MECHANISM AND KINETICS OF H_2S-CO_2 MIXTURE DISSOCIATION IN PLASMA OF A MICROWAVE DISCHARGE*

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Several experimental and theoretical investigations of plasma-chemical H_2S dissociation have addressed the effects of different gas compositions and various types of discharges (such as microwave [1, 2], radio-frequency [3, 4], arc, and glidarc [5] discharges). There are two primary reasons for these investigations: (1) the plasma-chemical process recovers both hydrogen (a valuable chemical reagent) and sulfur from H_2S (as in the conventional Claus process), and (2) plasmas can be used for selectively decomposing H_2S in air and other exhaust gases for environmental-control purposes. These studies have shown that, in plasmas with strong centrifugal force fields, H_2S can be dissociated with high specific rates and low specific energies of dissociation (0.8–1.0 eV/molecule) [1, 3, 6]. Furthermore, acid gases from both natural deposits and those produced in industrial processes often contain significant amounts of CO_2 in addition to H_2S. Unfortunately, CO_2 can have substantial, negative impacts on H_2S dissociation. In particular, CO_2 can significantly increase the process energy consumption and affect by-product composition. However, until this study, the influence of CO_2 on the plasma-chemical dissociation of H_2S has not been studied in detail. This study presents the results of a theoretical analysis of an experimental determination of the CO_2 effects over a wide range of CO_2 concentrations. This analysis identified the primary chemical reaction mechanism and the kinetics for the plasma-chemical dissociation of H_2S, including the generation of two undesirable by-products, SO_2 and COS.

EXPERIMENTS WITH HIGH CO_2 CONCENTRATIONS

The experiments analyzed here were jointly sponsored by the Gas Research Institute and the U.S. Department of Energy in order to determine the technical feasibility of operating a plasma-chemical waste-treatment process with acid gas compositions typical of more recent U.S. natural gas discoveries containing substantial amounts of CO_2. Previously, experiments for typical refinery acid gases (CO_2 concentrations of 0.0–16.1%) showed that CO_2 presented no technical barriers to the operation of a plasma-chemical process for converting H_2S into H_2 and S [7]. Therefore, these follow-up experiments studied the effects of CO_2 at much higher concentrations (30.0 to 65.0%) on the conversion of H_2S and its product distribution [6].

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EXPERIMENTAL APPARATUS

The apparatus used in these experiments consisted of five primary subsystems (shown in Fig. 1). The feed system used mass-flow controllers to meter H_2S, CO_2, and a "pipeline" natural gas from gas cylinders into a heated manifold. Water was metered into the feed system from a burette and vaporized in the manifold. The microwave system included a continuously variable, 2.2-kW magnetron (2.45 GHz); a directional coupler to measure forward and reverse power; and a resonant-cavity applicator, which represents a change from the original configuration [7].

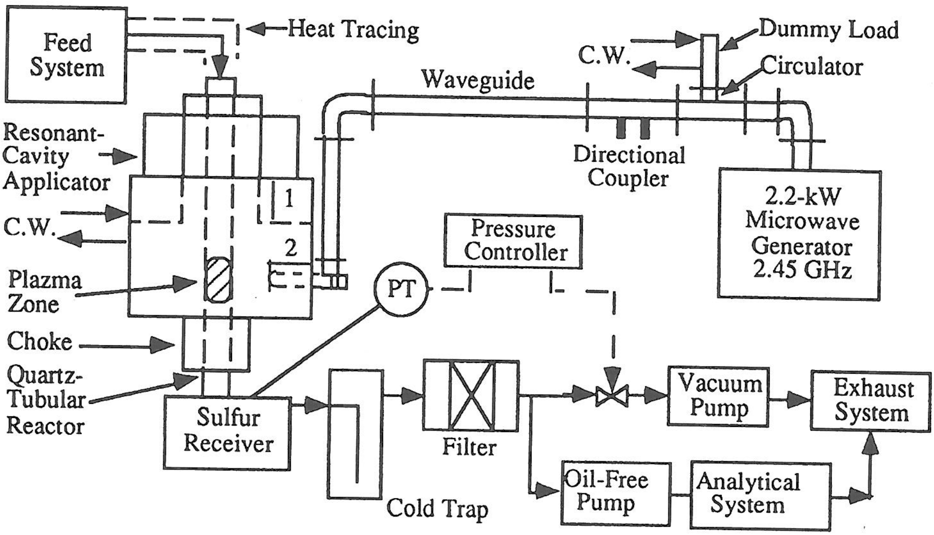

Figure 1. Schematic of Experimental Apparatus

The gas feed was injected tangentially, at high velocity, into a quartz-tubular reactor to produce the desired centrifugal force field [8]. This reactor extended through the applicator to the downstream sample-handling and analytical systems. Most of the sulfur was collected in the sulfur receiver, and the gas stream was then chilled to -10°C to remove additional sulfur. The cooled gases then passed through the primary vacuum pump to the exhaust system or were compressed into the analytical system. In these experiments, gas samples were collected and conversions and production rates were calculated from the results of off-line, mass-spectrographic analyses of both the feed and product gas samples.

These statistically designed experiments studied the effects of three variables – CO_2 (30–65%), H_2O (0–7%), and "pipeline" natural gas (0.0–0.2%) – to represent the typical hydrocarbons present in the industry's acid gases. In each experiment, H_2S was the balance gas, the total gas flow rate was 6.0 standard liters per minute, and the reactor operating pressure was 50 torr. The forward microwave power was 1.0 kW, and the net energy to the plasma ranged from 0.71 to 0.78 kW. Since the cold trap removed most of the water before the gas analyses, the results reported here were calculated by adding the theoretical amount of water to the reported results and then normalizing the resulting compositions to 100% [6].

These experiments showed that H_2S conversion was directly proportional to the CO_2 concentration, and this was the only variable with a significant effect. However, the high CO_2 concentrations had a serious negative impact on the H_2 yield by partly converting it to H_2O. Although the mechanism for the H_2 loss was not determined, clearly the CO_2 content in the feed must be kept low to maximize H_2 production.

THEORETICAL KINETIC MODEL OF H_2S-CO_2 DISSOCIATION

Plasma-chemical reactions are influenced by a number of processes – the energy transfer from electrons to molecules at the plasma boundary layer, the rates of chemical reactions, and the mass transport of reactants into the reaction zone and products from it (assumed to be convection, diffusion, and drift in the zero-dimensional model used here). Furthermore, only the thermal effect of the plasma was calculated, since H_2S dissociation requires a relatively low temperature and H_2S has a fast vibrational-translational relaxation rate. The centrifugal force field rapidly ejects heavy sulfur molecules and clusters into the colder, rotating gas flow around the plasma and is the main nonequilibrium effect for H_2S dissociation. This cooling decreases the rate of the reverse reaction and results in a product composition typical of a reaction at a much higher temperature than the observed gas-exit temperature. Therefore, the observed H_2S conversion is much greater than expected, and the latent heat load in the reaction zone is much smaller than expected. The time dependence of temperature in the reaction zone was considered as known.

By considering the high value of the specific energy input in these experiments, we have used a uniform model for the process wherein gas is rapidly heated in the reaction zone to its temperature (T_r), dissociation occurs, and chemical equilibrium is established before the products are quenched as they exit the reaction zone. This model can be represented by a set of stiff ordinary differential equations that describe the changes of all component concentrations during the heating, reaction, and quenching phases of the overall plasma-chemical process:

$$\frac{dY_i}{dt} = \frac{W_i}{\rho}, \qquad i = 1, .. n \qquad \text{chemical species}$$
$$P = RT\sum \frac{Y_i}{\mu_i} = const \qquad (1)$$
$$T = f(t)$$

Here, Y_i , X_i , and μ_i are the mass fraction, the mole fraction, and the molecular weight of the i^{th} component, respectively; ρ , T, and P are the gas phase density, temperature, and pressure, respectively; $W_i = \mu_i \sum (\vartheta''_{i,k} - \vartheta'_{i,k}) k_k \prod \left(\frac{X_j}{R} \frac{P}{T} \right)^{\vartheta}_{j,k}$ is the source members conditioned by variations of the i^{th} components due to chemical reactions in unit time; $\vartheta''_{i,k}, \vartheta'_{i,k}$ are the stoichiometric coefficients; and k_k are the chemical reaction rate constants. The appropriate chemical reactions and rate coefficients for H_2S-CO_2 dissociation were used in this analysis [9], and the heating and cooling rates and the reaction temperature were taken as parameters to be fitted to the experimental results.

Figure 2 shows the rapid changes in concentration for the principal species when a 50/50 mixture of H_2S and CO_2 is heated to 2500 K with a specific energy input of 1.5 eV/molecule; chemical equilibrium is established after 2×10^{-4} s. These concentration profiles show that the plasma-chemical process occurs in two stages. In the first stage, H_2S dissociates, and in the second, CO_2 decomposes. Sensitivity analyses have shown that the main reactions in the first stage are as follows:

$$H_2S + M \longrightarrow H + HS + M$$
$$H + H_2S \longrightarrow H_2 + HS \qquad (2)$$
$$HS + HS \longrightarrow H_2 + S_2$$

During the initial stage, CO_2 is essentially inert, but in the second stage, the "water-gas-shift" reverse reaction ($H_2 + CO_2 \longrightarrow CO + H_2O$) converts CO_2 into CO while consuming H_2. During this stage, however, the amount of (H_2-CO) changes very

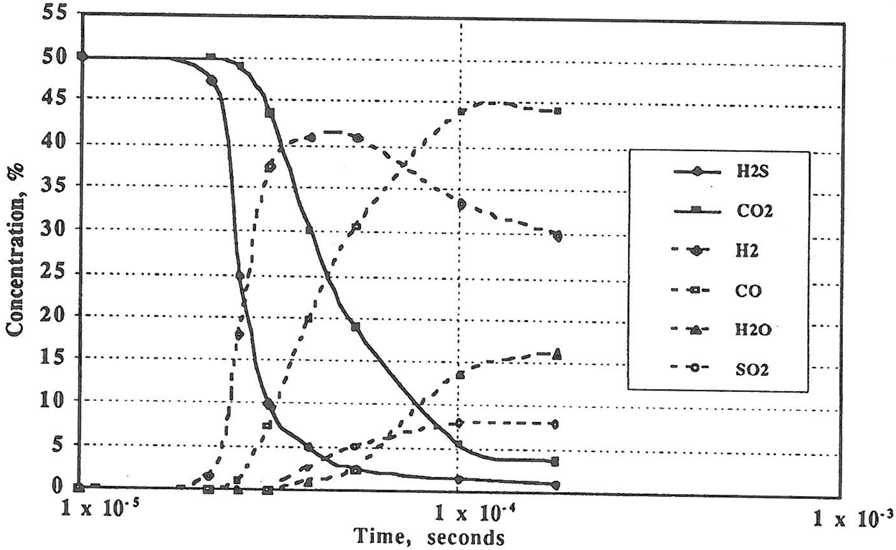

Figure 2. Kinetics of H_2S-CO_2 Dissociation

little compared with the first stage because the controlling reactions in the first stage have a significantly higher effective activation energy than those in the second. In addition, during the second stage, SO_2 and CO are co-produced via:

$$CO_2 + S \longrightarrow CO + SO$$
$$CO_2 + SO \longrightarrow CO + SO_2 \qquad (3)$$
$$SO + SO \longrightarrow SO_2 + S$$

Figure 2 also shows that the amount of (H_2-CO) depends on the gas residence time in the discharge. Therefore, by knowing the gas temperature in the reaction zone, one can determine the gas residence time in the discharge and characterize the process.

The equations for the model (1) were integrated for quenching rates (V) varying from 10^2 to 10^7 K/s and for E_v varying from 0.5 to 2.5 eV/molecule to determine their best values for fitting the experimental data. This analysis showed that as E_v increased, V had to be greater than 10^6 K/s to maintain the (H_2-CO) product content. Otherwise, the water-gas-shift reaction converts CO back into H_2. At the highest values of V, the (H_2-CO) content of the gas leaving the plasma reaction zone can be preserved. However, this led to higher SO_2 yields because more SO_2 is produced at the higher values of E_v, yet there is less opportunity for its reconversion reactions,

$$SO_2 + S \longrightarrow SO + SO$$
$$SO + CO \longrightarrow CO_2 + S, \qquad (4)$$

to destroy the SO_2 produced in the plasma zone. Thus, it should be possible to select a V that would maintain (H_2-CO) production and minimize SO_2 yield.

Discussion of Results

The experimental results were best described by the zero-dimensional model for E_v between 0.9 and 1.1 eV/molecule and V between 5×10^4 and 1×10^3 K/s. Both the experimental results and the analysis show that H_2S conversion decreases as H_2S concentration increases (see Fig. 3), because CO_2 removes H_2 in the second stage and, thereby, indirectly contributes to the dissociation of H_2S. H_2S conversion trends from higher to lower values of E_v as its concentration increases, because the plasma loses energy to the reactor (the "Non-Adiabatic Case") – which fits the experimental results quite well.

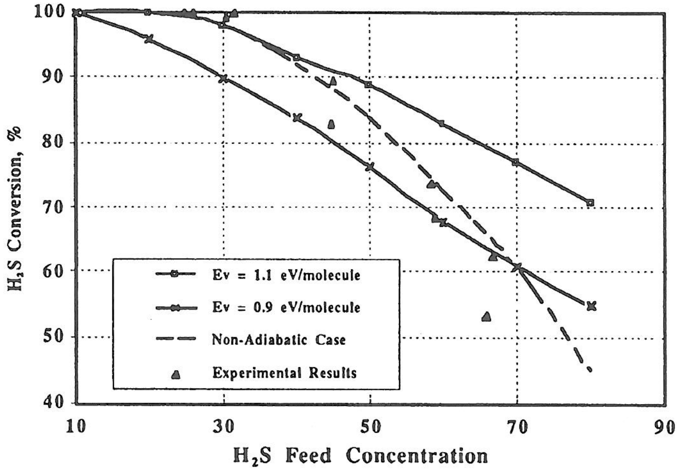

Figure 3. Comparison for H_2S Conversion

Both results also show good agreement for the H_2 yield decreasing as the CO_2 concentration increases (see Fig. 4) – another aspect of the reverse shift reaction in the post-discharge zone. Furthermore, H_2 yield could be increased by quenching with a higher rate to take advantage of the non-equilibrium regime of the plasma process and then quenching more slowly to allow CO to shift back to H_2. This is also consistent with recent experimental results [10].

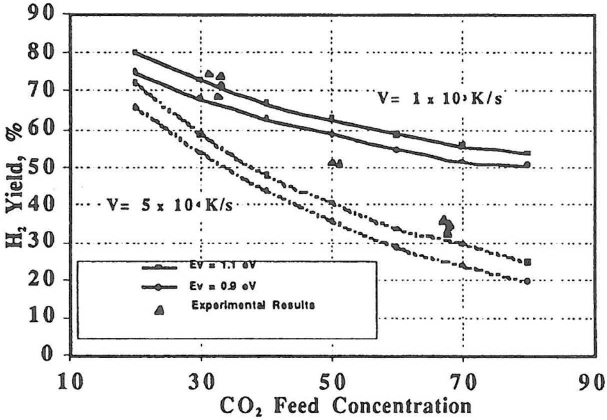

Figure 4. Comparison for H_2 Yields

The production of minor by-products (such as SO_2 and COS) was also a concern of this study. The observed COS production (see Fig. 5) agreed very closely with the predicted values and with the curve's shape. However, for SO_2, the experimental values were significantly lower than the theoretical results. This suggests that the gas handling procedure was removing SO_2 from the samples but not COS.

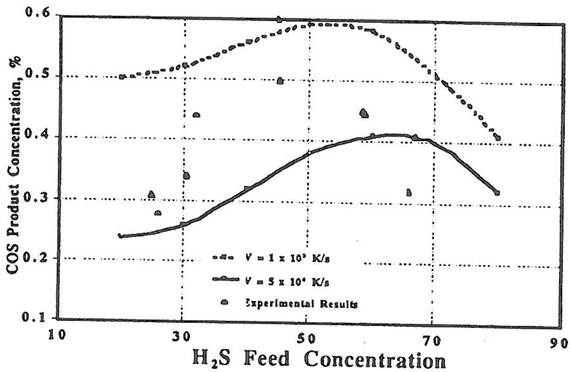

Figure 5. Comparison for COS Production

CONCLUSIONS

These results confirm that the dissociation of H_2S-CO_2 mixtures is a two-stage process: the H_2S is dissociated, plasma-chemically, in the first stage and the CO_2 reacts with H_2 to convert it to H_2O and co-produce CO in the second. The overall effect of the CO_2 was to increase the H_2S conversion and decrease its H_2 yield.

The influence of quenching rate on the process showed possible strategies for maximizing H_2 yield while minimizing SO_2 production, an undesirable by-product. Additionally, the correlation between the product H_2 and CO concentrations may be used to determine the gas residence time in the plasma reaction zone.

This model provides useful information about the production of minor by-products. In these experiments, COS was correctly reported by the off-line analytical procedure. However, an on-line procedure will be needed to accurately monitor condensable or soluble species like SO_2.

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