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Project Title:

Production of Elemental Sulfur and Methane from H₂S and CO₂
Derived from a Coal Desulfurization Process

by

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ABSTRACT

During the seventh quarter of the project, further simulations were performed to investigate the feasibility of producing elemental sulfur and methane from hydrogen sulfide and carbon dioxide by using the overall reaction of H₂S and CO₂ based on the following stoichiometry:

The results indicate that the number of stages needed to reach the final system equilibrium for recovering sulfur can be greatly affected by the factor of sulfur vapor pressure. Sulfur vapor pressure versus the system temperature follows a logarithmic relationship. The H₂S conversion and sulfur yield do not increase proportionally with the number of stages. The simulation indicates that a multiple stage system is more effective at a high reaction temperature range in raising the H₂S conversion and sulfur yield.

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Work Performed

The main scheme of the present process is that a rich gas stream of H_2S and CO_2 passes through a high temperature catalyst bed to form elemental sulfur, methane and water vapor. The overall reaction is as following^[1]:

A simulation for the above process is based on the removal of sulfur from the system by condensation when the reaction reaches an equilibrium. The residues are fed into the next stage. A new equilibrium reaches and sulfur is removed again. This process continues until the efficiency of sulfur removal from the reaction system becomes very low. Thermodynamically, the limitation is controlled by the sulfur vapor pressure of the condensed phase. The final product distributions at various reaction temperatures are shown in Table 1. Table 2 shows the product distribution at 25°C. The results in Table 1 and 2 strongly support the concept of continuous removal of sulfur from the system and clearly demonstrate the feasibility of the stoichiometric relations in Reaction (1).

The purpose of the simulation is to investigate the effects of major system variables on the equilibrium composition of the species in the system and to find out the optimum reaction temperature and the number of theoretical stages based on the vapor pressure of condensed sulfur.

Sulfur vapor pressure affects the condensation efficiency of sulfur which defines a limit for extraction of sulfur from the reaction system. The temperature of the condensed phase lies within the sulfur melting point at 112.8°C and the boiling point at 444.6°C^[2] at 1 atm. The

relationship of sulfur vapor pressure with temperature will determine the optimum value of reaction temperature in the first and second zones. It will also determine the experimental decision on how many stages are really needed to reach a practical equilibrium limit in a bench scale experiment. In this report, the theoretical effects of the reaction temperature and the number of stages on the H_2S conversion and sulfur yield are discussed. Further investigation will be performed along with the relevant bench scale experiments.

Figure 1 illustrates the relationship of sulfur vapor pressure with temperature at 1 atm from three independent sources^[2-4]. Due to the different research interests of the investigators, the sulfur vapor pressure data in these sources do not cover the same temperature range. However, they are consistent with each other in their tendencies and overlap areas within the temperature range of our interest and are accurate enough for the present purpose. Sulfur vapor pressure increases exponentially with the temperature. This feature makes the operation temperature of condensed sulfur very sensitive to the sulfur removal efficiency. High sulfur vapor pressure in the system will inhibit sulfur condensation or adsorption although high temperature will favor the main reaction to decompose H_2S and save the total cost of system energy usage. Therefore, there is a set of optimum values for each system configuration. Simulation will determine the optimum operating conditions.

In the previous simulation work, the effect of sulfur vapor pressure was not considered. The highest number of stages up to 10,000 was used in order to find the final extraction equilibrium point. When the number of stages increased over 1,000, the calculation reached beyond the significant figures of the computer. All the results of equilibrium

calculations in the last report are based on the first 1,000 stages.

During this period of work, the effect of sulfur vapor pressure is taken into account and the sulfur sink temperature is arbitrarily set as 150°C. This temperature is not yet an optimum temperature but it will help us to demonstrate the change of H₂S conversion and sulfur yield versus temperature and the number of stages under the inference of sulfur vapor pressure. From Figure 1, the sulfur vapor pressure at 150°C is 2×10^{-4} atm. After repeating the calculations with this sulfur pressure, the new result shows that the maximum effective number of stages is dropped to 220, at which point there will be no further sulfur extracted from the system.

Figure 2 shows the effects of reaction temperature (from 450 to 1100°C) and the number of theoretical stages (from 1 to 220 stages) on the equilibrium conversion of H₂S. In general, a high conversion is obtained at high temperature and large number of stages. The increase of temperature has a greater positive effect on the conversion due to the endothermic nature of H₂S decomposition reaction. When N equals to 1, the curve stands for a single stage or once-flow reactor. As the number of N increases, H₂S conversion does not increase proportionally with N values. If the reaction temperature is fixed, the relationship of the conversion versus the number of stages N can be approximately summarized by the equation below:

$$\text{Conversion of H}_2\text{S} = \alpha(T) + \beta(T) \cdot \text{LOG}_2(N) \quad (650 < T < 1000^\circ\text{C}) \quad (2)$$

where $\alpha(T)$ and $\beta(T)$ are the functions of reaction temperature. It is true that the higher the number of N, the higher the H₂S conversion. However, it also means that the larger the

dimension of the reaction system. Another feature illustrated in Figure 2 is that a multiple stage system has more positive effect on the H_2S conversion at the higher reaction temperatures range than at the low ones.

Figure 3 shows the effects of reaction temperature and the number of theoretical stages on the equilibrium yield of sulfur. The conclusion from Figure 3 is similar to that from Figure 2. The reason is that sulfur produced at each theoretical stage is almost completely recovered by the system. There is very little amount of by-products formed, such as COS, CS_2 and SO_2 . Therefore, almost all the sulfur decomposed from H_2S is recovered as elemental sulfur. For the yield of sulfur, an equation similar to equation (2) can be deduced:

$$\text{Yield of Sulfur} = \eta(T) + \lambda(T) \cdot \text{LOG}_2(N) \quad (650 < T < 1000^\circ\text{C}) \quad (3)$$

where $\eta(T)$ and $\lambda(T)$ are the functions of reaction temperature.

Actual number of stages and the temperature of reaction and sulfur sink will be chosen after detailed laboratory works. The key is to find out an effective mechanical configuration of the sulfur condensation system.

Future Work

A bench-scale experiment will be carried out to investigate the relationship between the system reaction temperature and sulfur sink temperature, the effects of both temperatures on the sulfur recovery efficiency. Another experiment will also be preformed to find out the ability of different kinds of materials on sulfur vapor condensation and adsorption.

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Table 1. Equilibrium Mole Fraction of the Related Species at the Final Stage before Cooling down the Reaction System to 25°C

Reaction Temperature (C)	CH ₄	CO	COS	CO ₂	CS ₂	H ₂	H ₂ O	H ₂ S	SO ₂	S ₂
450	0.0094	0.0142	0.0130	0.1710	0.0002	0.0301	0.0473	0.7149	0.0000	0.0000
500	0.0101	0.0294	0.0117	0.1614	0.0002	0.0586	0.0626	0.6661	0.0000	0.0000
550	0.0084	0.0513	0.0102	0.1468	0.0002	0.1000	0.0789	0.6042	0.0000	0.0000
600	0.0057	0.0760	0.0086	0.1269	0.0001	0.1532	0.0956	0.5339	0.0000	0.0000
650	0.0035	0.1024	0.0071	0.1038	0.0001	0.2138	0.1056	0.4635	0.0000	0.0000
700	0.0035	0.1137	0.0034	0.0633	0.0000	0.3574	0.1229	0.3357	0.0000	0.0000
750	0.0017	0.1294	0.0023	0.0515	0.0000	0.4382	0.1329	0.2439	0.0000	0.0000
800	0.0008	0.1415	0.0015	0.0436	0.0000	0.5028	0.1423	0.1675	0.0000	0.0000
850	0.0003	0.1506	0.0010	0.0386	0.0000	0.5419	0.1511	0.1164	0.0000	0.0000
900	0.0002	0.1576	0.0003	0.0318	0.0000	0.6188	0.1579	0.0334	0.0000	0.0000
950	0.0001	0.1632	0.0002	0.0294	0.0000	0.6224	0.1629	0.0218	0.0000	0.0000
1000	0.0000	0.1674	0.0001	0.0271	0.0000	0.6239	0.1665	0.0148	0.0000	0.0000
1050	0.0000	0.1707	0.0001	0.0253	0.0000	0.6233	0.1701	0.0105	0.0000	0.0000
1100	0.0000	0.1732	0.0000	0.0234	0.0000	0.6262	0.1734	0.0037	0.0000	0.0000

Table 2. Equilibrium Mole Fraction of the Related Species at the Final Stage after Cooling down the Reaction System to 25°C

Reaction Temperature (C)	CH4	CO	COS	CO2	CS2	H2	H2O	H2S	SO2	S2
450	0.0210	0.0000	0.0000	0.1915	0.0000	0.0000	0.0429	0.7447	0.0000	0.0000
500	0.0336	0.0000	0.0000	0.1890	0.0000	0.0000	0.0681	0.7093	0.0000	0.0000
550	0.0500	0.0000	0.0000	0.1845	0.0000	0.0000	0.1004	0.6650	0.0000	0.0000
600	0.0712	0.0000	0.0000	0.1743	0.0000	0.0000	0.1416	0.6130	0.0000	0.0000
650	0.0981	0.0000	0.0000	0.1597	0.0000	0.0000	0.1828	0.5594	0.0000	0.0000
700	0.1586	0.0000	0.0000	0.0820	0.0000	0.0000	0.3156	0.4437	0.0000	0.0000
750	0.2006	0.0000	0.0000	0.0577	0.0000	0.0000	0.3979	0.3438	0.0000	0.0000
800	0.2388	0.0000	0.0000	0.0377	0.0000	0.0000	0.4742	0.2494	0.0000	0.0000
850	0.2653	0.0000	0.0000	0.0262	0.0000	0.0000	0.5288	0.1797	0.0000	0.0000
900	0.3058	0.0000	0.0000	0.0000	0.0000	0.0287	0.6112	0.0543	0.0000	0.0000
950	0.3139	0.0000	0.0000	0.0000	0.0000	0.0235	0.6268	0.0358	0.0000	0.0000
1000	0.3188	0.0000	0.0000	0.0000	0.0000	0.0207	0.6359	0.0245	0.0000	0.0000
1050	0.3225	0.0000	0.0000	0.0000	0.0000	0.0162	0.6439	0.0174	0.0000	0.0000
1100	0.3242	0.0000	0.0000	0.0000	0.0000	0.0210	0.6486	0.0062	0.0000	0.0000

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Figure 1. Sulfur Vapor Pressure (atm) v.s. Temperature (°C)

Figure 2. Effects of Reaction Temperature and Number of Simulated Stages on the Conversion of H_2S with Sulfur Sink Temperature at 150°C

Figure 3. Effects of Reaction Temperature and Number of Simulated Stages on the Yield of Sulfur with Sulfur Sink Temperature at 150°C