Conf-920122--5

MICROWAVE PRODUCTION OF HYDROGEN AND SULFUR FROM HYDROGEN SULFIDE WASTES*

by

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ABSTRACT

A waste-treatment process is being developed that uses "cold" microwave plasma-chemical reactions to split hydrogen sulfide into elemental hydrogen and sulfur. A clean sulfur product can be recovered and sold, while product gases are purified and separated into streams containing hydrogen, hydrogen sulfide for recycle, and the process purge containing carbon dioxide and water.

Experiments with pure hydrogen sulfide at 0.5 to 1.5 L/min flow rates and microwave powers of 400 to 1,000 W confirmed that conversions of over 90% per pass at process energy requirements approaching 5 kcal/mol are possible. Experiments with impurities typical of petroleum refinery waste hydrogen sulfide streams have demonstrated that these impurities are compatible with the plasma dissociation process and that they do not create new waste treatment problems.

This technology has a long-term potential for saving 40 to 70 x 10^{12} Btu/yr in the refining industry, for an economic savings of $500 million to $1,000 million annually. Although the microwave process should show particular advantages for the petroleum refining industry, the low capital costs and modular nature of the new process should make it economically attractive in connection with the small-scale waste-treatment technologies currently used in the natural gas industry. Currently, in the U.S.S.R., a 500-kW demonstration microwave hydrogen sulfide treatment unit operating at near atmospheric pressure is being tested at the natural gas fields in Orenberg.

INTRODUCTION

Some years ago, a new approach for the direct decomposition of hydrogen sulfide was described in the Soviet scientific literature (Balebanov et al., 1985; Rusanov et al., 1985). A microwave discharge was used to create a "cold," nonequilibrium plasma that dissociates hydrogen sulfide into hydrogen and sulfur. This work, which was concerned with sweetening natural gas, was conducted at the I.V. Kurchatov Institute of Atomic Energy in Moscow.

A conceptual flow sheet for an H_2S waste-treatment process based on plasma dissociation appears in Fig. 1. Both fresh and recycled H_2S are fed to a plasma reactor, which is connected to a microwave generator with wave guides. The Soviet literature reported conversions ranging from 45 to 80% of the H_2S fed to the laboratory plasma reactor, with power consumption of 0.7 to 1.9 electron volts per H_2S molecule converted (eV/molecule). The process conditions were not reported, but they are believed to be close to ambient temperatures, at subatmospheric pressures. Low-temperature operation is one of the principal advantages of plasma dissociation, since very little energy is lost to heating the bulk gas.

In commercial operation, the process stream leaving the reactor contains hydrogen, molten sulfur, and unconverted H_2S. The product sulfur is cooled and collected to recover available process energy. The gas phase is compressed and sent to a purification step to recover the product hydrogen and to recycle the unconverted H_2S. Most of the energy used by the process is needed for generating the microwaves, although some energy is needed to operate the gas compressor.

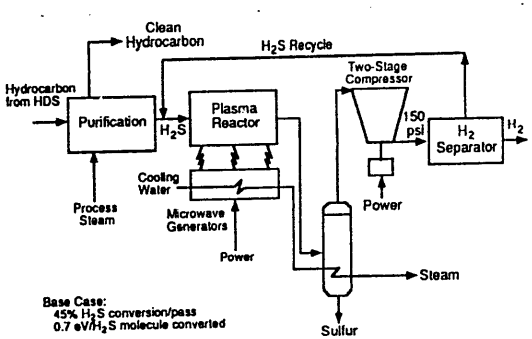

FIGURE 1 Conversion of Hydrogen Sulfide to Sulfur and Hydrogen by Plasma Dissociation Process

*Work supported by the U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, under Contract W-31-109-ENG-38.

EARLY PROCESS DEVELOPMENT PROGRAM AT ARGONNE

A program to investigate H_2S plasma dissociation was initiated at Argonne in 1987 to provide the U.S. Department of Energy (DOE) with experimental data on and process design evaluations of this technology. An Industrial Working Group was also established to review the Argonne program and provide direction from an industry perspective.

The experimental system developed for this program includes a multiple gas feed system, reactor, microwave-transport system, vacuum system, exhaust scrubber, analytical system, and auxiliary instrumentation (see Fig. 2). For safety, most of this apparatus was located in well-ventilated hoods. The scale of the equipment was for feed-gas flow rates of 0.5 to 1.5 L/min at microwave power levels of 400 to 1,000 W. Results for the early program effort have been described in a recent technical memorandum (Gorski et al., 1990). Some of the major findings may be summarized as follows:

1. Experimental data showed that the specific energy of H_2S dissociation is low enough for the plasma process to save energy compared with the Claus/SCOT-plus-reformer technology currently being used in the domestic petrochemical industry. This new technology has a long-term potential for saving 40 to 70 x 10^{12} Btu/yr in the refining industry, which translates into an economic savings of $500 to $1,000 million annually.

2. Specific energies of H_2S dissociation were estimated to be 0.5 to 0.8 eV/molecule, obtainable with 52 to 82% conversion per pass.

3. Even lower dissociation energies of 0.2 to 0.3 eV/molecule may be technically feasible. (For comparison, at 25 K the enthalpy of H_2S is $\Delta H = -0.21$ eV/molecule, and the Gibbs free energy is $\Delta G = -0.35$ eV/molecule.)

4. Typical refinery impurities are compatible with microwave plasma dissociation and even tend to stabilize the plasma.

5. Major reaction byproducts are CO and SO_2, while minor byproducts are CS_2 and COS.

Note that the specific energies of dissociation mentioned here may differ from theoretically calculated values because the gas temperatures in these experiments are greater than standard conditions and the distribution of the allotropes present in the liquid sulfur product leaving the plasma zone is unknown at this time. Based on this early work, a number of design improvements were made in the system. It is the typical results from these efforts which are reported in the remainder of this paper.

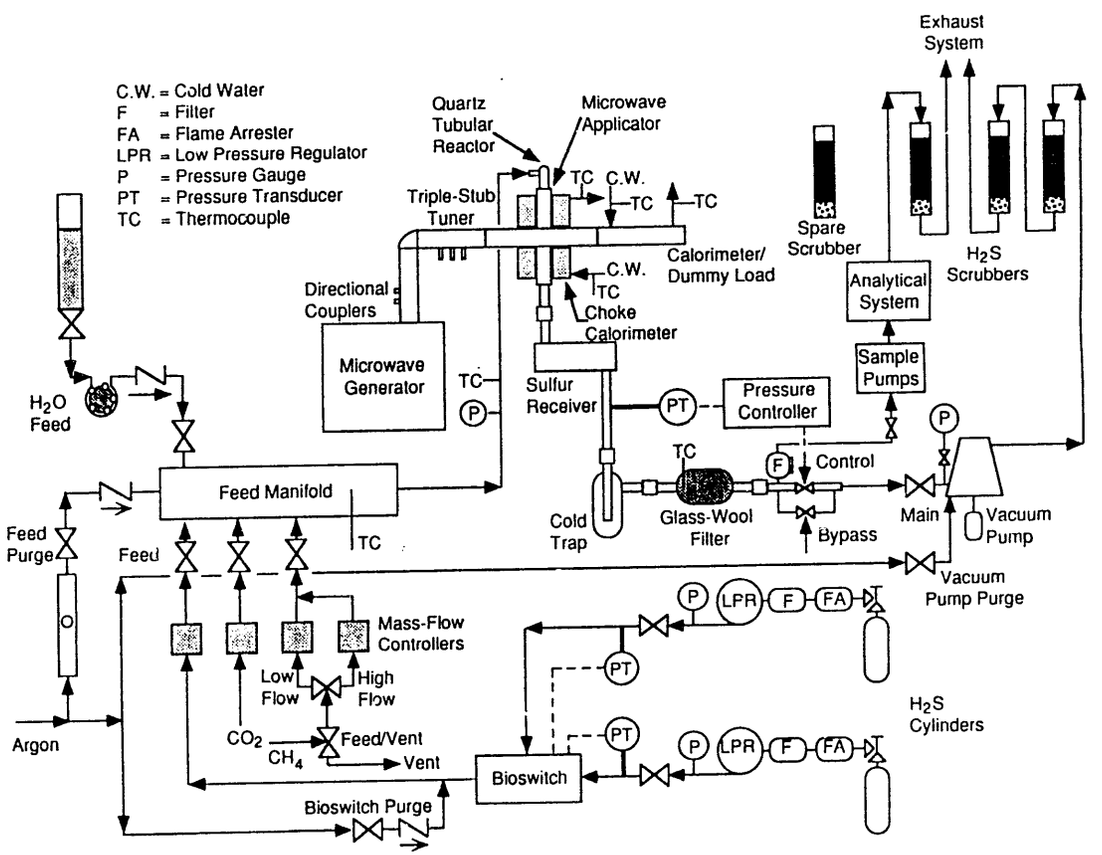

FIGURE 2. Schematic Diagram of Experimental System

SONIC SWIRL EXPERIMENTS

The general schematic for the recent experimental chemical-plasma reactor appears in Fig. 3. It should be noted that the 35-mm quartz reactor tube is closed by a dome just above the plasma zone, and all the gas must pass through an orifice that is drilled into the dome at a near-tangent so that a cyclonic flow is induced in the gas as the gas passes into the plasma zone. This approach results in two benefits:

1. The cyclonic-flow pattern improves the heat transfer from the glass surface and has alleviated the problem of quartz glass softening in the system from excess microwave power.

2. The cyclonic-flow design serves to de-entrain the sulfur from the hydrogen by condensing the sulfur on the walls of the reactor.

Typically, the experiments reported here were run at a pressure of 20 torr. Under these conditions, the operation of the plasma was quite stable, and the system operated for two hours without any difficulties.

The calculation of the flow rates through the orifice is not straightforward, because the leading edge of this orifice initiates nozzle flow conditions that easily place the flow into the supersonic regime. In Fig. 4, the Mach number through the orifice and the H_2S conversion at a 1,000-W power level are plotted for subatmospheric operation at 20 torr pressure. The Mach number was corrected by assuming a 0.33 orifice discharge coefficient. This work suggests that there is an optimal conversion point near sonic conditions.

Conversion Efficiency and Power Levels

Determining H_2S conversion efficiency as a function of input power level is one of the objectives of the experimental program and is important for the optimization of process recycle conditions. The non-normalized results for the analysis of the H_2S dissociation at two different energy levels appear in Table 1. For a 35-mm quartz reactor, the orifice size used in these experiments was 3 mm, with a gas flow rate of 0.75 standard L/min, and the plasma pressure was 20 torr.

Product hydrogen produced during the low-power run at 470 W shows an H_2S conversion efficiency that is 53.6% higher than for the 1,000-W case. This illustrates the motivation for operating the system at lower power with recycle.

It should be noted that the feed gas (a commercial grade of H_2S) contains traces of light hydrocarbons, which are not readily quantified during analysis. These light hydrocarbons are thought to

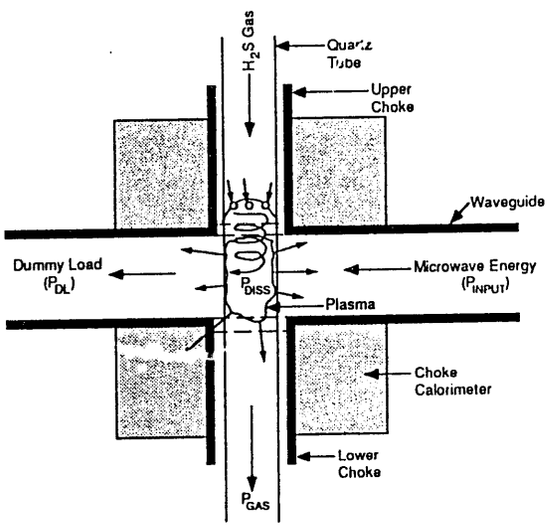

FIGURE 3 Schematic Diagram of Microwave-Induced-Plasma Experimental Apparatus

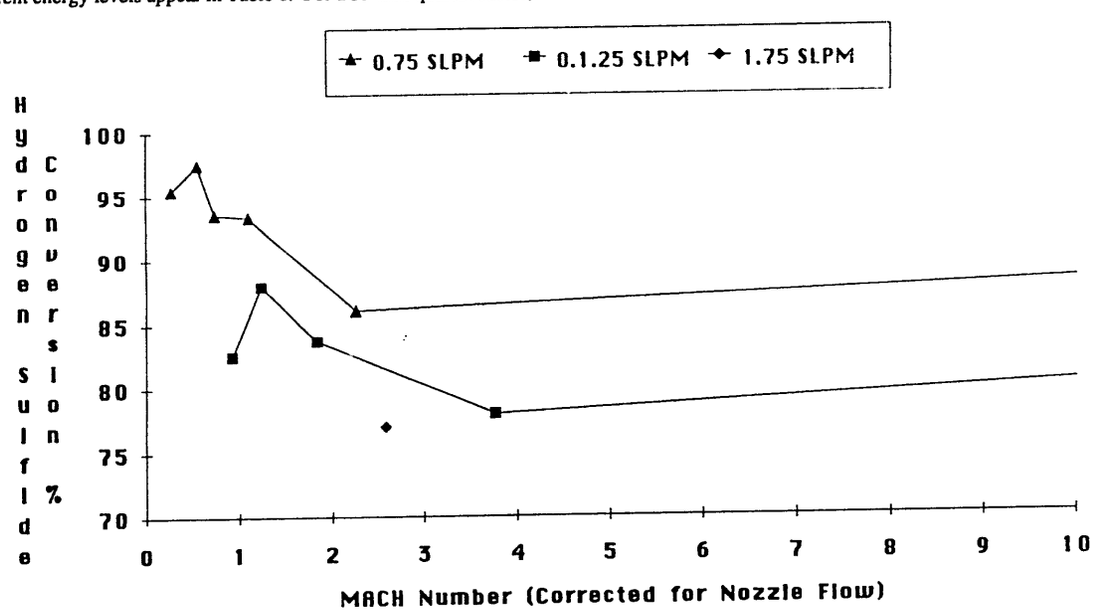

FIGURE 4 Sonic Flow Conditions and H_2S Conversion (correcting for nozzle effects shows that best conversion occurs close to sonic flow rates)

Table 1 H_2S Conversion as a Function of Power Level

Item	Feed	Product at 1,000 W	Product at 470 W
Component (mol %)			
H_2	0.01	95.1	68.6
H_2O	0.90	0.07	0.10
N_2	0.4	0.43	0.55
O_2	ND[a]	ND	ND
H_2S	98.5	3.5	29.8
Ar	0.068	0.056	0.012
CO_2	0.043	0.074	0.068
COS	0.015	0.0007	0.0043
SO_2	0.04	0.019	0.18
CS_2	0.004	0.59	0.69
Conversion (g·mol/h·W)	NA[b]	1.90×10^{-3}	2.90×10^{-3}

[a]ND = not detected.

[b]NA = not applicable.

be the source of carbon for the COS and CS_2 that appear in the product analysis.

Residence Times

A preheater tape around the gas-feed line was installed to maintain feed-gas temperatures between the ambient value and 400°C. Experimental results from preheating the feed gas (see Fig. 5) were matched against a control experiment, in which there was no preheating of the gas but the residence time was matched by decreasing the molar flow rate. These experiments clearly showed that it is residence time, and not preheating, that affects H_2S conversion.

CONCLUSIONS

The following conclusions may be drawn from the experimental program in H_2S conversion by a cold, nonequilibrium plasma:

1. A swirl-design reactor operating at near sonic velocities not only provides for an optimal conversion rate at a given flow, but it assists in de-entraining sulfur and keeping the reactor tube at sustainable temperatures.
2. At a set feed rate, higher conversion efficiencies at lower-power operation suggest that an optimal commercial design will include recycle.
3. At a set power level, residence time controls the conversion efficiency. The inlet temperature of the gas has a negligible effect.

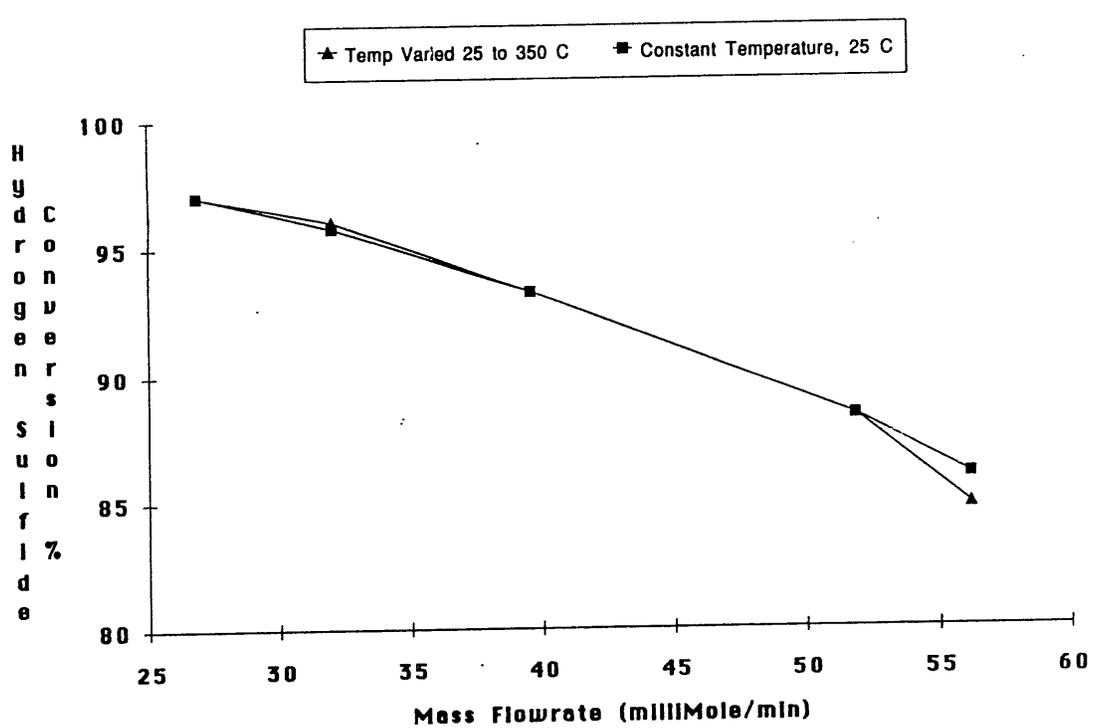

FIGURE 5 H_2S Conversion vs. Residence Time for the Feed Gas

ACKNOWLEDGMENTS

The research described in this paper is sponsored by the U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, Office of Industrial Technologies under contract W-31-109-Eng-38. The authors wish to acknowledge and thank Bruce Cranford (DOE) for his support and guidance of this research. The corporations and research institutes that are members of the Industrial Working Group are also acknowledged; we especially wish to thank Gas Research Institute; Electric Power Research Institute; Amoco Oil Company; UOP, Inc.; Varian Associates; and Wavemat, Inc.

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