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Project Title:

Production of Elemental Sulfur and Methane from H_2S and CO_2
Derived from a Coal Desulfurization Process

by

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ABSTRACT

During the tenth quarter of the project, bench scale experiments were performed to investigate the adsorption ability of different kinds of materials within sulfur vapor environment. Four kinds of adsorbents have been tested. The experimental results indicated that activated carbon was the best of four adsorbents tested. In addition to the baseline tests, several designs of activated carbon feed system have been tested. Under an inert environment, bench scale experiments were performed to investigate the characteristics and efficiency of activated carbon passing through the Co-Mo-Alumina catalyst bed. The results showed that activated carbon powder could easily be transported through the catalytic bed. The adsorption process may be applicable to promote conversion of H_2S in the H_2S and CO_2 reaction system.

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Work Performed

Adsorption of Sulfur Vapor on Selected Materials

The investigation was performed on two experimental systems. The first experimental system for adsorption of sulfur vapor on selected materials is schematically shown in Figure 1. Elemental sulfur is loaded in a Pyrex glass tube which is 1 inch in I.D. and 10 inches in length. A total amount of sulfur is approximately 30 grams. Oxygen free nitrogen is used to purge the inside glass tube to maintain an inert environment. The flowrate is controlled by a rotameter. The adsorbents are loaded into a small basket made of stainless steel screen. The amount of adsorbent used in the each run is around 400-500 mg. The Pyrex glass tube, containing the adsorbent basket and sulfur, is heated by a tubular furnace to reach the expected experimental temperatures. Two K-type thermocouples are used in the system. One measures the temperature of the adsorbent basket, the other is connected to the tubular furnace which monitors the upper temperature limit.

The adsorbents were obtained from commercial sources. The adsorbents tested were Al_2O_3 (two kinds of shape), CoO-MoO_3 -Alumina and activated carbon. Oxygen free nitrogen was purchased from Wright Brothers Inc., a distributor for the Matheson Gas Products. Sublimed sulfur powder was obtained from Fisher Scientific Inc. Cobalt-molybdenum (CoO-MoO_3 -Alumina, Crosfield 465, 1/20" extruded) was obtained from Crosfield Catalysts (4099 West 71st Street, Chicago, Illinois 60629). The aluminum oxide was purchased from Engelhard Corporation (120 Pine Street, Elyria, Ohio 44035). The activated carbon (mesh 12 x 40) was obtained from Autochem North America (Mineral Products Division, Three

Parkway, Philadelphia, PA 19102).

The second experimental system for investigating adsorption of sulfur vapor is schematically shown in Figure 2. The system consists of two sulfur vaporizers, three temperature controllers and an adsorption bed. The vaporizers are made of stainless steel with the dimension of 2.5 inches in O.D. and 7 inches in height. The connection tubings are all made of 1/4 inch stainless steel tubes. The temperature controllers (Omega, CN 9000A), K-type thermocouples (O.D. 1/16") were obtained from the Omega Technologies Company (One Omega Drive, Box 4047, Stamford, Connecticut 06907). And flexible electric heating tapes (AWH-051-060DSP) were purchased from Amptek Company (P.O. Box 1381, Stafford, Texas 77497). During the experiment, the temperature in the first sulfur vaporizer was set always higher than that in the second one in order to generate completely saturated sulfur vapor. The saturated sulfur vapor pressure produced by the system was estimated based on the relationship between sulfur vapor pressure and temperature diagram shown in Figure 3.

Experimental Condition and Procedures

Figure 3 shows 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 sufficient for the present purpose. The figure shows

that sulfur vapor pressure increases exponentially with the temperature. This feature makes the operation temperature of condensed sulfur very sensitive to the efficiency of sulfur removal from vapor phase. In order to experimentally investigate the effect of the different kinds of materials on sulfur vapor condensation and adsorption, the following experimental procedure was performed during the tests.

- (1) Load sulfur into the Pyrex glass tube.
- (2) Purge the tube with oxygen free nitrogen to make an inert environment.
- (3) Raise the furnace temperature to 150°C. This step was necessary to minimize the initial condensation of sulfur vapor on adsorbent surface. It might occur when there is a temperature difference between the hot glass tube and adsorbent basket containing the adsorbents which were dried and kept in the oven at 150°C.
- (4) Load the adsorbent of 400-500 mg on to a small basket made of stainless steel screen. Insert the basket into the tube.
- (5) Then raise the furnace temperature to a desired experimental value.
- (6) Stop purging of oxygen free N₂ when the desired temperature is reached.
- (7) After a predetermined duration of time, take out the basket and measure the weight change of the adsorbent.

Results and Discussion

The results of the experiment are tabulated in Tables 1 and 2. Four different types of adsorbents were tested during the investigation. They were Al₂O₃ (with two different shapes),

CoO-MoO₃-Alumina and activated carbon.

Table 1. Amount of Sulfur Adsorbed (wt % of adsorbent) at 290 ± 5°C

Temp (hours)	Activated Carbon	Co-Mo-Al ₂ O ₃ (extruded)	Al ₂ O ₃ (sphere type)	Al ₂ O ₃ (cylinder type)
0.17	4.3	-	-	-
0.5	20.1	0.0	0.0	2.6
1.0	43.9	0.0	0.0	2.8
2.0	47.2	3.3	0.0	6.3
3.0	52.9	5.4	12.3	5.0
5.0	70.8	2.6	11.7	6.1
5.0	-	3.2	-	-
8.0	74.2	28.9	12.5	8.7

Table 2. Amount of Sulfur Adsorbed (wt % of adsorbents) at 220 ± 5°C

Temp (hours)	Activated Carbon
5.0	8.9
8.0	23.6

The experimental results are also plotted in Figure 4. It indicates that activated carbon was the best adsorbents among the four adsorbents tested. The amount of sulfur adsorbed on the activated carbon increased with the experimental time and did not reach an equilibrium value within the duration of experiments. Capillary condensation occurring in the pores may be responsible for this behavior. In the case of Al₂O₃ (both sphere and cylinder types),

adsorption of sulfur almost remained constant for 3 hours. At higher temperature above 420°C, oxidation of activated carbon was observed because of leakage of a little amount of oxygen in the tube even though the purge step was performed prior to the experiment. For the equal period of experiment, the amount of sulfur adsorbed on activated carbon at lower temperature (e.g. 220°C) was smaller than that of at high temperature (e.g. 290°C). It was due to the fact that the lower the system temperature, the less vaporized sulfur ^[2-4] was available for adsorption (low partial pressure of sulfur). The results prove that this adsorption process is capable to remove sulfur vapor from gas mixtures, such as H₂S and CO₂ reaction system, and promote the conversion of H₂S.

The first experimental system shown in Figure 1 was not equipped to control the sulfur vapor mole fraction quantitatively with respect to the experimental temperature. It did not provide a perfect inert (oxygen free) circumstance for the investigation either. Therefore, the second experimental system shown in Figure 2 was built and some improvements on the experiment system were made for the further investigations. The experimental results proved that the second system for sulfur vapor adsorption could be operated at higher experimental temperature to investigate the condensation and adsorption effect of sulfur vapor on activated carbon without oxidizing it. The second system could control the sulfur vapor pressure effectively through its two sulfur vapor generators and extend the range of experimental temperature. Using the second system, it was expected to find at what temperature sulfur vapor could be effectively condensed or adsorbed by activated carbon. However, due to the fact that the stainless tubings which linked the sulfur tanks and the adsorption bed were

frequently blocked by condensing sulfur, the experiment could not run as smoothly as originally planned. Another fact was that the corrosive effect of sulfur vapor on adsorption bed at high temperatures caused difficulty in material balance of activated carbon samples before and after adsorption, even though the adsorption bed was made of stainless steel. Due to these problems, not much experiment data were generated from the second system.

During the process development phase of investigation, several designs of activated carbon feed system have been tested, which includes a small scale jet pump and a screw feeder. Both feed systems were tested under specific configurations. Selection of the feeder type will depend on the requirements of further process development. Under simulated inert environment, bench scale experiments were performed to investigate the characteristics and efficiency of activated carbon passing through the Co-Mo-Alumina catalyst bed. The experimental results showed that activated carbon powder could easily pass through the catalytic bed.

Future Work

Base on the experimental results of adsorption of sulfur vapor on activated carbon, a new experimental process shown in Figure 5 will be set up and tested in the next two quarters. The process will be a hybrid system of catalysis and adsorption. The detailed system description and design will be discussed in the next quarter by report. In view of the possible sulfur removal through adsorption, the catalytic reaction of H_2S and CO_2 will be carried out in a wider range of temperature to find out the optimum operating condition for the process.

References

- [1] Yang, Ralph T., *Gas Separation by Adsorption Processes*. Butterworth Publishers, Boston (1987).
- [2] Perry, Robert H. and Don Green, *Perry's Chemical Engineers' Handbook*. 6th edition, McGraw Hill Book Company, New York (1984).
- [3] Hultgren, Ralph, Pramod D. Desai, Donald T. Hawkins, Molly Gleiser, Kenneth K. Kelley (University of California, Berkeley) and Donald D. Wagman (U.S. National Bureau of Standards), *Selected Values of the Thermodynamic Properties of the Elements*. American Society for Metals (1973).
- [4] Barin, Ihsan, Ottmar Knacke and Oswald Kubaschewski, *Thermochemical Properties of Inorganic Substances, supplement*, Springer-Verlag Berlin Heidelberg New York (1977).

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Figure 1. Experimental Apparatus for Adsorption of Sulfur

Figure 2. New Experimental Apparatus for Adsorption of Sulfur

Figure 3. Sulfur Vapor Pressure (atm) v.s. Temperature (°C)

Figure 4. The Amount of Sulfur Adsorbed on Various Kind of Adsorbents at 290°C

Figure 5. New Experimental System for Sulfur Recovery

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