

SULFUR REMOVAL FROM HOT PRODUCER GAS

by

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INTRODUCTION

To obtain clean gas from coal, gasification and gas cleanup must be considered jointly in view of today's clean environment regulations. Much of the coal sulfur appears in the gas, and in addition, solid and tar particulates are present in concentrations that vary with the gasification process and coal composition. All gasification concepts undergoing development include some type of gas cleaning. Conventional practice could be followed using commercial equipment, but this requires gas cooling and scrubbing with liquid solutions. Disposal of liquid and solid wastes is required, and provision for recovering coal tar is necessary.

Low-Btu fuel gas for power generation is receiving serious consideration by the electric utilities because it offers a timely solution to the shortage of low-sulfur fuel. High-sulfur coals can be converted into gas and cleaned of sulfur before being burned for power generation. Commercialization of this practice will make large quantities of high-sulfur coal available for generating electricity. Probably the least complicated system for converting coal into low-Btu fuel gas is pressure gasification using mine-run coal which may have any free-swelling index from low to high and includes lignite.

Gasification in a fixed bed has been widely used commercially for over one hundred years and is still used today. Historically, the fixed-bed gas producer has required a feed of noncaking, lump-sized coal or coke. Recently, the Bureau of Mines at Morgantown, W. Va., has gasified many coals including strongly caking Pittsburgh seam (1),^{1/} high-volatile A bituminous (FSI 8-1/2), and coal 50 percent smaller than 1/4-inch screen size (run-of-mine) (2). These pioneering developments have demonstrated that deep, continuous stirring or agitation of the fuel bed is essential and beneficial to the gasification process. The bed stirring promotes gasification reactions and gas quality by breaking massive coke formations and maintaining permeability of the bed for better contact between gas and fuel. The stirring employed in this work is much more extensive than ever used previously, and it warrants being distinguished by being called the stirred fixed-bed, or simply the stirred bed to distinguish it from the conventional fixed bed.

^{1/} Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

The Morgantown Energy Research Center of the U.S. Bureau of Mines has evaluated many solid sorbents as an acceptor for hydrogen sulfide in hot producer gas. Results of those studies using simulated producer gas at 1,000° to 1,500° F have been reported in earlier papers (3)(4). This paper reports results obtained with a sintered iron oxide sorbent and gas from the stirred-bed producer.

EXPERIMENTAL

A mixture of iron oxide (hematite Fe_2O_3) and fly ash was the best sorbent found among more than thirty-two materials tested. Primary requirements were that the sorbent be readily available and relatively inexpensive, have reasonable sorption capacity and useful life, be easily regenerated for repeated use, and resist fusion or disintegration over the useful temperature range. Fly ash (as received) could be formed into a durable and regenerable sorbent, but its sorption capacity was improved by adding iron oxide, increasing the concentration to 36 percent from 15 percent originally present. Other oxides found in this fly ash but inactive included silica 35 percent, alumina 18 percent, and small percentages of oxides of calcium, magnesium, sodium, potassium, and titanium. Iron oxide concentrations greater than 40 percent were unsatisfactory because the bed fusion temperature was lowered and fusion took place during normal operations.

Pilot quantities of the fly ash-iron oxide sorbent were made by two catalyst manufacturers by mulling and extruding the mixture to form 1/4-inch-diameter cylinders with 1/4- to 3/8-inch lengths, which were then sintered to develop hardness. Mercury porosimeter measurements showed pore volume of one new sorbent was 0.36 cc per gram, but this decreased to 0.13 cc per gram and remained constant after 30 regenerations, as shown in figure 1. Surface area measured by nitrogen absorption ranged from 4.2 to 6.5 square meters per gram.

RESULTS AND DISCUSSION

Two sorption-regeneration cycles were completed, cleaning gas generated by the stirred-bed producer using Upper Freeport coal. Gas composition is given in figure 2. Gas from the producer was transferred to the sorbent bed at system pressure of 120 psig via a heated pipeline. Bed temperatures were controlled to give 1,100° and 1,200° F, and flow rates were adjusted to give gas hourly space velocities of 710 and 940, respectively. Hydrogen sulfide concentration averaged 380 grains per 100 scf, and the gas contained approximately 1/2 pound of dust, 1 pound of tar, and 5 pounds of steam per 1,000 scf. Figure 3 shows hydrogen sulfide in the gas leaving the sorbent bed had its concentration reduced to 10 and 20 grains per 100 scf and did not

increase until after six hours on steam. Removal was 95 percent and 97 percent effective with respect to hydrogen sulfide. Tar was not removed by the sorbent.

Data were obtained for cleaning the gas from Western Kentucky No. 9 coal using 820 hourly space velocity. Average H_2S concentrations in the feed gas were 588, 518, and 478 grains per 100 cubic feet and respective bed temperatures were 1,100°, 1,200°, and 1,300° F. Sorption capacity increased markedly as bed temperature increased. Figure 4 shows the grams of H_2S removed per gram of sorbent until concentration in gas leaving the bed reached 100 grains per 100 scf. The amount removed increased linearly between 1,100° and 1,300° F. Breakthrough was reached after approximately 4-1/2, 6, and 6-1/2 hours, respectively.

Reaction mechanism is chemisorption, whereby hydrogen sulfide diffuses throughout the sorbent and reacts with Fe_2O_3 forming FeS and FeS_2 . Analyzing the spent sorbent indicated the empirical composition was $FeS_{1.3}$. Iron oxide, Fe_2O_3 , was regenerated and the sulfur released as SO_2 by passing air or oxygen over the hot bed. With oxygen regeneration, the effluent gas was pure SO_2 until some oxygen passed through unreacted after regeneration was 90 percent complete.

CONCLUSIONS

Sintered sorbent made of iron oxide and fly ash is effective for removing hydrogen sulfide at temperature up to 1,500° F. Long life is indicated for this sorbent when used in a fixed bed. Its activity is good for the 1/4-inch-diameter extrusion, the only size for which data were obtained, but reduction in size should increase its activity.

REFERENCES

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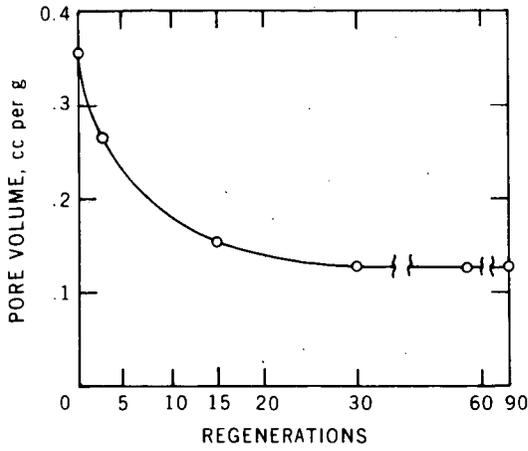


FIGURE 1. - Pore Volume Reaches Constant Value After 30 Regenerations

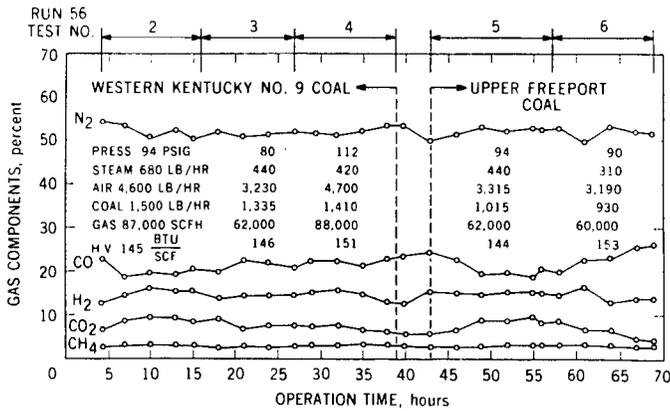


FIGURE 2. - Producer Gas Composition

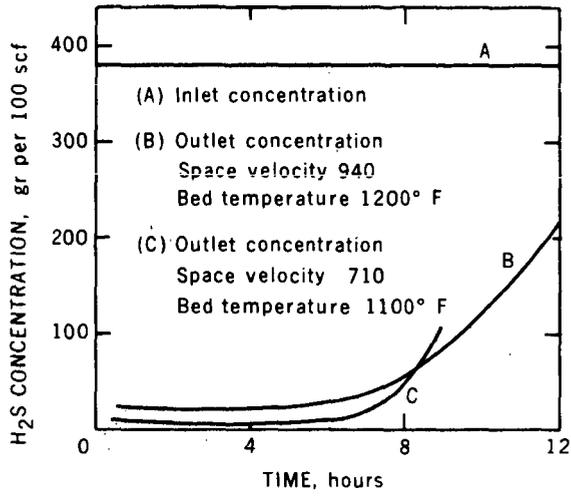


FIGURE 3. - Removing H₂S from Producer Gas

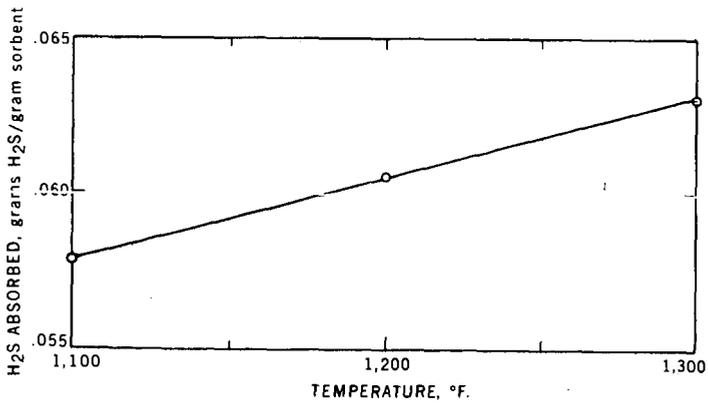


FIGURE 4. - Total H₂S Absorbed by an Fe₂O₃ Fly Ash Bed Until 100 grains/100 ft³ Breakthrough Occurred