experiments was also run at a pressure of 20 torr. At 20 torr, the operation of the plasma was quite stable, and the system was operated for two hours without any difficulties. The second series of experiments demonstrated the following:

- Feed-gas velocities at, or slightly less than, sonic values with a cyclonic flow pattern will yield the most efficient conversion of hydrogen sulfide in a plasma-chemical reactor.
- At a set feed rate, lower specific energies of hydrogen sulfide dissociation at lower input microwave power suggest that an optimal commercial design will include the recycle of unconverted hydrogen sulfide.
- At a set power level, residence time controls conversion efficiency. The inlet temperature of the gas has a negligible effect.

The first point can be explained by two factors, both of which will result in a lowering of the back-reaction rate between hydrogen and sulfur. First, the cyclonic flow pattern improves the heat transfer from the reactor surface and increases the rate of sulfur condensation. (This flow pattern has also alleviated an earlier problem in which excess microwave power softened the quartz.) Second, the cyclonic flow pattern serves to de-entrain the sulfur product from the hydrogen product by concentrating the liquid sulfur on the wall of the reactor.

The primary conclusion from the acid-gas experiments was that typical refinery acid-gas compositions are compatible with the microwave-plasma dissociation of hydrogen sulfide. Surprisingly, the other acid-gas constituents appeared to have increased the stability of the plasma; with the other species present, the maintenance of a hydrogen sulfide plasma required a lower microwave-power level than did the maintenance of pure hydrogen sulfide. Also, at a fixed power level, the conversion of hydrogen sulfide increased slightly, which translates into only slight or no increases in the specific energy of dissociation after the effect of dilution by the other species has been considered.

In general, there were relatively few by-products detected, and those by-products were found at relatively low concentrations. The major by-products were carbon monoxide and sulfur dioxide, which may (in part) be formed by the overall reaction

The highest gas-phase concentration observed for these by-products was 12% for carbon monoxide (75% conversion of the inlet carbon dioxide), but only 1.4% for sulfur dioxide. Very minor amounts of carbon disulfide and carbonyl sulfide were found in the gas phase of some, but not all, experiments (maximum concentrations were 0.6 and 0.03%, respectively). A similar cross section of by-products was found in the solid sulfur product. Overall, these by-products do not appear to present any processing difficulties — all of them should be treatable by using existing technology integrated into the plasma process.

1.2 Proposed Argonne Process Design for the Treatment of Hydrogen Sulfide Waste

The flow sheet proposed by Argonne for a process to treat hydrogen sulfide waste by means of plasma-chemical dissociation is shown in Figure 4. Note that this flow sheet was proposed on the basis that the design would be implemented at a refinery location, because a comparable analysis has not yet been conducted for a natural gas purification plant. As shown in the flow sheet, acid gas from an amine-purification system, which would contain carbon dioxide and water, is combined with recycled hydrogen sulfide and fed to the plasma reactor, which is connected to a microwave generator with wave guides. The process stream leaving the reactor would contain hydrogen, sulfur vapor, sulfur liquid, unconverted hydrogen sulfide, water, and, possibly, some impurities (such as carbonyl sulfide or carbon disulfide). The product sulfur

FIGURE 4 Proposed Argonne Process Concept for the Treatment of Hydrogen Sulfide Waste

would be cooled and collected in a scrubber. Some process energy could be recovered at this point. The scrubbing step would remove the bulk of the sulfur and some of the sulfur-containing impurities. Remaining traces of these undesirable compounds would be removed in an internal catalytic reducing unit. This unit would consume a small, but probably negligible, fraction of the hydrogen product. The purified gas phase would contain only hydrogen sulfide, hydrogen, carbon dioxide, and water; the purified gas would then be compressed and subsequently sent to a separations step to recover the hydrogen product, recycle the unconverted hydrogen sulfide, and purge water and carbon dioxide.

Most of the operating costs are for the energy needed to generate the microwaves, although some additional energy would be needed to operate pumps and compressors (Daniels et al. 1992). The capital costs of the Argonne version of the process have been estimated to be less than half those of Claus Sulfur Recovery Unit (CSRU)/Tail-Gas Cleanup Unit (TGCU) technology. A comparison of the annual operating costs of the plasma-chemical technology with those for the current CSRU/TGCU technology indicates that the plasma-chemical system might cost from $\$2.0$ to $4.0 \times 10^6/\text{yr}$ less to operate (assuming a sulfur production of 156 long ton/day). This difference is insensitive to the price of sulfur because both processes generate essentially the same amount of sulfur.

Because the plasma-chemical technology saves energy, it becomes more competitive when the cost of energy increases. Compared with conventional technology, the energy savings for the same scale of operation are probably between 550×10^6 and 950×10^6 Btu/day. Assuming that 90% of the plants ≥ 30 years old will use plasma-chemical technology and that the new capacity will use also plasma-chemical technology, the total energy savings for the U.S. refining industry could range from 40×10^{12} to 70×10^{12} Btu/yr in 2010.

2 Gas Research Institute Experimental Work at Argonne

The GRI research program at Argonne had three objectives and was divided into five tasks. The objectives were to (1) determine whether or not the plasma-chemical process could operate at atmospheric pressures, (2) determine the effect of acid-gas compositions of greater interest to the gas industry than the refinery compositions previously studied, and (3) test the feasibility of a direct plasma-desulfurization process for natural gas applications. The specific tasks are listed below.

- Task I: Modify the apparatus used in the original DOE program so that the experimental tasks of the GRI program can be performed.
- Task II: Determine the maximum operating pressure possible with this apparatus.
- Task III: Test acid-gas compositions containing up to 65% carbon dioxide.
- Task IV: Test a "pipeline" gas mixture containing up to 100 ppm hydrogen sulfide.
- Task V: Write report.

2.1 Task I: Modify Equipment

The experimental system originally developed for the DOE program included a gas-feed system, a plasma reactor, a microwave generator and applicator, a vacuum system, an exhaust scrubber, an analytical system, and auxiliary instrumentation. The modified version of this system is shown in Figures 5 and 6. For safety, most of the apparatus is located in well-ventilated hoods. The apparatus can produce feed-gas flow rates of 0.5-6.0 L/min and microwave power levels of up to 2.0 kW. The current configuration permits gaseous feed compositions containing hydrogen sulfide, carbon dioxide, water, and "pipeline" natural gas. The plasma reactor consists of a 35-mm quartz-tubular reactor with an internal diaphragm that has small holes drilled tangentially to the plasma zone. A preheater tape around the gas-feed line originally could maintain feed-gas temperatures between ambient and 400°C, but the current materials' limit is 250°C. After molten sulfur is collected, a cold trap and glass-wool filter remove additional traces of solid sulfur. The noncondensed/nonsolidified gaseous stream is compressed by an oil-free pump through the analytical system, from which gas samples are collected for mass-spectrometric analysis.

The first task of the GRI program involved replacing the microwave applicator with a resonant-cavity plasma reactor and modifying the existing feed system. The existing applicator

FIGURE 5 Experimental Apparatus

FIGURE 6 Laboratory Layout

might have been modified to provide additional tuning capabilities, but it was recommended that an alternative strategy be pursued, whereby the waveguide-style applicator was replaced with a resonant-cavity applicator. (A resonant-cavity applicator shapes the electric field while also centering it on the plasma zone in the tubular reactor.) The Industry Working Group for the DOE program recommended that the waveguide applicator be replaced, for the reasons stated above, and because a resonant-cavity reactor appears to be a more realistic configuration for an industrial system. The microwave applicator chosen is a tunable, resonant cavity capable of handling up to 3.0 kW. In the current experimental program, the resonant cavity is operated in the TM_{012} -mode, as shown in Figure 7, which produces an electrical field with cylindrical symmetry. The highest field strengths are centered on the plasma zone of the quartz-tubular reactor.

Because the existing apparatus was designed to operate at pressures below atmospheric pressure, many of the tubing fittings were selected for vacuum service and represent a potentially serious safety hazard if operated at, or above, atmospheric pressure. Therefore, this portion of the apparatus was redesigned to operate safely at pressures of up to 20 psig. At the same time, the plasma reactor was modified to eliminate the internal diaphragm. The modification consisted of the design of a metal insert that fit inside the quartz-tubular reactor and that had one nozzle (or more) drilled at the perimeter of the insert to direct the feed gas tangentially into the plasma zone of the reactor, as shown in Figure 7.

FIGURE 7 Detailed Diagram of Resonant-Cavity Applicator and the Feed Nozzle

The modifications to the feed system were tested by pressurizing the apparatus to 5 psig and observing that it held this pressure overnight. The resonant-cavity applicator was installed and inspected in our laboratory by a qualified individual from the manufacturer. The new applicator was demonstrated to surpass all its performance criteria.

2.2 Task II: Increase Operating Pressure

The objective of the first experiments with the modified apparatus was to increase the plasma operating pressure from the previous standard condition of 20 torr to atmospheric pressure. Achieving stable operation in the range of 500 to 760 torr would, however, have been considered a qualified success because pressure in this range would represent more than a 25-fold improvement, leaving less than a factor of 1.5 to reach atmospheric pressure. We believe that operation at atmospheric pressure should be easier in a commercial-scale system than in a laboratory system because the ratio of plasma volume to reactor surface area is much more favorable in a commercial-scale system operating at a lower frequency, longer wavelength.

The Task II experiments involved igniting a plasma according to established procedures at 20 torr and slowly increasing the pressure until it was quenched. The flow rate of hydrogen sulfide was 2.0 SLPM, and the input microwave power was set at 1.0 kW. While increasing the pressure from 20 to 50 torr, we observed very little change in the plasma, but further increases produced a visible flicker in the plasma that yielded variable conversions of hydrogen sulfide. These phenomena were accompanied by a steadily shrinking plasma, which eventually was quenched. This region of operation was also characterized by a decline in the conversion of hydrogen sulfide. During the procedure, the resonant-cavity applicator needed to be retuned with each incremental increase in pressure so that the reflected power, which also increased, could be minimized. Typically, we obtained reactor pressures of 150 torr, but with great care and patience, we obtained 200 torr on a few occasions.

We attempted two strategies to obtain greater increases in operating pressure, but neither strategy proved satisfactory. The first strategy was to increase the input power as we approached the 150-torr region, and the second strategy was to use argon as a "pilot light" to keep the plasma going until higher pressures were reached. In the latter case, the hydrogen sulfide plasma would extinguish when the argon was turned off. The result of the first strategy was that the quartz tubes melted because the plasma was not isolated (that is, the plasma was not centered in the core of the tubular reactor and was not touching the wall). As pressure increased, the bulk-gas temperature also increased; and because the plasma was still in contact with the inner surface of the tubing, localized heating of the reactor wall occurred, which quickly led to the failure of the tube.

In reviewing these results with both Canadian and Russian scientists, we learned that atmospheric operations are technically feasible (albeit with performance penalties). As pressure increases, thermal losses increase, which, in turn, cause the specific dissociation energy to increase. Furthermore, we learned from the Canadians that the key to obtaining an isolated plasma (and, therefore, to obtaining and maintaining a plasma at atmospheric pressures) was to use a

significantly higher hydrogen-sulfide flow rate than was possible in the current configuration of the Argonne apparatus. The Canadian work used gas flow rates of 10-50 SLPM, rates that were described as being more than adequate, but there appeared to be a threshold value. This value was not stated, although the Canadians apparently operated comfortably above it.

2.3 Task III: Test Acid-Gas Compositions

The Task III series of experiments tested acid-gas compositions typical of natural gas production. For the experiments, a statistical design in three variables was used — the concentrations of carbon dioxide, water, and natural gas in hydrogen sulfide. The plasma operating conditions were dictated by the results of Task II and required that a pressure of 50 torr be used so that a stable plasma — without flickering — could be maintained. The primary performance criteria for these experiments were the percentage conversion of hydrogen sulfide and the rate at which by-products formed. We also noted the conversion of carbon dioxide reflected power and the minimum power readings. The aforementioned criteria were determined by means of mass spectrometry.

As noted earlier, the specific energy of the dissociation of hydrogen sulfide is quite difficult to measure in a small-scale laboratory system because of uncontrolled losses to the apparatus. These losses include the microwave power reflected (or "broadcast") back to the source, bulk heating of the gas stream, conduction to the reactor (which was exacerbated by the contact between the plasma and the quartz tube), radiation to the applicator, and the chemical conversion of other species in the feed stream. Because many of these energy-transfer mechanisms are scale-dependent and we do not yet know their scale factors, we abandoned any pretense of measuring the dissociation energy in the experiments. The best engineering values for the dissociation energy of hydrogen sulfide would be from either the existing Russian industrial experimental facilities at L'vov and Orenburg or the "field experiment" proposed for the DOE commercialization program with industry. All of these plasma-chemical reactors are, or would be, commercial-scale reactors based on a 915-MHz microwave power source.

The range of gas compositions tested in these experiments is listed in Table 1. The mixtures were prepared by blending technical-grade gases in the laboratory by means of on-line mass-flow controllers. The "gas" component was a standard gas mixture typical of pipeline natural gas obtained from the Institute of Gas Technology (IGT). The carbon dioxide gas was purchased from AGA Gas, Inc., while the hydrogen sulfide came from Matheson Gas Products, Inc.

TABLE 1 Range of Gas Compositions^a
Tested

Gas Species	Range of Values (%)		
	Low	Center Point	High
Carbon dioxide	30.0	47.5	65.0
Water	0	3.5	7.0
Gas	0	0.1	0.2

^a The balance of the gas composition is hydrogen sulfide.

The other experimental conditions for this series of experiments were as follows:

- The total gas flow rate was 6 L/min; this rate was controlled by means of a new nozzle that was fabricated so that flow rates would match the Mach conditions used in the HEPTI experimental system;
- The plasma reactor pressure was 50 torr; and
- The microwave power level was 1.0 kW.

In each of the experiments, the resonant cavity was tuned to minimum reflected power while in the TM_{012} mode.

The statistical design of these experiments was a full-factorial design in three variables with three center-point experiments; this scheme yielded a design matrix of 11 experiments, which were scheduled in a random order. Table 2 provides the complete list of these experiments with their run order and individual gas compositions. In one experiment, the reactor pressure rose to 80 torr because sulfur partially plugged the glass-wool filter; as a result of the partial plugging, the conversion of hydrogen sulfide dropped significantly below the conversions observed for other experiments in the matrix. Therefore, this experiment was repeated after more cooling was added to the sulfur receiver to remove more sulfur before it reached the glass-wool filter. Only the results from the repeated experiment were included in the subsequent data analysis.

Each experiment was identified by a unique information sheet, or run sheet. Each run sheet included the experimental series identification, statistical design identification, randomized experimental run number, date, name of operator, and a brief abstract of operations alerting the operators that the experiment will use mixtures of hydrogen sulfide, carbon dioxide, water, and the pipeline gas. This information was followed by specific operating instructions. A typical experiment started with a detailed standard procedure for the checkout, start-up, and calibration of the various subsystems that made up the laboratory apparatus. The procedure included completing a checklist of items and manually logging in data (for example, regulator pressure settings and manual hydrogen-sulfide detector readings). The completed checklist is part of the permanent file for all the written records from each experiment.

The run sheet identified the reactor inlet nozzle; the flow rates of hydrogen sulfide, carbon dioxide, and pipeline gas; system operating pressure (50 torr); microwave power (1.0 kW); and the inventory of sample tubes required for the off-line analyses. The flow rates were set on the mass-flow controllers, and the system was allowed to equilibrate before a feed sample was collected. Water was then introduced by means of a precision peristaltic metering pump into a

TABLE 2 Task III Experimental Sequence and Feed Compositions

Experiment	Feed Compositions from the Statistical Design (%)			Balance Gas, Hydrogen Sulfide (%)
	Carbon Dioxide	Water	Gas	
GRI III-1	30	0	0	70
GRI III-5	30	0	0.2	69.8
GRI III-9C	47.5	3.5	0.1	48.9
GRI III-7	30	7	0.2	62.8
GRI III-2	65	0	0	35
GRI III-8	65	7	0.2	27.8
GRI III-9A	47.5	3.5	0.1	48.9
GRI III-9B	47.5	3.5	0.1	48.9
GRI III-3	30	7	0	63
GRI III-4	65	7	0	28
GRI III-6	65	0	0.2	34.8

heated mixing volume (if water was needed in a particular experiment).^{*} The pressure controller was set at 50 torr, the plasma was ignited, the microwave power was adjusted to 1.0 kW, and finally the resonant cavity was tuned for minimum reflected power.

The operators waited until the system had stabilized, as evidenced by a flat trace on the binary gas analyzer, and then commenced to gather data and collect product samples. Each product sample was collected for five volume changes through a 125-mL gas-sample tube. For each experiment, the following data were gathered: experiment number, time, computer data-log file (12 thermocouples and 4 flow meters were data-logged), reactor, inlet nozzle, forward power, reverse power, pressure, gas temperature in, gas temperature out, binary gas analyzer reading, and cooling-water flow rates for the reactor jacket, the reactor base, the microwave circulator, and the dummy load.

After at least 625 mL had passed through the sample tubes, the sample tube was removed from the apparatus and labeled, and then the microwave power to the plasma was decreased to a minimum value (just slightly above a value that would create a flicker in the plasma that would be apparent to the unaided eye). The operators waited until the system restabilized (typically within 5 min) and then commenced to gather a second set of data and collect a second product sample.

^{*} Water is always condensed ahead of the feed and product sample collection so that although the sample is not dehydrated, it contains only a fraction of the water in the actual stream. See Appendix A for an explanation of how water was accounted for in the material balance analysis.

Unfortunately, in most of the experiments, the accumulated sulfur in the cold trap and on the glass-wool filter forced a system shutdown before a valid, steady-state sample could be collected.

After the minimum-power portion of the experiment, the system was purged with argon while the experiment was shut down. Another standard checklist, which was also included in the experimental folder, was used for the shutdown process. At the conclusion of the experiments, the sample tubes were taken to the Argonne Analytical Chemistry Laboratory, where the gas compositions were determined by means of mass spectrometry.

Table 3 lists the calculated conversions and by-product concentrations in the product stream, as well as the temperature of this stream as it entered the sulfur receiver, for each of the experiments included in the analysis of these experimental results.

The conversions of hydrogen sulfide ranged from 53 to >99% when the result for experiment 9A is discounted (as will be explained shortly). The four experiments with the high concentration of carbon dioxide yielded conversions of hydrogen sulfide clustered above 99%. Unlike the conversions of hydrogen sulfide, the conversions of carbon dioxide showed a more uniform distribution — their values ranged from 36 to 50% (experiment 9A excluded). The concentrations of carbonyl sulfide were greater than the concentrations of carbon disulfide, except in experiments 5A and 7A. Experiments 8A and 4A yielded notably higher concentrations of sulfur dioxide than did the rest of the data set, in which the concentrations ranged from 30 to 80 ppm. The gas temperature leaving the plasma zone was significantly hotter (ranging from 260

TABLE 3 Summary of Task III Experimental Results

Standard Order	Hydrogen Sulfide Conversion (%)	Carbon Dioxide Conversion (%)	Carbonyl Sulfide Production (%)	Carbon Disulfide Production (%)	Sulfur Dioxide Production (%)	T _g (°C)
1B	62.53	43.41	0.46	0.15	0.003	314
2A	99.98	49.75	0.60	0.04	0.002	351
3A	73.97	47.42	0.54	0.11	0.003	313
4A	99.91	43.52	0.38	0.02	0.900	260
5A	53.38	36.66	0.36	0.46	0.006	340
6A	99.36	45.86	0.46	0.09	0.003	280
7A	68.57	42.19	0.54	0.60	0.008	349
8A	99.94	47.81	0.42	0.06	2.100	321
9A ^a	37.80	20.45	0.28	0.14	0.006	276
9B	83.10	47.04	0.81	0.13	0.003	367
9C	89.78	46.87	0.65	0.13	0.003	276

^a Note that in the statistical analysis of these experiments, the 9A results were replaced by the average of the 9B and 9C results.

to 367°C) than the inlet temperature (80 to 90°C) for all the experiments. Appendix A provides the results, as they were originally reported, for the feed and product analyses. The normalized results are also provided in Appendix A.

The percent change for all components in the system has been included in the results, as have atomic balances for hydrogen and carbon. However, because water was partially condensed after it had been through the plasma reactor (and was fully condensed before the analytical work was carried out), the water concentrations were calculated. The water concentration in the feed was taken from the precision pump that feeds the water to the steam generator. The initial presence of water in the product steam was inferred from the carbon monoxide present in the product analysis. The oxygen atom produced from the conversion of carbon dioxide to carbon monoxide was assumed to produce one molecule of water. Thus, for a first-order estimate, the concentration of water was set equal to the concentration of carbon monoxide. (Note that the production of carbonyl sulfide production was two orders of magnitude less than that of carbon monoxide.) On the basis of the first-order estimate, the composition of the stream was normalized to yield 100%. The partial condensation of water vapor in the experimental apparatus presents a serious complication to the closure of element balances — it introduces a systematic error as water content increases. Nevertheless, it should be emphasized that the relative ratios of noncondensable components in the gas stream remain unaffected by this error (see Appendix A). Finally, the spreadsheet formulae used in these calculations have been retained for completeness of documentation (the formulae are not reproduced here).

An analysis of the results from all the experiments in this series was conducted by using standard methods (Box et al. 1978). The statistical plots and analyses of variance summaries generated by this analysis are shown in Appendix B. This analysis encompassed three steps. First, the experimental data were transformed by the Yates' algorithm to determine the effects of each independent variable. The effects were then plotted on a probability plot to identify the statistically significant variables. Finally, the significant variables were evaluated by using analyses of variance to determine how well the variables described the experimental results.

The analysis showed that, for these experiments, only the concentration of carbon dioxide gas had a significant effect on the conversion of hydrogen sulfide. The coefficients of all the other variables and their cross-effects appeared to be random noise. Nevertheless, when the four experiments with the high concentrations of carbon dioxide were excluded from the data set and a new, two-factorial design was extracted, water was found to have a significant effect on promoting the conversion of hydrogen sulfide, while the concentration of pipeline gas inhibited the conversion of hydrogen sulfide. The apparent promoting effect of oxygen-containing species may be related to the effect hypothesized by Strelkova.* The diluting effect of carbon dioxide can be explained by hydrogen sulfide becoming the "limiting reagent" instead of the microwave power. This phenomenon can be seen in Figure 8, in which the conversion of hydrogen sulfide is plotted versus the concentration of hydrogen sulfide for all 11 experiments. As the concentration of hydrogen sulfide decreases from 70 to 50%, the conversion increases approximately linearly. As

* Personal communication from M.I. Strelkova to J.B.L. Harkness, July 1992.

FIGURE 8 Hydrogen Sulfide Conversion as a Function of Hydrogen Sulfide Concentration

the concentration of hydrogen sulfide continues to decrease, the conversion clearly levels off in the 99-100% region. Figure 8 also shows the substantial difference between the results from experiment 9A and those of the rest of the data set. Because of this difference, the results from experiment 9A were replaced by the average of its companion, center-point experiments in the data analysis

The conversion of carbon dioxide was a weak function of several factors, including its own concentration (positive); the second-order effects between the concentration of carbon dioxide and the concentration of water (negative, the water-gas shift reaction), as well as between the concentrations of carbon dioxide and pipeline gas (positive); and the first-order effect of the concentration of pipeline gas (negative). High concentrations of carbon dioxide will favor the formation of water at the expense of hydrogen; consequently, the full value of hydrogen is lost. In addition, the overall amount of carbon dioxide converted suggests that the concentrations of carbon dioxide in the range studied here will represent a significant source of energy losses in a process designed to convert hydrogen sulfide. The mechanism for these losses is both chemical — the energy required to convert the carbon dioxide — and sensible — the energy required to heat carbon dioxide and carbon monoxide in the product stream.

The data analysis showed a weak relationship between the production of carbonyl sulfide and two second-order effects: the concentrations of carbon dioxide and water plus the concentrations of water and pipeline gas. The former second-order effect inhibited the production of carbonyl sulfide, while the latter second-order effect promoted it. The net effect was a very slight production of carbonyl sulfide. On the other hand, the production of carbon disulfide was a much stronger function of three variables — the concentration of carbon dioxide, the concentration

of pipeline gas, and the second-order effect of carbon dioxide and pipeline gas. The concentration of pipeline gas promoted the production of carbonyl sulfide, while the concentration of carbon dioxide and the second-order effect of carbon dioxide and pipeline gas inhibited the production of carbonyl sulfide. That the production of carbonyl sulfide strongly depends on the very low concentration of the pipeline gas suggests a direct reaction between methane (or one of the other hydrocarbons in the mixture) and the activated sulfur species from the plasma.

The production of sulfur dioxide showed a very unusual pattern. If pipeline gas was present in an experiment, the production of sulfur dioxide was low; if not, it was high. The other variables had only a minor effect on the production of sulfur dioxide. This phenomenon could be explained by a couple of mechanisms. In the first mechanism, the hydrocarbons in the pipeline-gas mixture promote the production of carbon disulfide in competition with the mechanism that forms sulfur dioxide. In the second mechanism, which may be in addition to the first, the dissociation products of the hydrocarbons are acting as very strong reducing agents to remove sulfur dioxide from the product stream.

Other dependent variables of interest included the temperature of the plasma at the outlet, the reflected microwave power during the experiment, and the minimum forward power for stable operation and its companion reverse power. The variations in the gas temperature exiting the plasma zone appeared to be completely random with respect to the independent variables studied here. However, the minimum operating power showed a net increase in the presence of water, probably because of the water-gas shift reaction, whereby carbon monoxide is converted back into carbon dioxide. The reverse power during the minimum-operating-power phase of the experiments showed a small — barely statistically significant — increase in the presence of carbon dioxide plus pipeline gas.

2.4 Task IV: Direct Treatment of Crude Gas

The Task IV experiments were designed to explore the feasibility of the direct treatment of crude gas. Like the experiments in Task III, the Task IV experiments were planned around a statistical design, but the design was simpler than that used in the Task III experiments. Only two variables were used in a full-factorial design, without any center points, which yielded a total of four experiments. The two variables studied were hydrogen sulfide and carbon dioxide. In these experiments, the IGT pipeline gas was the balance gas; the compositions are summarized in Table 4.

TABLE 4 Compositions of Experimental Gases^a

Gas Species	Low Value	High Value
Hydrogen sulfide	50 ppm	100 ppm
Carbon dioxide	1.0%	3.0%

The four, two-factorial experiments, summarized in Table 5, were run in a

^a The balance of the gas composition is IGT pipeline gas.

random order. The complete record of experimental data appears in Appendix C. The experiments were conducted with a total gas flow rate of 4 SLPM (Mach number = 0.283 with a single 0.12-in. nozzle), in order to conserve the pipeline gas, and at a reactor pressure of 50 torr. The microwave input power was 1.0 kW, and the resonant-cavity applicator was tuned for minimum reflected power after the plasma was ignited. The experimental procedure used for the Task IV experiments was the same as that used for the Task III experiments. The detailed results from these experiments are also presented in Appendix C.

TABLE 5 Summary of the Four, Two-Factorial Experiments

Experiment	Hydrogen Sulfide (ppm)	Carbon Dioxide (%)	Order
GRI-IV 1	50	1.0	1
GRI-IV 2	100	1.0	4
GRI-IV 3	50	3.0	3
GRI-IV 4	100	3.0	2

During the Task IV experiments, we could see the characteristic blue glow of hydrogen sulfide dissociation, but the analytical results of the gas feed for hydrogen sulfide were inconsistent with the metered flows. We subsequently determined that the mass-spectrographic analyses were systematically under-reporting the concentrations of hydrogen sulfide when they were in the range of 10-100 ppm. Although the analytical reports showed that the product stream contained ≤ 2 ppm of hydrogen sulfide, the actual value could have been as much as 20 or 30 ppm, a value that would not meet the pipeline specifications for hydrogen sulfide.

Moreover, we observed that a significant proportion of the hydrocarbon components were destroyed in the feed stream, as summarized in Figure 9. Although the methane losses averaged only 1.6%, the average conversion of the other hydrocarbons in the pipeline gas increased steadily with increasing carbon number until 15% of the propane and approximately 33% of the total "higher hydrocarbons" were destroyed. In individual experiments, as much as 50% of the "higher hydrocarbons" were destroyed. Not only would these be unacceptable losses in a commercial process, but carbon deposition on the reactor wall very quickly becomes conductive and screens the gas stream from the microwave energy, which causes the plasma to shut down or a quartz tube to melt.

With a substantial fraction of the hydrocarbons being converted, hydrogen was the major plasma product in the gas stream, averaging 1% of the total plasma product stream. In addition, the conversion of carbon dioxide averaged 1.2%, but more carbon monoxide was detected in the total plasma product stream than could be accounted for by the conversion of carbon dioxide. Clearly, some of the hydrocarbon was being oxidized by the atomic oxygen produced by the dissociation of carbon dioxide and/or water.

FIGURE 9 Hydrocarbon Conversion as a Function of the Number of Carbon Atoms in the Molecule

3 Significance of Results

The results from these experiments indicate that the plasma-chemical technology is technically capable of treating acid gases containing high concentrations of carbon dioxide. Nevertheless, elevated concentrations of carbon dioxide will extract an economic penalty in the form of excess energy consumption. Furthermore, plasma chemistry does not appear to be an appropriate technology for removing traces of hydrogen sulfide from crude natural gas because of unacceptable hydrocarbon losses. In view of prior research by the Russians and Canadians at pressures of up to 1 atm, the 200-torr limit in the Argonne apparatus does not represent a limit on the technology — only a limit on the current configuration of this particular experimental apparatus.

3.1 Conversions of Hydrogen Sulfide

The results of Task III experiments showed conversions of hydrogen sulfide ranging from 80 to 100%. The experiments with the highest conversions contained the highest concentrations of carbon dioxide and showed only trace amounts of hydrogen sulfide in the plasma product. These high conversions were achieved, in part, by the dilution of hydrogen sulfide by carbon dioxide. At the lowest concentrations of hydrogen sulfide, the hydrogen sulfide became the "rate-limiting species," in that more than enough microwave energy was available to drive the dissociation reaction.

Because a fixed microwave power level of 1.0 kW was chosen for the experimental design, power was excessive, as indicated by the fact that all the experiments had a minimum forward power of less than 0.5 kW (down to 0.25 kW). However, carbon dioxide had only a minor effect on minimum forward power (which was most strongly affected by water concentration), probably because such a large fraction (35 to 50%) of the carbon dioxide was also being dissociated in the plasma process. The mechanism for the water effect is probably the reverse of the water-gas shift reaction, whereby carbon dioxide is produced from the carbon monoxide produced by the dissociation reaction. The dissociation of carbon dioxide consumes additional, unproductive energy and represents an economic penalty from a hydrogen sulfide waste-treatment perspective.

In the Task IV experiments, uncertainties about the analytical procedure clouded the results of the hydrogen sulfide conversion; however, because the hydrocarbon losses in the plasma were unacceptable, the uncertainties about the procedure were not of practical significance.

3.2 Formation of By-Products

The total sulfur-containing impurities in the plasma product stream were very similar to the distribution and concentrations observed in our earlier work with concentrations of carbon dioxide ranging from 0.0 to 16.1%. Moreover, the concentrations of carbonyl sulfide, carbon disulfide, and sulfur dioxide appeared to be amenable to treatment by the internal catalytic-reduction step proposed for the Argonne process for the treatment of hydrogen sulfide waste. Some of the related conclusions from these experiments are as follows:

- Carbon dioxide inhibited the formation of carbon disulfide.
- The water-gas shift reaction contributed to minimizing the production of carbonyl sulfide.
- Methane had a significant effect on inhibiting the formation of sulfur dioxide.

3.3 Implications of Process Design

The negative impacts of high concentrations of carbon dioxide suggest that the removal of some fraction of the carbon dioxide from the plasma-reactor feed stream should be considered in an industrial-scale process. Nevertheless, even with high concentrations of carbon dioxide, the amount of sulfur-containing impurities appears to have been low enough to be treatable by the internal catalytic reduction step included in Argonne's proposed process for the plasma-chemical treatment of hydrogen sulfide waste.

The application of this technology in the natural gas industry appears to depend upon finding a profitable use for the product hydrogen. It could be used as a fuel at the site of a gas-purification facility, but its highest value would be realized if a nearby consumer would purchase the hydrogen for use as a chemical reagent.

4 References

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Appendix A:

Task III: Test Acid-Gas Compositions

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Task III: Test Acid-Gas Compositions

Tests at nine different operating conditions for the treatment of hydrogen sulfide in the presence of water, carbon dioxide, and natural gas by means of the microwave system with the resonant cavity took place between 15 July 1992 and September 1992. The tests employed a randomized factorial design. All experiments employed the resonant cavity with a 35-mm quartz tube fitted with the same inlet flow nozzle.

Experimental conditions for the system varied (carbon dioxide = 30-65%, water = 0-7%, and natural gas = 0-0.2%). The system flow rate was 6 L/min through a new nozzle that was fabricated so that flow rates would match the Mach conditions used in the Kurchatov Institute's experimental system. The pressure in the plasma reactor was held at 50 Torr. The microwave power level was 1,000 W. The natural gas mixture being used for these tests was obtained from the Institute of Gas Technology (IGT), and the carbon dioxide cylinder was obtained from AGA Gas, Inc. The resonant cavity was tuned to minimize reflected power for each of the experiments while in the TM₀₁₂ mode. The specific run conditions are listed in Table A.1.

The analytical chemistry results for the feed and product streams are given as they were received and then in normalized form (Feed-N or Prod-N). The percent change for all components in the system has been included, as have the atomic balances for hydrogen and carbon (see Table A.2). All Analytical Chemistry Laboratory reference numbers (ACL No.) appear on the appended spreadsheets (Tables A.3-A.11).

The water-gas shift reaction was important during all of these experiments:

However, because water was partially condensed after the plasma reactor and was fully condensed before analytical work, the water concentrations were calculated. The feed concentration was calculated from the water feed rate of the precision pump feeding the water to the system generators, and the gas flow rates were measured by the mass-flow controllers. Water initially present in the product steam was inferred from the reverse of the water-gas shift reaction and set equal to the carbon monoxide present in the product analysis. The partial condensation of water vapor by the system presented a serious complication to the closure of element balances; there was a systematic error as water content increased. It should be emphasized that the relative ratios of noncondensable components in the gas stream remained unaffected by this phenomenon.

TABLE A.1 Experimental Conditions

[illegible]

TABLE A.2 Material Balance
Closure for GRI Task III
Experiments

Experiment	Hydrogen Closure (%)	Carbon Closure (%)
1 A	0.602	-0.431
1 B	-0.609	-6.126
2 A	15.856	-8.951
3 A	-0.794	-0.459
4 A	6.121	-5.310
5 A	0.253	-3.940
6 A	11.602	-9.859
7 A	-5.230	10.554
8 A	10.933	-0.367
9 A	-2.771	-1.860
9 B	0.412	-2.908
9 C	-3.563	-1.915

TABLE A.3 Tests of Acid-Gas Composition: Experiment 1A

Component	ACL No.		ACL No.		Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	92-383-03	Feed (%)	92-383-04	Prod (%)							
H ₂ S:34.075	66.200	65.843	58.900	57.166	-13.179	2.011	0	132.411	114.960	0.000	0.000
H ₂ :2.011	0.030	0.030	6.400	6.212	20717.361	2.011	0	0.060	12.491	0.000	0.000
He:4.003	0.050	0.050	0.050	0.049	-2.419	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.060	0.060	0.060	0.058	-2.419	4.022	12.011	0.240	0.234	0.717	0.699
H ₂ O:18.005	0.050	0.050	3.000	2.912	5754.883	2.011	0	0.100	5.855	0.000	0.000
CO:28.005	0.170	0.169	3.000	2.912	1622.024	0	12.011	0.000	0.000	2.031	34.972
N ₂ :28.013	0.400	0.398	0.200	0.194	-51.209	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.400	0.398	0.400	0.388	-2.419	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.050	0.050	0.050	0.049	-2.419	6.033	24.022	0.300	0.293	1.195	1.166
O ₂ :31.999	0.001	0.001	0.001	0.001	-2.419	0	0	0.000	0.000	0.000	0.000
HCl:36.458	0.300	0.298	0.400	0.388	30.109	1.005	0	0.300	0.390	0.000	0.000
Ar:39.948	0.139	0.138	0.039	0.038	-72.621	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	32.600	32.424	30.300	29.408	-9.303	0	12.011	0.000	0.000	389.448	353.217
C ₃ H ₈ :44.077	0.040	0.040	0.040	0.039	-2.419	8.044	36.033	0.320	0.312	1.434	1.399
COS:60.069	0.038	0.038	0.120	0.116	208.152	0	12.011	0.000	0.000	0.454	1.399
SO ₂ :64.063	0.006	0.006	0.004	0.004	-34.946	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.008	0.008	0.070	0.068	753.837	0	12.011	0.000	0.000	0.096	0.816
Total	100.542	100.000	103.034	100.000				133.730	134.536	395.373	393.668
	Dry	1.000		0.971				% Clos.	0.602	% Clos.	-0.431

TABLE A.4 Tests of Acid-Gas Composition: Experiment 1B

Component	ACL No.		ACL No.		Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	92-0471-01	Feed (%)	92-0471-02	Prod (%)							
H ₂ S:34.075	66.700	66.691	28.400	24.989	-62.530	2.011	0	134.116	50.254	0.000	0.000
H ₂ :2.011	0.010	0.010	35.400	31.149	311428.597	2.011	0	0.020	62.640	0.000	0.000
He:4.003	0.060	0.060	0.090	0.079	32.004	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.010	0.010	0.014	0.012	23.203	4.022	12.011	0.040	0.050	0.120	0.148
H ₂ O:18.005	0.240	0.240	13.800	12.143	4960.140	2.011	0	0.483	24.419	0.000	0.000
CO:28.005	0.012	0.012	13.800	12.143	101102.793	0	12.011	0.000	0.000	0.144	145.847
N ₂ :28.013	0.108	0.108	0.600	0.528	388.902	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.600	0.600	0.200	0.176	-70.666	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.990	0.990	0.540	0.475	-51.999	6.033	24.022	5.972	2.867	23.779	11.414
O ₂ :31.999	0.001	0.001	0.120	0.106	10460.291	0	0	0.000	0.000	0.000	0.000
HCl:36.458	0.001	0.001	0.001	0.001	-11.998	1.005	0	0.001	0.001	0.000	0.000
Ar:39.948	0.045	0.045	0.010	0.009	-80.444	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	31.100	31.096	20.000	17.598	-43.407	0	12.011	0.000	0.000	373.494	211.372
C ₃ H ₈ :44.077	0.110	0.110	0.060	0.053	-51.999	8.044	36.033	0.885	0.425	3.963	1.902
COS:60.069	0.012	0.012	0.460	0.405	3273.426	0	12.011	0.000	0.000	0.144	4.862
SO ₂ :64.063	0.006	0.006	0.003	0.003	-55.999	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.008	0.008	0.150	0.132	1550.046	0	12.011	0.000	0.000	0.096	1.585
Total	100.013	100.000	113.648	100.000				141.517	140.655	401.740	377.130
Dry		0.998		0.879	H ₂ O-Gas Corr.	Mol Out	0.878572	% Clos.	-0.609	% Clos.	-6.126

TABLE A.5 Tests of Acid-Gas Composition: Experiment 2A

Component	ACL No.		ACL No.		Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	Feed (%)	92-0430-01	Feed-N (%)	Prod (%)	Prod-N (%)						
H ₂ S:34.075	31.700		31.677	0.010	0.007	2.011	0	63.702	0.015	0.000	0.000
H ₂ :2.011	0.010		0.010	14.300	10.534	2.011	0	0.020	21.183	0.000	0.000
He:4.003	0.040		0.040	0.340	0.250	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.001		0.001	0.001	0.001	4.022	12.011	0.004	0.003	0.012	0.009
H ₂ O:18.005	0.300		0.300	36.000	26.518	2.011	0	0.603	53.328	0.000	0.000
CO:28.005	0.108		0.108	36.000	26.518	0	12.011	0.000	0.000	1.296	318.507
N ₂ :28.013	0.012		0.012	1.000	0.737	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.270		0.270	0.180	0.133	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.001		0.001	0.001	0.001	6.033	24.022	0.006	0.004	0.024	0.018
O ₂ :31.999	0.001		0.001	0.260	0.192	0	0	0.000	0.000	0.000	0.000
HCl:36.458	0.001		0.001	0.010	0.007	1.005	0	0.001	0.007	0.000	0.000
Ar:39.948	0.012		0.012	0.011	0.008	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	67.600		67.550	47.000	34.621	0	12.011	0.000	0.000	811.343	415.829
C ₃ H ₈ :44.077	0.001		0.001	0.001	0.001	8.044	36.033	0.008	0.006	0.036	0.027
COS:60.069	0.006		0.006	0.600	0.442	0	12.011	0.000	0.000	0.072	5.308
SO ₂ :64.063	0.008		0.008	0.002	0.001	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.003		0.003	0.041	0.030	0	12.011	0.000	0.000	0.036	0.363
Total	100.074		100.000	135.757	100.000			64.344	74.546	812.819	740.061
	Dry		0.997		0.735			% Clos.	15.856	% Clos.	-8.951

TABLE A.6 Tests of Acid-Gas Composition: Experiment 3A

Component	ACL No.		ACL No.		Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	92-0442-03	Feed (%)	92-0442-04	Prod (%)							
H ₂ S:34.075	62.300	58.355	18.100	15.188	-73.973	2.011	0	117.551	36.430	0.000	0.000
H ₂ :2.011	0.010	0.009	38.200	32.054	342108.534	2.011	0	0.019	64.460	0.000	0.000
He:4.003	0.140	0.131	0.370	0.310	136.756	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	1.080	1.012	0.220	0.185	-81.752	4.022	12.011	4.069	0.742	12.150	2.217
H ₂ O:18.005	7.000	6.557	19.260	16.161	146.482	2.011	0	13.186	32.500	0.000	0.000
CO:28.005	0.252	0.236	19.260	16.161	6746.730	0	12.011	0.000	0.000	2.835	194.111
N ₂ :28.013	0.028	0.026	2.140	1.796	6746.730	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.570	0.534	0.120	0.101	-81.140	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.110	0.103	0.020	0.017	-83.712	6.033	24.022	0.622	0.101	2.475	0.403
O ₂ :31.999	0.001	0.001	0.180	0.151	16025.009	0	0	0.000	0.000	0.000	0.000
HCl:36.458	0.001	0.001	0.001	0.001	-10.417	1.005	0	0.001	0.001	0.000	0.000
Ar:39.948	0.140	0.131	0.049	0.041	-68.646	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	35.100	32.877	20.600	17.286	-47.424	0	12.011	0.000	0.000	394.888	207.616
C ₃ H ₈ :44.077	0.010	0.009	0.002	0.002	-82.083	8.044	36.033	0.075	0.013	0.338	0.060
COS:60.069	0.011	0.010	0.540	0.453	4297.730	0	12.011	0.000	0.000	0.124	5.442
SO ₂ :64.063	0.004	0.004	0.003	0.003	-32.812	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.004	0.004	0.110	0.092	2363.543	0	12.011	0.000	0.000	0.045	1.109
Total	106.761	100.000	119.175	100.000				135.322	134.248	412.855	410.959
Dry		0.934		0.838				% Clos.	-0.794	% Clos.	-0.459

TABLE A.7 Tests of Acid-Gas Composition: Experiment 4A

Component	ACL No. 92-0442-05		ACL No. 92-0442-06		Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	Feed (%)	Feed-N (%)	Prod (%)	Prod-N (%)							
H ₂ S:34.075	27.600	25.826	0.030	0.022	-99.913	2.011	0	51.936	0.045	0.000	0.000
H ₂ :2.011	0.010	0.009	12.600	9.428	100651.165	2.011	0	0.019	18.959	0.000	0.000
He:4.003	0.030	0.028	0.030	0.022	-20.039	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.360	0.337	0.009	0.007	-98.001	4.022	12.011	1.355	0.027	4.046	0.081
H ₂ O:18.005	7.000	6.550	34.398	25.737	292.930	2.011	0	13.172	51.757	0.000	0.000
CO:28.005	0.090	0.084	34.398	25.737	30461.187	0	12.011	0.000	0.000	1.012	309.129
N ₂ :28.013	0.010	0.009	0.010	0.007	-20.039	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.170	0.159	0.130	0.097	-38.853	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.036	0.034	0.001	0.001	-97.779	6.033	24.022	0.203	0.005	0.809	0.018
O ₂ :31.999	0.001	0.001	0.220	0.165	17491.473	0	0	0.000	0.000	0.000	0.000
HCl:36.458	0.001	0.001	0.001	0.001	-20.039	1.005	0	0.001	0.001	0.000	0.000
Ar:39.948	0.046	0.043	0.023	0.017	-60.019	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	71.500	66.904	50.500	37.785	-43.524	0	12.011	0.000	0.000	803.588	453.835
C ₃ H ₈ :44.077	0.004	0.004	0.001	0.001	-80.010	8.044	36.033	0.030	0.006	0.135	0.027
COS:60.069	0.005	0.005	0.380	0.284	5977.054	0	12.011	0.000	0.000	0.056	3.415
SO ₂ :64.063	0.003	0.003	0.900	0.673	23888.373	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.003	0.003	0.020	0.015	433.075	0	12.011	0.000	0.000	0.034	0.180
Total	106.869 Dry	100.000 0.934	133.651	100.000 0.743				66.716 % Clos.	70.800 6.121	809.680 % Clos.	766.685 -5.310

TABLE A.8 Tests of Acid-Gas Composition: Experiment 5A

Component	ACL No.		ACL No.		Prod-N (%)	Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	92-0383-05 Feed (%)	Feed-N (%)	92-0383-06 Prod (%)	Prod-N (%)								
H ₂ S:34.075	66.000	65.771	34.300	30.662	-53.381	2.011	0	132.266	61.661	0.000	0.000	0.000
H ₂ :2.011	0.030	0.030	28.200	25.209	84221.528	2.011	0	0.060	50.695	0.000	0.000	0.000
He:4.003	0.020	0.020	0.010	0.009	-55.148	0	0	0.000	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.250	0.249	0.250	0.223	-10.296	4.022	12.011	1.002	0.899	2.992	2.684	2.684
H ₂ O:18.005	0.160	0.159	11.700	10.459	6459.587	2.011	0	0.321	21.033	0.000	0.000	0.000
CO:28.005	0.297	0.296	11.700	10.459	3433.784	0	12.011	0.000	0.000	3.555	125.622	125.622
N ₂ :28.013	0.033	0.033	1.200	1.073	3161.955	0	0	0.000	0.000	0.000	0.000	0.000
NO _x :30	0.400	0.399	0.200	0.179	-55.148	0	0	0.000	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.045	0.045	0.001	0.001	-98.007	6.033	24.022	0.271	0.005	1.077	0.021	0.021
O ₂ :31.999	0.001	0.001	0.130	0.116	11561.488	0	0	0.000	0.000	0.000	0.000	0.000
HCl:36.458	0.020	0.020	0.020	0.018	-10.296	1.005	0	0.020	0.018	0.000	0.000	0.000
Ar:39.948	0.046	0.046	0.028	0.025	-45.398	0	0	0.000	0.000	0.000	0.000	0.000
CO ₂ :44.010	33.000	32.886	23.300	20.828	-36.664	0	12.011	0.000	0.000	394.988	250.171	250.171
C ₃ H ₈ :44.077	0.005	0.005	0.001	0.001	-82.059	8.044	36.033	0.040	0.007	0.180	0.032	0.032
COS:60.069	0.033	0.033	0.360	0.322	878.586	0	12.011	0.000	0.000	0.395	3.865	3.865
SO ₂ :64.063	0.005	0.005	0.006	0.005	7.645	0	0	0.000	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.003	0.003	0.460	0.411	13654.575	0	12.011	0.000	0.000	0.036	4.939	4.939
Total	100.348 Dry	100.000 0.998	111.866	100.000 0.895				133.979 % Clos.	134.318 0.253	403.223 % Clos.	387.336 -3.940	

TABLE A.9 Tests of Acid-Gas Composition: Experiment 6A

Component	ACL No.		ACL No.		Change (%)	Prod-N (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	92-0383-05 1-2-2d (%)	Feed-N (%)	92-0383-06 Prod (%)	92-0383-06 Prod (%)								
H ₂ S:34.075	30.400	30.410	0.260	0.260	-99.362	0.194	2.011	0	61.155	0.390	0.000	0.000
H ₂ :2.011	0.010	0.010	14.300	14.300	106528.412	10.666	2.011	0	0.020	21.450	0.000	0.000
He:4.003	0.040	0.040	0.200	0.200	272.827	0.149	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.260	0.260	0.110	0.110	-68.453	0.082	4.022	12.011	1.046	0.330	3.124	0.985
H ₂ O:18.005	0.140	0.140	34.104	34.104	18064.113	25.438	2.011	0	0.282	51.157	0.000	0.000
CO:28.005	0.315	0.315	34.104	34.104	7972.939	25.438	0	12.011	0.000	0.000	3.785	305.541
N ₂ :28.013	0.035	0.035	0.696	0.696	1382.785	0.519	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.280	0.280	0.130	0.130	-65.380	0.097	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.504	0.504	0.063	0.063	-90.679	0.047	6.033	24.022	3.042	0.284	12.111	1.129
O ₂ :31.999	0.001	0.001	0.220	0.220	16304.371	0.164	0	0	0.000	0.000	0.000	0.000
HCl:36.458	0.001	0.001	0.001	0.001	-25.435	0.001	1.005	0	0.001	0.001	0.000	0.000
Ar:39.948	0.012	0.012	0.017	0.017	5.634	0.013	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	67.900	67.923	49.300	49.300	-45.861	36.773	0	12.011	0.000	0.000	815.824	441.683
C ₃ H ₈ :44.077	0.056	0.056	0.007	0.007	-90.679	0.005	8.044	36.033	0.451	0.042	2.019	0.188
COS:60.069	0.006	0.006	0.460	0.460	5616.675	0.343	0	12.011	0.000	0.000	0.072	4.121
SO ₂ :64.063	0.003	0.003	0.003	0.003	-25.435	0.002	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.003	0.003	0.090	0.090	2136.960	0.067	0	12.011	0.000	0.000	0.036	0.806
Total	99.966 Dry	100.000 0.999	134.065	134.065		100.000 0.746			65.996 % Clos.	73.653 11.602	836.971 % Clos.	754.454 -9.859

TABLE A.10 Tests of Acid-Gas Composition: Experiment 7A

Component	ACL No.		ACL No.		Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	92-0442-03	Feed (%)	92-0442-04	Prod (%)							
H ₂ S:34.075	62.800	58.756	22.400	18.466	-68.572	2.011	0	118.159	37.135	0.000	0.000
H ₂ :2.011	0.030	0.028	33.800	27.864	99170.753	2.011	0	0.056	56.034	0.000	0.000
He:4.003	0.020	0.019	0.020	0.016	-11.890	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.135	0.126	0.008	0.007	-94.779	4.022	12.011	0.508	0.027	1.517	0.079
H ₂ O:18.005	7.000	6.549	19.800	16.322	149.226	2.011	0	13.171	32.825	0.000	0.000
CO:28.005	0.001	0.001	19.800	16.322	174480.685	0	12.011	0.000	0.000	0.011	196.049
N ₂ :28.013	0.438	0.410	0.700	0.577	40.815	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.400	0.374	0.140	0.115	-69.161	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.013	0.012	0.008	0.007	-45.778	6.033	24.022	0.073	0.040	0.292	0.158
O ₂ :31.999	0.110	0.103	0.400	0.330	220.400	0	0	0.000	0.000	0.000	0.000
HCl:36.458	1.200	1.123	0.100	0.082	-92.657	1.005	0	1.128	0.083	0.000	0.000
Ar:39.948	0.086	0.080	0.280	0.231	186.870	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	34.600	32.372	22.700	18.713	-42.194	0	12.011	0.000	0.000	388.822	224.764
C ₃ H ₈ :44.077	0.002	0.002	0.001	0.001	-55.945	8.044	36.033	0.015	0.007	0.067	0.030
COS:60.069	0.028	0.026	0.540	0.445	1599.267	0	12.011	0.000	0.000	0.315	5.347
SO ₂ :64.063	0.013	0.012	0.008	0.007	-45.778	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.006	0.006	0.600	0.495	8711.014	0	12.011	0.000	0.000	0.067	5.941
Total	106.882	100.000	121.305	100.000				133.111	126.149	391.092	432.368
Dry		0.935		0.837				% Clos.	-5.230	% Clos.	10.554

TABLE A.11 Tests of Acid-Gas Composition: Experiment 8A

Component	ACL No.		ACL No.		Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	92-0430-03	Feed (%)	92-0430-04	Prod (%)							
H ₂ S:34.075	26.500	24.804	0.020	0.015	-99.941	2.011	0	49.881	0.030	0.000	0.000
H ₂ :2.011	0.010	0.009	11.600	8.529	91024.519	2.011	0	0.019	17.152	0.000	0.000
He:4.003	0.070	0.066	0.040	0.029	-55.111	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.140	0.131	0.050	0.037	-71.944	4.022	12.011	0.527	0.148	1.574	0.442
H ₂ O:18.005	7.000	6.552	36.000	26.470	304.000	2.011	0	13.176	53.231	0.000	0.000
CO:28.005	0.001	0.001	36.000	26.470	2827902.323	0	12.011	0.000	0.000	0.011	317.931
N ₂ :28.013	0.270	0.253	1.100	0.809	220.041	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.030	0.215	0.120	0.088	-59.014	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.001	0.001	0.001	0.001	-21.444	6.033	24.022	0.006	0.004	0.022	0.018
O ₂ :31.999	0.170	0.159	0.320	0.235	47.869	0	0	0.000	0.000	0.000	0.000
HCl:36.458	0.001	0.001	0.001	0.001	-21.444	1.005	0	0.001	0.001	0.000	0.000
Ar:39.948	0.031	0.029	0.070	0.051	77.384	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	72.400	67.766	48.100	35.367	-47.810	0	12.011	0.000	0.000	813.939	424.791
C ₃ H ₈ :44.077	0.001	0.001	0.001	0.001	-21.444	8.044	36.033	0.008	0.006	0.034	0.026
COS:60.069	0.006	0.006	0.420	0.309	5398.893	0	12.011	0.000	0.000	0.067	3.709
SO ₂ :64.063	0.003	0.003	2.100	1.544	54888.934	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.004	0.004	0.060	0.044	1078.334	0	12.011	0.000	0.000	0.045	0.530
Total	106.838	100.000	136.003	100.000				63.617	70.572	815.693	747.447
Dry		0.934		0.735				% Clos.	10.933	% Clos.	-8.367

TABLE A.12 Tests of Acid-Gas Composition: Experiment 9A

Component	ACL No.		ACL No.		Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	92-0422-01 Feed (%)	Feed-N (%)	92-0422-02 Prod (%)	Prod-N (%)							
H ₂ S:34.075	46.400	44.968	30.800	27.969	-37.803	2.011	0	90.431	56.246	0.000	0.000
H ₂ :2.011	0.030	0.029	10.900	9.898	33944.230	2.011	0	0.058	19.905	0.000	0.000
He:4.003	0.170	0.165	2.400	2.179	1222.820	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.018	0.017	0.090	0.082	368.499	4.022	12.011	0.070	0.329	0.210	0.982
H ₂ O:18.005	3.500	3.392	9.900	8.990	165.036	2.011	0	6.821	18.079	0.000	0.000
CO:28.005	0.001	0.001	9.900	8.990	927527.177	0	12.011	0.000	0.000	0.012	107.979
N ₂ :28.013	0.280	0.271	0.700	0.636	134.249	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.300	0.291	0.120	0.109	-62.520	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.002	0.002	0.010	0.009	368.499	6.033	24.022	0.012	0.055	0.047	0.218
O ₂ :31.999	0.001	0.001	0.320	0.291	29883.909	0	0	0.000	0.000	0.000	0.000
HCl:36.458	0.030	0.029	0.120	0.109	274.799	1.005	0	0.029	0.110	0.000	0.000
Ar:39.948	0.110	0.107	0.035	0.032	-70.186	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	52.300	50.686	44.400	40.319	-20.454	0	12.011	0.000	0.000	608.791	484.271
C ₃ H ₈ :44.077	0.001	0.001	0.001	0.001	-6.300	8.044	36.033	0.008	0.007	0.035	0.033
COS:60.069	0.022	0.021	0.280	0.254	1092.542	0	12.011	0.000	0.000	0.256	3.054
SO ₂ :64.063	0.015	0.015	0.006	0.005	-62.520	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.004	0.004	0.140	0.127	3179.490	0	12.011	0.000	0.000	0.047	1.527
Total	103.184 Dry	100.000 0.966	110.122	100.000 0.910				97.430 % Clos.	94.730 -2.771	609.397 % Clos.	598.063 -1.860

TABLE A.13 Tests of Acid-Gas Composition: Experiment 9B

Component	ACL No. 92-0430-05		ACL No. 92-0430-06		Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	Feed (%)	Feed-N (%)	Prod (%)	Prod-N (%)							
H ₂ S:34.075	46.200	44.843	9.700	7.580	-83.096	2.011	0	90.179	15.244	0.000	0.000
H ₂ :2.011	0.010	0.010	24.500	19.146	197158.305	2.011	0	0.020	38.504	0.000	0.000
He:4.003	0.020	0.019	0.080	0.063	222.054	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.110	0.107	0.040	0.031	-70.722	4.022	12.011	0.429	0.126	1.282	0.375
H ₂ O:18.005	3.500	3.397	28.000	21.882	544.109	2.011	0	6.832	44.004	0.000	0.000
CO:28.005	0.001	0.001	28.000	21.882	2254280.632	0	12.011	0.000	0.000	0.012	262.821
N ₂ :28.013	0.210	0.204	1.500	1.172	475.097	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.280	0.272	0.140	0.109	-59.743	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.001	0.001	0.001	0.001	-19.486	6.033	24.022	0.006	0.005	0.023	0.019
O ₂ :31.999	0.001	0.001	0.320	0.234	24054.078	0	0	0.000	0.000	0.000	0.000
HCl:36.458	0.030	0.029	0.020	0.016	-46.324	1.005	0	0.029	0.016	0.000	0.000
Ar:39.948	0.044	0.043	0.136	0.106	148.860	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	52.600	51.055	34.600	27.039	-47.039	0	12.011	0.000	0.000	613.222	324.771
C ₃ H ₈ :44.077	0.001	0.001	0.001	0.001	-19.486	8.044	36.033	0.008	0.006	0.035	0.028
COS:60.069	0.009	0.009	0.810	0.633	7146.223	0	12.011	0.000	0.000	0.105	7.603
SO ₂ :64.063	0.006	0.006	0.003	0.002	-59.743	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.003	0.003	0.130	0.102	3388.922	0	12.011	0.000	0.000	0.035	1.220
Total	103.026	100.000	127.961	100.000				97.503	97.904	614.715	596.838
Dry		0.966		0.781				% Clos.	0.412	% Clos.	-2.908

TABLE A.14 Tests of Acid-Gas Composition: Experiment 9C

Component	ACL No. 92-0430-05		ACL No. 92-0430-06		Change (%)	M.W. (H)	M.W. (C)	H (in)	H (out)	C (in)	C (out)
	Feed (%)	Feed-N (%)	Prod (%)	Prod-N (%)							
H ₂ S:34.075	46.500	45.026	6.000	4.603	-89.776	2.011	0	90.548	9.257	0.000	0.000
H ₂ :2.011	0.010	0.010	27.300	20.945	216207.573	2.011	0	0.019	42.121	0.000	0.000
He:4.003	0.040	0.039	0.160	0.123	216.934	0	0	0.000	0.000	0.000	0.000
CH ₄ :16.033	0.150	0.145	0.060	0.046	-68.307	4.022	12.011	0.584	0.185	1.745	0.553
H ₂ O:18.005	3.500	3.389	30.383	23.311	587.815	2.011	0	6.815	46.878	0.000	0.000
CO:28.005	0.013	0.013	30.383	23.311	185080.980	0	12.011	0.000	0.000	0.151	279.983
N ₂ :28.013	0.117	0.113	0.117	0.090	-20.766	0	0	0.000	0.000	0.000	0.000
NO _x :30	0.440	0.426	0.130	0.100	-76.590	0	0	0.000	0.000	0.000	0.000
C ₂ H ₆ :30.055	0.657	0.636	0.072	0.055	-91.317	6.033	24.022	3.838	0.333	15.282	1.327
O ₂ :31.999	0.001	0.001	0.280	0.215	22085.392	0	0	0.000	0.000	0.000	0.000
HCl:36.458	0.120	0.116	0.020	0.015	-86.794	1.005	0	0.117	0.015	0.000	0.000
Ar:39.948	0.034	0.033	0.044	0.034	2.538	0	0	0.000	0.000	0.000	0.000
CO ₂ :44.010	51.600	49.965	34.600	26.546	-46.871	0	12.011	0.000	0.000	600.125	318.843
C ₃ H ₈ :44.077	0.073	0.071	0.008	0.006	-91.317	8.044	36.033	0.569	0.049	2.547	0.221
COS:60.069	0.008	0.008	0.650	0.499	6337.725	0	12.011	0.000	0.000	0.093	5.990
SO ₂ :64.063	0.006	0.006	0.003	0.002	-60.383	0	0	0.000	0.000	0.000	0.000
CS ₂ :76.139	0.004	0.004	0.130	0.100	2475.090	0	12.011	0.000	0.000	0.047	1.198
Total	103.273	100.000	130.340	100.000				102.490	98.839	619.990	608.116
Dry		0.966		0.767				% Clos.	-3.563	% Clos.	-1.915

Appendix B:

Statistical Design Analysis of Experimental Results for Acid-Gas Compositions

Appendix B:

Statistical Design Analysis of Experimental Results for Acid-Gas Compositions

This appendix reports the results of a statistical analysis* of the Task III experimental results reported in Appendix A. The analysis involved a three-step procedure, which began with the calculation of the effect of each of the independent variables on the major dependent variables. The calculation used the Yates' algorithm* (this operation is a transform function that separates the effect of each of the independent variables on the dependent variables in the experiments) to calculate the values of the first-order effects of the independent variables (carbon dioxide concentration = CO_2 Conc, water concentration = H_2O Conc, and pipeline gas concentration = Gas Conc), the second-order effects of the interactions between pairs of the primary variables (the carbon-dioxide concentration/water-concentration interaction = $\text{CO}_2 \text{ C} \times \text{H}_2\text{O C}$, the carbon-dioxide concentration/pipeline-gas concentration interaction = $\text{CO}_2 \text{ C} \times \text{Gas C}$, and the water-concentration/pipeline-gas concentration interaction = $\text{H}_2\text{O C} \times \text{Gas C}$), and the third-order effect of the interaction among all three primary variables (carbon-dioxide concentration/water-concentration/pipeline-gas concentration interaction = $\text{CO}_2 \text{ C} \times \text{H}_2\text{O C} \times \text{Gas C}$).

In the second step, the results of the statistical design were interpreted by taking the results of the full complement of experiments. For the majority of experiments, most of the cross-effects are insignificant and can be treated as random noise. Hence, a plot of these points should be expected to follow a random (normal Gaussian) distribution. One may then conclude that any values that significantly depart from the normal distribution curve are not random and therefore are significant. A normal Gaussian distribution plotted on a "probability plot" graph would appear as a straight line. Hence, any effects, or cross-effects, that depart from the straight line are significant effects and should be considered further. The error bars shown on these plots are calculated from nonsignificant effects by assuming they are random noise.

The third step involved an ANOVA (analysis of variance) evaluation* on the "significant" variable(s) by means of a simple linear model to determine how well the variable(s) described the actual experimental results. In this section of the analysis, the "significant" variables identified in the previous step were included in the first iteration of the evaluation. Then, variables were added or deleted, depending on the calculated probability that an effect was random. If the weakest variable had a probability of less than 0.10 (10% chance of being random), then the next strongest variable was added to the model, and the ANOVA evaluation was repeated until a variable showed a greater than 10% chance of being random. The "significant" variables were then taken to be the set of variables minus this last variable. Similarly, when the weakest variable of the initial set had a greater than 10% chance of being random, the variables were deleted until the same test was met. (In the following pages, exceptions to this test are discussed in greater detail.)

* From DESIGN-EASE analysis.

This analysis is presented in the following pages for the major dependent variables of interest in this study — the conversions of hydrogen sulfide and carbon dioxide and the production of carbonyl sulfide, carbon disulfide, sulfur dioxide, and total impurities (the sum of carbonyl sulfide, carbon disulfide, and sulfur dioxide production).

B.1 Hydrogen Sulfide Conversion

TABLE B.1.1 Effect of Independent Variables on the Percent Conversion of Hydrogen Sulfide

Independent Variable	Coefficient	Effect
Mean	82.205000	82.205000
CO ₂ Conc	17.592500	35.185000
H ₂ O Conc	3.392500	6.785000
CO ₂ C x H ₂ O C	-3.265000	-6.530000
Gas Conc	-1.892500	-3.785000
CO ₂ C x Gas C	1.745000	3.490000
H ₂ O C x Gas C	0.550000	1.100000
CO ₂ C x H ₂ O C x Gas C	-0.387500	-0.775000

Mean of center points: 86.44 %.

FIGURE B.1 Parameters Affecting the Conversion of Hydrogen Sulfide

TABLE B.1.2 Model Developed on the Basis of CO₂ Concentration Being the Only Significant Variable Affecting the Conversion of Hydrogen Sulfide

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	2475.968450	1	2475.9684500	77.284	0.0000
Curvature	39.131400	1	39.1314000	1.221	0.3012
Error	256.299350	8	32.0374187		
Residual	233.988150	6	38.9980250		
Pure Error	22.311200	4	11.1556000		
COR TOTAL	2771.399200	10			

Root MSE = 5.660161. R-Squared = 0.9075.

Dep. Mean = 82.205000. Adj. R-Squared = 0.8844.

C.V. = 6.89%.

TABLE B.1.3 Parameters for the Model Defined in Table B.1.2

Variable	Parameter Estimate	DF	Sum of Squares	t for H0 Parameter = 0	Prob > t
Intercept	82.205000	1		41.078	0.0000
CO ₂ Conc	17.592500	1	2475.968450	8.791	0.0000

Standard Error = 2.0011690.

TABLE B.1.4 Residual Analysis for the Model Defined in Table B.1.2

Std Ord	Actual Value	Predicated Value	Residual	Standardized Residual	Cook's D	t Value	Run Ord
1	62.530000	64.612500	-2.082500	-0.4248	0.030	-0.405	1
2	99.980000	99.797500	0.182500	0.0372	0.000	0.035	5
3	73.970000	64.612500	9.357500	1.9090	0.607	2.333	9
4	99.910000	99.797500	0.112500	0.0230	0.000	0.022	10
5	53.380000	64.612500	-11.232500	-2.2915	0.875	-3.347	2
6	99.360000	99.797500	-0.437500	-0.0893	0.001	-0.084	11
7	68.570000	64.612500	3.957500	0.8073	0.109	0.790	4
8	99.940000	99.797500	0.142500	0.0291	0.000	0.027	6

Discussion. With greater than 95% confidence, the probability plot of the coefficients of the variables indicate that CO₂ Conc strongly enhanced the conversion of hydrogen sulfide. The effect of CO₂ Conc appeared to be essentially linear, since the mean of the center-point experiments is quite close to the mean of the eight experiments comprising the basic factorial design. All other coefficients of the variables lie on a straight line and, therefore, appeared to be consistent with random noise. This finding would indicate that none of the other variables (H₂O Conc, Gas Conc) nor any of the various cross-effects were significant.

There is no obvious mechanistic reason for the dominating effect of CO₂ Conc on the conversion of hydrogen sulfide. One possible explanation is that the oxygen produced from the dissociation of carbon dioxide is promoting hydrogen sulfide dissociation, as proposed by Strelkova.* Another possibility is that carbon dioxide simply diluted the hydrogen sulfide; therefore, at the lowest hydrogen sulfide concentrations (27.8-35%) associated with the highest carbon dioxide concentrations, hydrogen sulfide became "the limiting reagent" instead of the available microwave power, which was held constant at 1.0 kW in these experiments. This phenomenon could also explain why none of the other variables appeared to be significant. The subset of data at the low value of CO₂ Conc constitutes an independent factorial design in two variables — H₂O Conc and Gas Conc. If this subset is evaluated separately by means of Yates' algorithm (see Table B.1.5), the effect of these variables is seen to be fairly large. The effect of H₂O Conc is to promote hydrogen sulfide dissociation, while the effect of Gas Conc was to inhibit its dissociation.

TABLE B.1.5 Subset Evaluation by Means of Yates' Algorithm

Experiment	H ₂ S Conversion (%)	Yates' Coefficient	Variable
1	62.5	64.613	Mean
3	74	13.315	H ₂ O Conc
5	53.4	-7.275	Gas Conc
7	68.6	1.875	H ₂ O Conc × Gas Conc

* Personal communication from M.I. Strelkova to J.B.L. Harkness, July 1992.

B.2 Carbon Dioxide Conversion

TABLE B.2.1 Effect of Independent Variables on the Percent Conversion of Carbon Dioxide

Independent Variable	Coefficient	Effect
Mean	44.577500	44.577500
CO ₂ Conc	2.157500	4.315000
H ₂ O Conc	0.657500	1.315000
CO ₂ C x H ₂ O C	-1.727500	-3.455000
Gas Conc	-1.447500	-2.895000
CO ₂ C x Gas C	1.547500	3.095000
H ₂ O C x Gas C	1.212500	2.425000
CO ₂ C x H ₂ O C x Gas C	0.832500	1.665000

Mean of center points: 46.96%.

FIGURE B.2 Parameters Affecting the Conversion of Carbon Dioxide

TABLE B.2.2 Model Developed on the Basis of CO₂ Concentration, CO₂ Concentration × H₂O Concentration, CO₂ Concentration × Gas Concentration, and Gas Concentration Being the Primary Variables Affecting the Conversion of Carbon Dioxide

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	97.032600	4	24.2581500	5.837	0.0400
Curvature	12.350038	1	12.3500379	2.972	0.1453
Error	20.778617	5	4.1557233		
Residual	20.764150	3	6.9213833		
Pure Error	0.014467	2	0.0072333		
COR TOTAL	130.161255	10			

Root MSE = 2.038559.

R-Squared = 0.8404.

Dep. Mean = 44.577500.

Adj. R-Squared = 0.6807.

C.V. = 4.57%.

TABLE B.2.3 Parameters for the Model Defined in Table B.2.2

Variable	Parameter Estimate	DF	Sum of Squares	t for H0 Parameter = 0	Prob > t
Intercept	44.577500	1		61.850	0.0000
CO ₂ Conc	2.157500	1	37.238450	2.993	0.0303
CO ₂ C × H ₂ O C	-1.727500	1	23.874050	-2.397	0.0619
Gas Conc	-1.447500	1	16.762050	-2.008	0.1009
CO ₂ C × Gas C	1.547500	1	19.158050	2.147	0.0846

Standard Error = 0.7207395.

TABLE B.2.4 Residual Analysis for the Model Defined in Table B.2.2

Std Ord	Actual Value	Predicated Value	Residual	Standardized Residual	Cook's D	t Value	Run Ord
1	43.410000	43.687500	-0.277500	-0.2223	0.016	-0.204	1
2	49.750000	48.362500	1.387500	1.1115	0.412	1.139	5
3	47.420000	47.142500	0.277500	0.2223	0.016	0.204	9
4	43.520000	44.907500	-1.387500	-1.1115	0.412	-1.139	10
5	36.660000	37.697500	-1.037500	-0.8311	0.230	-0.807	2
6	45.860000	48.562500	-2.702500	-2.1648	1.562	-4.224	11
7	42.190000	41.152500	1.037500	0.8311	0.230	0.807	4
8	47.810000	45.107500	2.702500	2.1648	1.562	4.224	6

Discussion. With 95% confidence, the probability plot indicated that two variables inhibited carbon dioxide conversion. The most significant inhibitor appeared to be the $\text{CO}_2 \text{ C} \times \text{H}_2\text{O C}$ cross-effect, and Gas Conc was the next variable in importance. However, when the ANOVA evaluation was carried out with these variables, the results indicated that neither could account for the variations observed for the carbon dioxide conversion in these experiments. $\text{CO}_2 \text{ Conc}$ alone yielded a better fit of the actual results than the combination of the $\text{CO}_2 \text{ C} \times \text{H}_2\text{O C}$ and Gas Conc variables, but the overall fit was very weak — a very low F-value. Adding $\text{CO}_2 \text{ C} \times \text{Gas C}$ and then both the $\text{CO}_2 \text{ C} \times \text{H}_2\text{O C}$ and Gas Conc variables increased the F-value of the model, but the fit was still very weak. At this point, the probability value for the Gas Conc was slightly over 0.10, which was less than half of its probability in the initial test of the model. This value indicates that these variables are not independent variables as required for a true ANOVA evaluation. The mostly likely explanation is that the variables are interrelated by the water-gas shift reaction, which is consistent with some of the other observations for these experiments.

B.3 Carbonyl Sulfide Production

TABLE B.3.1 Effect of Independent Variables on the Percent Production of Carbonyl Sulfide

Independent Variable	Coefficient	Effect
Mean	0.470000	0.470000
CO ₂ Conc	-0.005000	-0.010000
H ₂ O Conc	0.000000	0.000000
CO ₂ C × H ₂ O C	-0.065000	-0.130000
Gas Conc	-0.025000	-0.050000
CO ₂ C × Gas C	-0.000000	-0.000000
H ₂ O C × Gas C	0.035000	0.070000
CO ₂ C × H ₂ O C × Gas C	0.010000	0.020000

Mean of center points: 0.73%.

FIGURE B.3 Parameters Affecting the Production of Carbonyl Sulfide

TABLE B.3.2 Model Developed on the Basis of CO₂ Concentration × H₂O Concentration and H₂O Concentration × Gas Concentration Being the Only Significant Variables Affecting the Production of Carbonyl Sulfide

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	0.043600	2	0.0218000	8.117	0.0150
Curvature	0.147491	1	0.1474909	54.917	0.0001
Error	0.018800	7	0.0026857		
Residual	0.006000	5	0.0012000		
Pure Error	0.012800	2	0.0064000		
COR TOTAL	0.209891	10			

Root MSE = 0.051824. R-Squared = 0.9104.

Dep. Mean = 0.470000. Adj. R-Squared = 0.8720.

C.V. = 11.03%.

TABLE B.3.3 Parameters for the Model Defined in Table B.3.2

Variable	Parameter Estimate	DF	Sum of Squares	t for H0 Parameter = 0	Prob > t
Intercept	0.470000	1		25.652	0.0000
CO ₂ C × H ₂ O C	-0.065000	1	0.033800	-3.548	0.0094
H ₂ O C × Gas C	0.035000	1	0.009800	1.910	0.0977

Standard Error = 0.0183225.

TABLE B.3.4 Residual Analysis for the Model Defined in Table B.3.2

Std Ord	Actual Value	Predicated Value	Residual	Standardized Residual	Cook's D	t Value	Run Ord
1	0.460000	0.440000	0.020000	0.4882	0.048	0.464	1
2	0.600000	0.570000	0.030000	0.7322	0.107	0.709	5
3	0.540000	0.500000	0.040000	0.9763	0.191	0.973	9
4	0.380000	0.370000	0.010000	0.2441	0.012	0.229	10
5	0.360000	0.370000	-0.010000	-0.2441	0.012	-0.229	2
6	0.460000	0.500000	-0.040000	-0.9763	0.191	-0.973	11
7	0.540000	0.570000	-0.030000	-0.7322	0.107	-0.709	4
8	0.420000	0.440000	-0.020000	-0.4882	0.048	-0.464	6

Discussion. At a 50% confidence level, two variables appear significant for carbonyl sulfide production — both second-order effects. The Gas C $\times$ H₂O C cross-effect enhanced carbonyl sulfide production, while at the other end of the spectrum, the CO₂ C $\times$ H₂O C cross-effect inhibited it. The relative strength of the second-order effects could also account for the nonlinearity of the data, with the mean of the center-point experiments being almost twice the mean of the eight experiments from the statistical design. Although the effect of Gas Conc did not lie on the line with the random effects, it did not meet any of the statistical tests for "significance" and, therefore, was not used in the model. Overall, the model showed a rather weak relationship between the two "significant" variables and the experimental results for carbonyl sulfide production.

Also noteworthy was the finding that the pipeline gas was present at trace levels (0-0.2%), while carbon dioxide was a major component (30-65%). With this observation in mind, it is interesting to compare the significance of the Gas C $\times$ H₂O C cross-effect in enhancing carbonyl sulfide formation with the inhibitory effect of CO₂ C $\times$ H₂O C. The fact that both of these variables involve water strongly suggests the carbonyl sulfide formation reaction(s) are, in some manner, related to the water-gas shift reaction.

B.4 Carbon Disulfide Production

TABLE B.4.1 Effect of Independent Variables on the Percent Production of Carbon Disulfide

Independent Variable	Coefficient	Effect
Mean	0.191375	0.191375
CO ₂ Conc	-0.138625	-0.277250
H ₂ O Conc	0.006125	0.012250
CO ₂ C × H ₂ O C	-0.018875	-0.037750
Gas Conc	0.111125	0.222250
CO ₂ C × Gas C	-0.088875	-0.177750
H ₂ O C × Gas C	0.021375	0.042750
CO ₂ C × H ₂ O C × Gas C	-0.023625	-0.047250

Mean of center points: 0.13%.

FIGURE B.4 Parameters Affecting the Production of Carbon Disulfide

TABLE B.4.2 Model Developed on the Basis of CO₂ Concentration, Gas Concentration, and CO₂ Concentration × Gas Concentration Being the Only Significant Variables Affecting the Production of Carbon Disulfide

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	0.315715	3	0.1052385	56.025	0.0001
Curvature	0.008219	1	0.0082187	4.375	0.0814
Error	0.011271	6	0.0018784		
Residual	0.011271	4	0.0028176		
Pure Error	0.000000	2	0.0000000		
COR TOTAL	0.335205	10			

Root MSE = 0.043341. R-Squared = 0.9664.

Dep. Mean = 0.191375. Adj. R-Squared = 0.9440.

C.V. = 22.65%.

TABLE B.4.3 Parameters for the Model Defined in Table B.4.2

Variable	Parameter Estimate	DF	Sum of Squares	t for H0 Parameter = 0	Prob > t
Intercept	0.191375	1		12.489	0.0000
CO ₂ Conc	-0.138625	1	0.153735	-9.047	0.0001
Gas Conc	0.111125	1	0.098790	7.252	0.0003
CO ₂ C × Gas C	-0.088875	1	0.063190	-5.800	0.0012

Standard Error = 0.0153233.

TABLE B.4.4 Residual Analysis for the Model Defined in Table B.4.2

Std Ord	Actual Value	Predicated Value	Residual	Standardized Residual	Cook's D	t Value	Run Ord
1	0.150000	0.130000	0.020000	0.6526	0.106	0.623	1
2	0.041000	0.030500	0.010500	0.3426	0.029	0.320	5
3	0.110000	0.130000	-0.020000	-0.6526	0.106	-0.623	9
4	0.020000	0.030500	-0.010500	-0.3426	0.029	-0.320	10
5	0.460000	0.530000	-0.070000	-2.2841	1.304	-4.190	2
6	0.090000	0.075000	0.015000	0.4895	0.060	0.461	11
7	0.600000	0.530000	0.070000	2.2841	1.304	4.190	4
8	0.060000	0.075000	-0.015000	-0.4895	0.060	-0.461	6

Discussion. The data set for carbon disulfide production appeared to have some curvature, since the mean of the center-point experiments was less than the mean of the eight-factorial experiments by four times the standard error of the model. At a 95% confidence level, three variables appeared significant, as seen in the probability plot of the coefficients of the effects. The Gas Conc was the most significant variable enhancing carbon disulfide formation, while two variables appeared to inhibit its formation — CO₂ Conc and the second-order effect of CO₂ C × Gas C. These variables modeled the experimental results quite well (high F Value), and the probability that the effect of a variable was random was less than 1% for each of these variables.

Mechanistically, the findings suggest the direct reaction of methane (or one of the other hydrocarbons in the mixture) with, perhaps, polyatomic sulfur ions to form carbon disulfide. In these experiments, the pipeline gas concentration was very low (0-0.2%), while carbon dioxide was present as a bulk component (30-65%). With this observation in mind, it is interesting to compare the magnitude of the Gas Conc effect in enhancing carbon disulfide formation with the inhibitory effect of CO₂ Conc. Both of these effects are roughly equal in magnitude, in spite of the disparity in their concentrations. The inhibitory effects of CO₂ Conc suggest that the pathway which leads to carbon disulfide formation produces carbon dioxide as a reaction product. It is possible that raising the carbon dioxide level in the system served to inhibit the formation of carbon disulfide by driving the by-product formation reaction backwards.

B.5 Sulfur Dioxide Production

TABLE B.5.1 Effect of Independent Variables on the Percent Production of Sulfur Dioxide

Independent Variable	Coefficient	Effect
Mean	0.378125	0.378125
CO ₂ Conc	0.373125	0.746250
H ₂ O Conc	0.374625	0.749250
CO ₂ C × H ₂ O C	0.374125	0.748250
Gas Conc	0.151125	0.302250
CO ₂ C × Gas C	0.149125	0.298250
H ₂ O C × Gas C	0.150125	0.300250
CO ₂ C × H ₂ O C × Gas C	0.149625	0.299250

Mean of center points: 0.003%.

FIGURE B.5 Parameters Affecting the Production of Sulfur Dioxide

TABLE B.5.2 Model Developed on the Basis of CO₂ Concentration, H₂O Concentration, and CO₂ Concentration × H₂O Concentration Being the Only Significant Variables Affecting the Production of Sulfur Dioxide

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	3.356285	3	1.1187618	9.323	0.0112
Curvature	0.307023	1	0.3070228	2.558	0.1608
Error	0.720017	6	0.1200029		
Residual	0.720017	4	0.1800044		
Pure Error	0.000000	2	0.0000000		
COR TOTAL	4.383326	10			

Root MSE = 0.346414. R-Squared = 0.8357.

Dep. Mean = 0.378125. Adj. R-Squared = 0.7262.

C.V. = 91.61%.

TABLE B.5.3 Parameters for the Model Defined in Table B.5.2

Variable	Parameter Estimate	DF	Sum of Squares	t for H0 Parameter = 0	Prob > t
Intercept	0.378125	1		3.087	0.0215
CO ₂ Conc	0.373125	1	1.113778	3.047	0.0226
Gas Conc	0.374625	1	1.122751	3.059	0.0223
CO ₂ C × Gas C	0.374125	1	1.119756	3.055	0.0224

Standard Error = 0.1224760.

TABLE B.5.4 Residual Analysis for the Model Defined in Table B.5.2

Std Ord	Actual Value	Predicated Value	Residual	Standardized Residual	Cook's D	t Value	Run Ord
1	0.003000	0.004500	-0.001500	-0.0061	0.000	-0.006	1
2	0.002000	0.002500	-0.000500	-0.0020	0.000	-0.002	5
3	0.003000	0.005500	-0.002500	-0.0102	0.000	-0.009	9
4	0.900000	1.500000	-0.600000	-2.4495	1.500	-5.999	10
5	0.006000	0.004500	0.001500	0.0061	0.000	0.006	2
6	0.003000	0.002500	0.000500	0.0020	0.000	0.002	11
7	0.008000	0.005500	0.002500	0.0102	0.000	0.009	4
8	2.100000	1.500000	0.600000	2.4495	1.500	5.999	6

Discussion. The data set for sulfur dioxide production appeared to be linear when the means of the center-point experiments were compared with the eight factorial-design experiments. However, the probability plot of the coefficients of the effects produced two distinct populations at a 95% confidence level. The groups of three variables that were found to be "significant" in enhancing sulfur dioxide production were those that did not involve Gas Conc. All variables in which Gas Conc was included inhibited sulfur dioxide production, which is especially noteworthy because the pipeline gas was present only at trace levels. The "nonpipeline gas" variables modeled the experimental results weakly (low F Value), but the probability that their effects were random was also low in each case (slightly greater than 2%).

B.6 Total Impurity Production

TABLE B.6.1 Effect of Independent Variables on the Percent Total Production of Impurities

Independent Variable	Coefficient	Effect
Mean	1.039500	1.039500
CO ₂ Conc	0.229500	0.459000
H ₂ O Conc	0.380750	0.761500
CO ₂ C × H ₂ O C	0.290250	0.580500
Gas Conc	0.237250	0.474500
CO ₂ C × Gas C	0.060250	0.120500
H ₂ O C × Gas C	0.206500	0.413000
CO ₂ C × H ₂ O C × Gas C	0.136000	0.272000

Mean of center points: 0.863%.

FIGURE B.6 Parameters Affecting the Production of Impurities

TABLE B.6.2 Model Developed on the Basis of H₂O Concentration Being the Only Significant Variable Affecting the Production of Impurities

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	1.159536	1	1.1595361	4.467	0.0675
Curvature	0.067997	1	0.0679974	0.262	0.6226
Error	2.076506	8	0.2595633		
Residual	2.063706	6	0.3439510		
Pure Error	0.012800	2	0.0064000		
COR TOTAL	3.304040	10			

Root MSE = 0.509474.

R-Squared = 0.3715.

Dep. Mean = 1.039537.

Adj. R-Squared = 0.2144.

C.V. = 49.01%.

TABLE B.6.3 Parameters for the Model Defined in Table B.6.2

Variable	Parameter Estimate	DF	Sum of Squares	t for H ₀ Parameter = 0	Prob > t
Intercept	1.039537	1		5.771	0.0004
H ₂ O Conc	0.380712	1	1.159536	2.114	0.0675

Standard Error = 0.1801261.

TABLE B.6.4 Residual Analysis for the Model Defined in Table B.6.2

Std Ord	Actual Value	Predicated Value	Residual	Standardized Residual	Cook's D	t Value	Run Ord
1	0.613000	0.658825	-0.045825	-0.1039	0.002	-0.098	1
2	0.643000	0.658825	-0.015825	-0.0359	0.000	-0.034	5
3	0.653000	1.420250	-0.767250	-1.7389	0.504	-2.012	9
4	1.300000	1.420250	-0.120250	-0.2725	0.012	-0.258	10
5	0.826000	0.658825	0.167175	0.3789	0.024	0.360	2
6	0.553000	0.658825	-0.105525	-0.2392	0.010	-0.226	11
7	1.148000	1.420250	-0.272250	-0.6170	0.063	-0.594	4
8	2.580000	1.420250	1.159750	2.6285	1.152	5.142	6

Discussion. When summed together, the three by-products (carbonyl sulfide, carbon disulfide, and sulfur dioxide) were viewed as total impurities for the system. At the 50% level, the probability plot of the coefficients of the variables showed that none of the variables appeared to be significant for the production of the total impurities. A straight line could describe all of the coefficients of the variables, which would be consistent with random noise. The ANOVA evaluation of this data set showed that two variables very weakly modeled the experiments. The H₂O Conc and CO₂ C × H₂O C variables slightly enhanced the production of total impurities. In view of the mechanistic trends that emerge for each of these individual by-products, total impurities, as a dependent variable, does not appear to be useful for characterizing the performance of the plasma-chemical dissociation of hydrogen sulfide.

B.7 Reverse Power

TABLE B.7.1 Effect of Independent Variables on Reverse Power (Watts)

Independent Variable	Coefficient	Effect
Mean	249.625	249.625
CO ₂ Conc	-4.875	-9.750
H ₂ O Conc	-5.375	-10.750
CO ₂ C × H ₂ O C	14.125	28.250
Gas Conc	2.875	5.750
CO ₂ C × Gas C	-0.125	-0.250
H ₂ O C × Gas C	-2.125	-4.250
CO ₂ C × H ₂ O C × Gas C	10.875	21.750

Mean of center points: 230 W.

FIGURE B.7 Parameters Affecting Reverse Power

TABLE B.7.2 Model Developed on the Basis of CO₂ Concentration x H₂O Concentration and CO₂ Concentration x H₂O Concentration x Gas Concentration Being the Only Significant Variables Affecting Reverse Power

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	2542.250	2	1271.1250	6.722	0.0235
Curvature	840.306818	1	840.3068182	4.444	0.0730
Error	1323.625	7	189.0892857		
Residual	523.625	5	104.7250		
Pure Error	800.	2	400.0		
COR TOTAL	4706.181818	10			

Root MSE = 5.51%.

R-Squared = 0.7187.

Dep. Mean = 249.625.

Adj. R-Squared = 0.5982.

C.V. = 5.51%.

TABLE B.7.3 Parameters for the Model Defined in Table B.7.2

Variable	Parameter Estimate	DF	Sum of Squares	t for H0 Parameter = 0	Prob > t
Intercept	249.625	1		51.345	0.0
CO ₂ x H ₂ O	14.125	1	1596.125	2.905	0.0228
CO ₂ C x H ₂ O C x Gas C	10.875	1	946.125	2.237	0.0604

Standard Error = 4.86.

TABLE B.7.4 Residual Analysis for the Model Defined in Table B.7.2

Std Ord	Actual Value	Predicated Value	Residual	Standardized Residual	Cook's D	t Value	Run Ord
1	258	252.875	5.125	0.4714	0.044	0.447	1
2	242	246.375	-4.375	-0.4024	0.032	-0.380	5
3	245	246.375	-1.375	-0.1265	0.003	-0.118	9
4	242	252.875	-10.875	-1.4000	0.200	-1.000	10
5	290	274.625	15.375	1.4143	0.400	1.528	2
6	230	224.625	5.375	0.4944	0.049	0.470	11
7	225	224.625	0.375	0.0345	0.000	0.032	4
8	265	274.625	-9.625	-0.8854	0.157	-0.872	6

Discussion. In these experiments, between 20 and 30% of the microwave energy was reflected back to the source by the plasma. This reflection and the large differences between the 1.0-kW input power and the values obtained for the minimum forward power suggest that the power level was too high for the feed rate of hydrogen sulfide. Some of the variation in the data is explained by the second-order effect of $\text{CO}_2 \text{ C} \times \text{H}_2\text{O}$ and the third-order effect of $\text{CO}_2 \text{ C} \times \text{H}_2\text{O} \text{ C} \times \text{Gas C}$. However, the model is weak (low F Value), and the differences between the actual and the predicated values are larger than the calculated standard error in over half the experiments.

B.8 Minimum Forward Power

TABLE B.8.1 Effect of Independent Variables on Minimum Forward Power (Watts)

Independent Variable	Coefficient	Effect
Mean	343.75	343.75
CO ₂ Conc	6.25	12.50
H ₂ O Conc	56.25	112.50
CO ₂ C × H ₂ O C	-31.25	-62.50
Gas Conc	18.75	37.50
CO ₂ C × Gas C	31.25	62.50
H ₂ O C × Gas C	-43.75	-87.50
CO ₂ C × H ₂ O C × Gas C	-31.25	-62.50

FIGURE B.8 Parameters Affecting Minimum Forward Power

TABLE B.8.2 Model Developed on the Basis of H₂O Concentration and H₂O Concentration x Gas Concentration Being the Only Significant Variables Affecting Minimum Forward Power

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	40,625.00	2	20,312.50	5.353	0.0389
Curvature	360,085.22	1	360,085.22	94.893	0.0000
Error	26,562.50	7	3,794.64		
Residual	26,562.50	5	5,312.50		
Pure Error	0.00	2	0.00		
COR TOTAL	427,272.72	10			

Root MSE = 61.601.

R-Squared = 0.9378.

Dep. Mean = 343.750.

Adj. R-Squared = 0.9112.

C.V. = 17.92%.

TABLE B.8.3 Parameters for the Model Defined in Table B.8.2

Variable	Parameter Estimate	DF	Sum of Squares	t for H0 Parameter = 0	Prob > t
Intercept	343.750	1		15.783	0.0000
H ₂ O Conc	56.250	1	25,312.5	2.583	0.0363
H ₂ O C x Gas C	-43.750	1	15,312.5	-2.009	0.0845

Standard Error = 21.8.

TABLE B.8.4 Residual Analysis for the Model Defined in Table B.8.2

Std Ord	Actual Value	Predicated Value	Residual	Standardized Residual	Cook's D	t Value	Run Ord
1	250	243.750	6.250	0.1283	0.003	0.120	1
2	200	243.750	-43.750	-0.8984	0.161	-0.886	5
3	450	443.750	6.250	0.1283	0.003	0.120	9
4	400	443.750	-43.750	-0.8984	0.161	-0.886	10
5	250	331.250	-81.250	-1.6684	0.557	-1.933	2
6	450	331.250	118.750	2.4384	1.189	4.501	11
7	400	356.250	43.750	0.8984	0.161	0.886	4
8	350	356.250	-6.250	-0.1283	0.003	-0.120	6

Discussion. The data were very weakly modeled (low F Value) by H₂O Conc and H₂O C × Gas C. Furthermore, the differences between the actual and the predicted values were significantly larger than the standard error in several experiments.

B.9 Minimum Reverse Power

TABLE B.9.1 Effect of Independent Variables on Minimum Reverse Power (Watts)

Independent Variable	Coefficient	Effect
Mean	76.00	76.00
CO ₂ Conc	-7.00	-14.00
H ₂ O Conc	-1.50	-3.00
CO ₂ C × H ₂ O C	5.50	11.00
Gas Conc	-4.75	-9.50
CO ₂ C × Gas C	12.25	24.50
H ₂ O C × Gas C	-4.75	-9.50
CO ₂ C × H ₂ O C × Gas C	-7.75	-15.50

FIGURE B.9 Parameters Affecting Minimum Reverse Power

TABLE B.9.2 Model Developed on the Basis of CO₂ Concentration x Gas Concentration Being the Only Significant Variable Affecting Minimum Reverse Power

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Model	1,200.50	1	1,200.50	6.431	0.0349
Curvature	23,598.55	1	23,598.55	126.407	0.0000
Error	1,493.50	8	186.69		
Residual	1,493.500	6	248.92		
Pure Error	0.00	2	0.00		
COR TOTAL	26,292.55	10			

Root MSE = 13.66.

R-Squared = 0.9432.

Dep. Mean = 76.00.

Adj. R-Squared = 0.9290.

C.V. = 17.98%.

TABLE B.9.3 Parameters for the Model Defined in Table B.9.2

Variable	Parameter Estimate	DF	Sum of Squares	t for H0 Parameter = 0	Prob > t
Intercept	76.00	1		15.733	0.0000
CO ₂ C x Gas C	12.25	1	1200.50	2.536	0.0349

Standard Error = 4.83.

TABLE B.9.4 Residual Analysis for the Model Defined in Table B.9.2

Std Ord	Actual Value	Predicated Value	Residual	Standardized Residual	Cook's D	t Value	Run Ord
1	110.00	88.25	21.75	1.8381	0.563	2.193	1
2	45.00	63.75	-18.75	-1.5846	0.418	-1.759	5
3	90.00	88.25	1.75	0.1479	0.004	0.140	9
4	78.00	63.75	14.25	1.2043	0.242	1.240	10
5	70.00	63.75	6.25	0.5282	0.046	0.506	2
6	85.00	88.25	-3.25	-0.2747	0.013	-0.260	11
7	62.00	63.75	-1.75	-0.1479	0.004	-0.140	4
8	68.00	88.25	-20.25	-1.7113	0.488	-1.964	6

Discussion. The reverse power measured at the minimum forward power was weakly modeled by $\text{CO}_2 \text{ C} \times \text{Gas C}$. Again, the differences between the actual and the predicted values were two to four times the standard error for several of the experiments.

Appendix C:

**Experimental Results for
Task IV: Direct Treatment of Crude Gas**

TABLE C.1b Calculated Values for Conversions of Gas Species Studied

Experiment	Changes between the Feed and Product Analyses (%)				
	H ₂	H ₂ S	H ₂ O	CO	CO ₂
1 A	607.07	-96.00	1.01	3,738.40	-0.03
1B	2,276.47	N/A	0.06	69,993.4	-8.28
2 A	824.55	-98.00	-0.05	33.27	-0.05
3 A	576.62	-96.03	1.49	1,929.87	-0.64
4 A	1,430.86	-98.00	2.06	1,941.15	0.00
	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ +	O ₂
1 A	-1.21	-1.58	-8.17	-30.07	8.23
1B	-2.48	2.69	-9.03	-9.94	0.06
2 A	-0.27	-2.61	-18.22	-33.37	-25.32
3 A	-2.88	-6.31	-16.96	-32.34	485.54
4 A	-1.34	-5.79	-16.50	-48.97	-14.60
Average	-1.43	-4.07	-14.96	-36.19	

C.2 Methane Conversion

In all of the experiments, some methane was destroyed by the plasma: the amount converted ranged from 0.25 to 2.88%. The data were analyzed by using Yates' algorithm to identify the important variables for methane conversion. In this analysis, the average value of experiments 1A and 1B was used for experiment 1. The results are shown in Table C.2, where the calculated values for methane conversion are shown in the column headed "% Conv." and the Yates' coefficients are given under "Effect" for the three variables listed in the final column. The analysis suggests that hydrogen sulfide inhibits methane conversion, while carbon dioxide promotes it. These conclusions are consistent with a simple mechanistic interpretation where the hydrogen produced by the dissociation of hydrogen sulfide would force the methane dissociation backwards, whereas carbon dioxide dissociation produces oxygen species that could react with the products of methane dissociation and, thereby, enhance the forward reaction.

C.3 Ethane Conversion

The destruction of the ethane in the feed gas was significantly greater than the methane losses for each of the experiments and ranged from 1.6 to 6.3% (again, experiment 1 is the average of experiments 1A and 1B). The Yates' analysis showed that (1) carbon dioxide had an

TABLE C.2 Analysis of Methane Conversion

Exp. No.	% Conv.	Effect	Variable
1	1.845	1.58375	Mean
2	0.27	-1.5575	H ₂ S Conc
3	2.88	1.0525	CO ₂ Conc
4	1.34	0.0175	H ₂ S Conc x CO ₂ Conc

even stronger effect on ethane destruction than on methane and (2) the inhibiting effect of hydrogen sulfide was negligible in the case of ethane. The results are shown in Table C.3.

C.4 Propane Conversion

The trend in hydrocarbon conversion continued with more propane being destroyed (8-18%) than ethane. In light of the low propane concentrations in the feed gases and the relatively equal magnitudes of the effects, no definitive conclusions can be drawn from these results. Both hydrogen sulfide and carbon dioxide seem to be stronger promoters of propane conversion than ethane or methane, while their interaction appears to inhibit it. Probably the same mechanism for the promotion of methane conversion by carbon dioxide is at work in this case. Hydrogen sulfide appears to be enhancing the dissociation of the higher hydrocarbons by providing hydrogen atoms to react with the broken hydrocarbon chains, which prevents the back reaction to reform the original species. The results are shown in Table C.4.

C.5 Higher Hydrocarbons Conversion

The losses of the heavier hydrocarbons were still greater, continuing the trend. Again, both hydrogen sulfide and carbon dioxide seem to be stronger promoters of conversion of these hydrocarbon species than of the lighter species, but the interaction effect is negligible in this case. The data are consistent with all of the mechanisms hypothesized above. The results are shown in Table C.5.

C.6 Carbon Dioxide Conversion

The conversions for carbon dioxide ranged from 0 to over 8%, with a mean value of 1.2% converted. A Yates' algorithm analysis showed no significant difference between the three independent variables for these results. The results are shown in Table C.6.

TABLE C.3 Analysis of Ethane Conversion

Exp. No.	% Conv.	Effect	Variable
1	2.14	4.2125	Mean
2	2.61	-0.025	H ₂ S Conc
3	6.31	3.675	CO ₂ Conc
4	5.79	-0.495	H ₂ S Conc x CO ₂ Conc

TABLE C.4 Analysis of Propane Conversion

Exp. No.	% Conv.	Effect	Variable
1	8.605	15.07125	Mean
2	18.22	4.5775	H ₂ S Conc
3	16.96	3.3175	CO ₂ Conc
4	1.34	-5.0375	H ₂ S Conc x CO ₂ Conc

TABLE C.5 Analysis of Higher Hydrocarbons Conversion

Exp. No.	% Conv.	Effect	Variable
1	20.005	33.67125	Mean
2	33.37	14.9975	H ₂ S Conc
3	32.34	13.9675	CO ₂ Conc
4	48.97	1.6325	H ₂ S Conc x CO ₂ Conc

TABLE C.6 Analysis of Carbon Dioxide Conversion

Exp. No.	% Conv.	Effect	Variable
1	4.17	1.21375	Mean
2	0.05	-2.3775	H ₂ S Conc
3	0.64	-1.7875	CO ₂ Conc
4	0	1.7375	H ₂ S Conc x CO ₂ Conc

TABLE C.7 Analysis of IGT Cylinders

Cylinder Number	Component	Mole Percent
GC185	Oxygen	<0.003
	Nitrogen	2.62 ± 0.01
	Carbon dioxide	1.010 ± 0.007
	Methane	90.47 ± 0.07
	Ethane	4.02 ± 0.01
	Propane	0.999 ± 0.008
	i-Butane	0.311 ± 0.005
	n-Butane	0.306 ± 0.005
	i-Pentane	0.103 ± 0.004
	n-Pentane	0.103 ± 0.004
	n-Hexane	0.053 ± 0.003
	Total	100.00
GC2754	Oxygen	<0.003
	Nitrogen	2.54 ± 0.01
	Carbon dioxide	0.996 ± 0.007
	Methane	90.61 ± 0.07
	Ethane	4.00 ± 0.01
	Propane	0.999 ± 0.008
	i-Butane	0.300 ± 0.005
	n-Butane	0.301 ± 0.005
	i-Pentane	0.101 ± 0.004
	n-Pentane	0.099 ± 0.004
	n-Hexane	0.053 ± 0.003
	Total	100.0

	A	B	C	D	E	F
1	GRI Tests of the Direct Treatment of Crude Gas					
2	Series GRI - IV 4/10/92 - 6/1/92					
3	Experiment 1A					
4	ACL	92-0293-01		92-0293-04		
5	Component	Feed 1A	FEED 1A	Prod 1A	PROD 1A	CHANGE
6		%	%	%	%	%
7	Adjustment		1.01041		1.000302	
8	H2S	0.005	0.0050	0.0002	0.0002	-96.00
9	H2	0.08	0.0792	0.56	0.5598	607.07
10	CH4	91	90.0624	89	88.9731	-1.21
11	H2O	0.01	0.0099	0.01	0.0100	1.01
12	CO	0.01	0.0099	0.38	0.3799	3738.40
13	N2	2.7	2.6722	3.1	3.0991	15.98
14	C2H6	3.9	3.8598	3.8	3.7989	-1.58
15	O2	0.07	0.0693	0.075	0.0750	8.23
16	Ar	0.015	0.0148	0.015	0.0150	1.01
17	CO2	2	2.0000	2	1.9994	-0.03
18	C3H8	1.1	1.0887	1	0.9997	-8.17
19	Other	0.13	0.1287	0.09	0.0900	-30.07
20						
21	TOTAL	101.02	99.9999	100.0302	100.0000	
22						
23	Experiment 2A					
24	ACL	92-0339-01		92-0339-02		
25	Component	Feed 2A	FEED 2A	Prod 2A	PROD 2A	CHANGE
26		%	%	%	%	%
27	Adjustment		1.00003		1.000522	
28	H2S	0.01	0.0100	0.0002	0.0002	-98.00
29	H2	0.08	0.0800	0.74	0.7396	824.55
30	CH4	90.3	90.2973	90.1	90.0530	-0.27
31	H2O	0.02	0.0200	0.02	0.0200	-0.05
32	CO	0.03	0.0300	0.04	0.0400	33.27
33	N2	2.8	2.7999	2.9	2.8985	3.52
34	C2H6	3.9	3.8999	3.8	3.7980	-2.61
35	O2	0.087	0.0870	0.065	0.0650	-25.32
36	Ar	0.076	0.0760	0.087	0.0870	14.42
37	CO2	1	1.0000	1	0.9995	-0.05
38	C3H8	1.1	1.1000	0.9	0.8995	-18.22
39	Other	0.6	0.6000	0.4	0.3998	-33.37
40						
41	TOTAL	100.003	100.0000	100.0522	100.0000	
42						

	A	B	C	D	E	F
1	GRI-IV Direct Treatment of Crude Gas					
2						
3	Experiment 1B					
4	ACL#	92-0495-01		92-495-02		
5	Component	Feed	FEED-N	Prod	PROD-N	CHANGE
6		%	%	%	%	%
7	H2S:34.075	0.005	0.005	0.005	0.005	0.062
8	H2:2.011	0.08	0.080	1.9	1.900	2276.473
9	He:4.003	0.038	0.038	0.057	0.057	50.093
10	CH4:16.033	90.6	90.547	88.3	88.303	-2.478
11	H2O:18.005	0.03	0.030	0.03	0.030	0.062
12	CO:28.005	0.001	0.001	0.7	0.700	69943.401
13	N2:28.013	0.9	0.899	0.9	0.900	0.062
14	NOx:30	0.001	0.001	0.001	0.001	0.062
15	C2H6:30.055	3.8	3.798	3.9	3.900	2.695
16	O2:31.999	0.06	0.060	0.06	0.060	0.062
17	HCl:36.458	0.001	0.001	0.001	0.001	0.062
18	Ar:39.948	0.04	0.040	0.04	0.040	0.062
19	CO2:44.010	2.4	2.399	2.2	2.200	-8.276
20	C3H8:44.077	1.1	1.099	1	1.000	-9.035
21	COS:60.069	0.001	0.001	0.001	0.001	0.062
22	SO2:64.063	0.001	0.001	0.001	0.001	0.062
23	CS2:76.139	0.001	0.001	0.001	0.001	0.062
24	C4s,C5s:58-7	1.000	0.999	0.900	0.900	-9.944
25						
26	TOTAL	100.059	100.000	99.997	100.000	
27		Dry	1.000		1.000	

	A	B	C	D	E	F
43	GRI Tests of the Direct Treatment of Crude Gas					
44	Series GRI - IV 4/10/92 - 6/1/92					
45	Experiment 3A					
46	ACL	92-0326-04		92-0326-05		
47	Component	Feed 3A	FEED 3A	Prod 3A	PROD 3A	CHANGE
48		%	%	%	%	%
49	Adjustment		1.021465		1.006432	
50	H2S	0.005	0.0050	0.0002	0.0002	-96.03
51	H2	0.09	0.0881	0.6	0.5962	576.62
52	CH4	90.5	88.5982	86.6	86.0465	-2.88
53	H2O	0.02	0.0196	0.02	0.0199	1.49
54	CO	0.03	0.0294	0.6	0.5962	1929.87
55	N2	2.7	2.6433	4.4	4.3719	65.40
56	C2H6	3.9	3.8180	3.6	3.5770	-6.31
57	O2	0.078	0.0764	0.45	0.4471	485.54
58	Ar	0.059	0.0578	0.073	0.0725	25.58
59	CO2	3	3.0000	3	2.9808	-0.64
60	C3H8	1.1	1.0769	0.9	0.8942	-16.96
61	Other	0.6	0.5874	0.4	0.3974	-32.34
62						
63	TOTAL	102.082	100.0000	100.6432	100.0000	
64						
65	Experiment 4A					
66	ACL	92-0326-01		92-0326-03		
67	Component	Feed 4A	FEED 4A	Prod 4A	PROD 4A	CHANGE
68		%	%	%	%	%
69	Adjustment		1.020526		0.999952	
70	H2S	0.01	0.0100	0.0002	0.0002	-98.00
71	H2	0.08	0.0784	1.2	1.2001	1430.86
72	CH4	90	88.1898	87	87.0042	-1.34
73	H2O	0.02	0.0196	0.02	0.0200	2.06
74	CO	0.03	0.0294	0.6	0.6000	1941.15
75	N2	2.9	2.8417	3.1	3.1001	9.10
76	C2H6	3.9	3.8216	3.6	3.6002	-5.79
77	O2	0.098	0.0960	0.082	0.0820	-14.60
78	Ar	0.053	0.0519	0.093	0.0930	79.08
79	CO2	3	3.0000	3	3.0001	0.00
80	C3H8	1.1	1.0779	0.9	0.9000	-16.50
81	Other	0.8	0.7839	0.4	0.4000	-48.97
82						
83	TOTAL	101.991	100.0002	99.9952	100.0000	
84						

	G	H	I	J	K	L	M	N
1	GRI Tests of the Direct Treatment of Crude Gas							
2	Series GRI - IV							
3								
4	Experiment 1A							
5	Comp.		M.W. (H)	M.W. (C)	H(in)	H(out)	C(in)	C(out)
6								
7								
8	H ₂ S		2.011	0	0.010055	0.000402	0	0
9	H ₂		2.011	0	0.159222	1.12582	0	0
10	CH ₄		4.022	12.011	362.2312	357.8499	1081.74	1068.656
11	H ₂ O		2.011	0	0.019903	0.020104	0	0
12	CO		0	12.011	0	0	0.118873	4.562802
13	N ₂		0	0	0	0	0	0
14	C ₂ H ₆		6.033	24.022	23.28629	22.91848	92.72058	91.25604
15	O ₂		0	0	0	0	0	0
16	Ar		0	0	0	0	0	0
17	CO ₂		0	12.011	0	0	24.022	24.01475
18	C ₃ H ₈		8.064	36.033	8.779011	8.061565	39.22794	36.02212
19	Other		12.096	60.055	1.556279	1.088311	7.726715	5.403318
20								
21	TOTAL				396.0419	391.0646	1245.5562	1229.9153
22					% Clos.	1.256767	% Clos.	1.271705
23								
24	Experiment 2A							
25	Comp.		M.W. (H)	M.W. (C)	H(in)	H(out)	C(in)	C(out)
26								
27								
28	H ₂ S		2.011	0	0.02011	0.000402	0	0
29	H ₂		2.011	0	0.160875	1.487364	0	0
30	CH ₄		4.022	12.011	363.1757	362.1931	1084.561	1081.626
31	H ₂ O		2.011	0	0.040219	0.040199	0	0
32	CO		0	12.011	0	0	0.360319	0.480189
33	N ₂		0	0	0	0	0	0
34	C ₂ H ₆		6.033	24.022	23.52799	22.91344	93.68299	91.23597
35	O ₂		0	0	0	0	0	0
36	Ar		0	0	0	0	0	0
37	CO ₂		0	12.011	0	0	12.011	12.00473
38	C ₃ H ₈		8.064	36.033	8.870134	7.253814	39.63511	32.41278
39	Other		12.096	60.055	7.257382	4.835876	36.03192	24.00947
40								
41	TOTAL				403.0524	398.7242	1266.2821	1241.7696
42					% Clos.	1.0739	% Clos.	1.9358

	G	H	I	J	K	L	M	N
43	GRI Tests of the Direct Treatment of Crude Gas							
44	Series GRI - IV							
45								
46	Experiment 3A							
47	Comp.		M.W. (H)	M.W. (C)	H(in)	H(out)	C(in)	C(out)
48								
49								
50	H2S		2.011	0	0.010055	0.0004	0	0
51	H2		2.011	0	0.177187	1.198889	0	0
52	CH4		4.022	12.011	356.3421	346.0792	1064.153	1033.505
53	H2O		2.011	0	0.039375	0.039963	0	0
54	CO		0	12.011	0	0	0.352758	7.160543
55	N2		0	0	0	0	0	0
56	C2H6		6.033	24.022	23.03427	21.58	91.71709	85.92652
57	O2		0	0	0	0	0	0
58	Ar		0	0	0	0	0	0
59	CO2		0	12.011	0	0	36.033	35.80272
60	C3H8		8.064	36.033	8.683998	7.211217	38.80339	32.22245
61	Other		12.096	60.055	7.105089	4.807478	35.2758	23.86848
62								
63	TOTAL				395.3921	380.9172	1266.3355	1218.4858
64					% Clos.	3.660904	% Clos.	3.92698
65								
66	Experiment 4A							
67	Comp.		M.W. (H)	M.W. (C)	H(in)	H(out)	C(in)	C(out)
68								
69								
70	H2S		2.011	0	0.02011	0.000402	0	0
71	H2		2.011	0	0.157644	2.413316	0	0
72	CH4		4.022	12.011	354.6994	349.9308	1059.248	1045.007
73	H2O		2.011	0	0.039411	0.040222	0	0
74	CO		0	12.011	0	0	0.353083	7.206946
75	N2		0	0	0	0	0	0
76	C2H6		6.033	24.022	23.05546	21.71984	91.80148	86.48335
77	O2		0	0	0	0	0	0
78	Ar		0	0	0	0	0	0
79	CO2		0	12.011	0	0	36.033	36.03473
80	C3H8		8.064	36.033	8.691988	7.257948	38.83909	32.43126
81	Other		12.096	60.055	9.482169	4.838632	47.07768	24.02315
82								
83	TOTAL				396.1462	386.2012	1273.3522	1231.1866
84					%Clos.	2.5105	% Clos.	3.3114

END

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