Conversion of Organic Sulfur in the Presence of Hydrogen Sulfide

Four samples of catalyst were supplied by the Girdler Corporation, Gas Processes Division, which the manufacturer at first expected would be capable of converting as much as 75 grains of organic sulfur per 100 cu. ft. in the presence of as much as 600 grains of hydrogen sulfide per 100 cu. ft., leaving not more than 0.1 grain of organic sulfur per 100 cu. ft. in the purified gas.

This expectation was based on experiments by the Girdler Corp., wherein over 2,000 grains of sulfur (as carbon disulfide) were reduced to about 2 grains per 100 cu. ft., or better than 99.9 percent conversion. With 75 grains of organic sulfur per 100 cu. ft., 99.9 percent conversion would leave only 0.075 grain per 100 cu. ft. in the purified gas. These catalysts could be operated to serve simultaneously as shift conversion catalysts, under suitable operating conditions.

Girdler's instructions called for first reducing the catalyst at 370° C. followed by sulfiding with hydrogen containing a high concentration of hydrogen sulfide. These provisions were carried out, and the first Morgantown experiment was begun. The results of these experiments are shown in table 6.

In these first experiments, no steam was added to the gas. Instead of a reduction in organic sulfur content, there was actually an increase at 400° C. With no organic sulfur added, but with hydrogen sulfide being added, as much as 17 grains of organic sulfur were synthesized at this temperature.

Lowering the temperature to 260° C. gave about 24 percent conversion. With no organic sulfur added, but with hydrogen sulfide added, some organic sulfur was synthesized, but to a smaller extent than at the higher temperature.

At Girdler's suggestion, 20 mol percent of steam was added. This gave only slight improvement in performance, so the steam was increased to 40 to 50 percent. Results of runs with steam addition are given in table 6. No thiophene was added in these tests, because the catalyst was not claimed to be effective for thiophene conversion and it was desired to first obtain satisfactory conversion with the simple types of organic sulfur.

Hydrogen sulfide inlet concentrations were varied from 0 to 1,000 grains per 100 cu. ft. Inlet organic sulfur concentrations were varied from 18 to 40 grains per 100 cu. ft. Organic sulfur in the outlet gas ranged from 2.0 to 5.0 grains per 100 cu. ft. These data indicate that the organic sulfur in the outlet gas represents an equilibrium value dependent on the concentration of carbon monoxide and hydrogen sulfide. Carbon monoxide appears to have more effect than does the hydrogen sulfide in establishing this equilibrium. The nature of this equilibrium condition is further brought out by the fact that when 100 percent hydrogen was used as carrier gas, containing as high as 720 grains of hydrogen sulfide and 15.9 grains of organic sulfur per 100 cu. ft., the outlet gas contained as little as 0.041 grain of organic sulfur.

TABLE 6. - Results of first experiment

Run No.	Gas used	Catalyst temp., °C.	Sp. vel., hr.-1	Steam content, Mol percent	H_2S in inlet gas, gr./100 cu. ft.	Total org. S in inlet gas, gr. S/100 cu. ft.	Approx. concentration of individual compounds in inlet gas, gr. S/100 cu. ft.			Total org. S in outlet gas, gr. S/100 cu. ft.
							CS_2	C_2H_5SH	C_4H_4S	
1	Syn.	400	700	-	700	16	6	6	4	18.2
	do.	400	700	-	750	15	9	6		17.0
	do.	400	700	-	700	0				17.4
	do.	260	700	-	650	0				3.8
	do.	260	700	-	620	13	4	4	5	9.5
	do.	200	700	-	570	13	4	4	5	12.1
2	do.	400	700	20	600	15	6	3	6	15.0
3	do.	400	400	50	750	19	12	7		4.5
	do.	400	700	50	750	19	12	7		4.5
	do.	400	700	50	800	21	11	10		5.0
	do.	400	700	50	1,000	19	11	8		4.1
	do.	200	200	50	1,000	12	12			6.1
	do.	400	700	50	0	40	40			2.0
	do.	400	700	50	300	40	40			2.0
	do.	400	700	50	10	19	12	7		3.0
	do.	400	700	50	380	25	13	12		2.7
	do.	400	700	50	360	27	13	14		2.8
	H_2	400	700	50	260	16	8	8		.055
	do.	400	700	50	720	16	8	8		.044

The fact that the equilibrium organic sulfur in the treated gas does not depend nearly so much on the organic sulfur-hydrogen sulfide relationship as on the carbon monoxide-hydrogen sulfide-hydrogen relationship accounts for the very high (over 99.9%) conversion obtained in Girdler's earlier work. Thus, in that work, with over 2,000 grains of organic sulfur per 100 cu. ft. in the inlet gas, the equilibrium amount in the treated gas was about the same as in the present work, where the inlet concentration was not over 40 grains per 100 cu. ft.

The work on this catalyst reveals that it does not give enough conversion of organic sulfur to serve as a single treatment for removing organic sulfur from synthesis gas, since such gas must be purified to contain less than 0.1 grain of total sulfur per 100 cu. ft. The Bureau's results were confirmed by later work by the Girdler Corp., which is understood to be making further studies with a view toward improving the catalyst.

The catalyst might have value in synthesis-gas purification as a preliminary step to reduce the organic sulfur concentration from a very high level to a level that could be completely removed by some different secondary treatment, for example, by means of water scrubbing under pressure (following hydrogen sulfide removal) or by means of alkalized iron.

The catalyst might also be of value in purifying fuel gas or city gas, where it would be sufficient merely to reduce the organic sulfur concentration to perhaps 2 grains per 100 cu. ft. In this application, the lower carbon monoxide content in manufcatured city gas would favor better organic sulfur conversion.

The feature of this catalyst is that the hot gas leaving the gasifier could be treated for organic sulfur conversion without removal of hydrogen sulfide, and hence without cooling the gas. Processes that involve removal of hydrogen sulfide, then reheating and hot catalytic conversion of organic sulfur to hydrogen sulfide, followed by cooling to again remove hydrogen sulfide would require one additional cooling step and one additional heating step. With the Girdler catalyst - if performance is adequate for the degree of purification required - no heating of the gas is required and only one cooling step.

The possible application of this catalyst to the purification of gases containing no carbon monoxide - for example, ammonia synthesis gas - is evident.

Cobalt Molybdate Catalyst; Platinized-Alumina Catalyst

Because of references found in the literature, it was believed that cobalt molybdate might prove to be a good catalyst for organic sulfur conversion. A sample of this catalyst, supplied by Harshaw Chemical Co., was therefore investigated. At the same time, a sample of platinized-alumina catalyst, obtained from Baker & Co., Inc., was studied. This latter catalyst in which platinum is supported on activated alumina, was thought to have possibilities because of the known properties of activated alumina and platinum separately to serve as catalysts for organic sulfur conversion.

Neither the cobalt molybdate nor the platinized-alumina catalyst was found to be satisfactory for purification of synthesis gas. Space velocities from 350 to 700 and catalyst temperatures from 400° to 600° C., and hydrogen sulfide concentrations from 0 to 340 grains per 100 cu. ft. were employed. The cobalt molybdate catalyst indicated some value in converting thiophene, but only at temperatures so high as to preclude its use if waste heat is to be utilized. As in the case of the Girdler catalyst, both catalysts showed an equilibrium value for organic sulfur (presumably COS) when no organic sulfur was contained in the inlet gas. This was evidently another case of reaction between carbon monoxide and hydrogen sulfide. Data are summarized in table 7.

Simultaneous Removal of Organic Sulfur and Hydrogen Sulfide (Huff Catalysts)

Because of the promising results obtained by Huff in the work already cited,32/ it was decided to try that method of total sulfur removal under the more favorable conditions possible in the purification of synthesis gas. Because gasification pilot-plant work had already indicated the absence of tar or oil condensates and because it was believed possible to free the gas from dust at elevated temperatures, maintaining such elevated temperatures at a reasonably constant level, it was felt that perhaps much better results might be obtained in applying the method to synthesis gas purification.

Catalyst selection was made on the basis of the best performances obtained in the work cited; the original catalyst as well as modifications and substitutions made during the course of the investigation have been designated as "Huff catalyst," and this designation will be used in this report for catalysts used to absorb organic sulfur and hydrogen sulfide simultaneously, catalyst being regenerated by burning off sulfur with air.