

CLEANUP OF HOT COAL GAS WITH CARBON-BASED SORBENTS

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INTRODUCTION

Integrated Gasification Combined Cycle (IGCC) power systems are emerging as the most promising technology to convert high sulfur coal into electricity. Illinois Basin coal is a proven feedstock for IGCC, e.g., the Destec process in Terre Haute, IN. Hot gas cleanup for desulfurization is needed to accelerate the successful demonstration and commercialization of advanced coal gasification systems worldwide. In IGCC processes, hydrogen sulfide is removed from the coal gas before it enters the turbine. To achieve maximum efficiency in IGCC systems, H₂S should be removed from the fuel gas while hot. Although H₂S can be removed quite effectively by cooling the hot gases to temperatures less than 100°C, removal of H₂S at 300-800°C can lead to significant increases (up to 3%) in overall thermal efficiency. More efficient IGCC processes expand for markets hot gas cleanup sorbents and for high sulfur Illinois coal.

Numerous metals and mixed metal compounds have been studied as possible desulfurization sorbents. Current leading sorbents include zinc titanate and Z-Sorb (a proprietary zinc-oxide-based sorbent). However, not only are these sorbents expensive (up to \$7-15/lb), they are also prone to chemical and/or physical degradation during cycling. Zinc titanate suffers from spalling due to formation of sulfide and sulfate which have 2 to 3 times higher molar volume than the oxide. Z-Sorb degrades in the presence of steam present in coal gas. Both sorbents sinter during regeneration and typically their reactivity drops by around 50 percent in just 50 cycles.

One may conclude by reviewing the literature on hot gas cleanup sorbents that while research on sorbent materials has been extensive, continuing efforts are important because these sorbents are not yet used commercially in coal gasification processes, and there is still time for the development of improved sorbents. Another reason to encourage research in this area is that not all gasification systems are alike, and because of these differences in operating conditions and requirements, it is likely that more than one type of sorbent will be needed to satisfy the market. Every sorbent examined to date has had at least one major deficiency that prevents its widespread use. The fact that there is still ample opportunity to develop new types of sorbents for hot gas cleanup provides incentive for research on new types of materials.

One material that should be examined in more detail as a potential hot gas cleanup sorbent is carbon. Although, the use of carbon for hot gas cleanup has significant potential, the possibility of using carbon-based materials to remove sulfur containing gases from the products of coal gasification has been overlooked as other sorbents such as zinc ferrite, zinc titanate, and copper oxides have been extensively studied. Carbon has several advantages compared to metal-based hot gas cleanup sorbents: 1) the harsh coal gas environment should not affect the properties of the carbon during operation (carbon will not gasify in a reducing atmosphere at temperatures less than 700°C), 2) carbon, itself, adsorbs large quantities of H₂S, meaning that it could be used as an active support for metals such as copper and zinc which also adsorb H₂S; most metal-based sorbents have an inert support matrix, sometimes constituting up to 60% of the mass of the sorbent, 3) carbon will not chemically spall unlike metal based sorbents and it is more physically stable, since there is little or no volumetric change in a carbon-based sorbent due to sulfur loading, and 4) coal, which is used to make the carbon-based sorbents, is a very inexpensive starting material.

EXPERIMENTAL PROCEDURES

Sorbent Preparation

Activated chars were produced from size-graded Illinois coal in a fluidized-bed reactor (2 in. ID) under controlled preoxidation, pyrolysis, and activation conditions. Preoxidation of the chars was typically performed for 2 hr at 225°C, pyrolysis for 1 hr at 425°C and activation in steam for 2-6 hr at 825°C. Coal samples were activated until a specified carbon conversion was achieved (10-50%). Chars were oxidized using nitric acid (45 wt. % HNO₃) to achieve oxygen concentrations on the chars of up to 15 wt. %. An thermal desorption treatment (200-1000°C) was used to prepare chars with varying amounts of oxygen, which served as a starting material for the metal impregnation step. Various metals (Zn, Cu, etc.) known to chemically react with H₂S were added to the activated char using either incipient wetness or ion exchange methods.

Fixed-Bed Breakthrough Experiments

H₂S removal tests were performed on the various carbon-based sorbents produced in this study. A simulated coal gas stream was used containing 0-50% CO₂, 49-99.5% N₂, and 0.5-1% H₂S at 1 atm and 400-550°C. Initial H₂S adsorption experiments were performed using a 1 cm I.D. 316L stainless steel reactor, but since H₂S reacts with stainless steel at the temperatures examined, only total sulfur measurements are reported for those experiments and not breakthrough times. The measurement technique used to determine the total sulfur added to the carbon is discussed below.

A quartz reactor with a 1.5 cm O.D. and a fritted quartz plate was used for the sulfidation breakthrough tests. The fittings and tubing entering and exiting the reactor are made of teflon in order to minimize the adsorption of H₂S onto anything other than the sorbent being tested. Breakthrough curves were developed at space velocities of about 2000 hr⁻¹ (200 cm³/min) for packed-beds containing the carbon-based sorbents. H₂S influent and effluent concentrations were measured with a mass spectrometer (MS). For most experiments, breakthrough curves were run until the effluent concentration reached 200-300 ppmv. At which time, the experiment was terminated and the breakthrough curve was integrated to yield the total H₂S capacity and the time to breakthrough. Total sulfur analysis was performed on valid samples as a quality assurance/quality control (QA/QC) procedure.

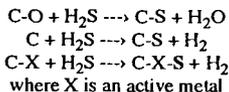
Total Sulfur Measurements

After adsorption and regeneration experiments, total adsorbed sulfur was determined by elemental analysis of the char using a solid state infrared detector (LECO SC-32). Samples were combusted in an oxygen atmosphere where the sulfur oxidizes to SO₂ and were then measured by a solid state infrared detector. The measured SO₂ was then converted to total percentage of sulfur. The sulfur content of samples before and after H₂S adsorption experiments was measured in order to calculate the total sulfur adsorbed.

RESULTS AND DISCUSSION

The best carbon-based sorbents developed for H₂S removal to date had a breakthrough time to 200 ppmv outlet H₂S concentration of over six hours and sulfidation capacities of up to 13 wt. % were observed. Numerous adsorption experiments were performed to evaluate the adsorption capacities and breakthrough times of various carbon-based sorbents. Activated, nitric acid oxidized, desorbed (with more active carbon sites), and metal impregnated chars were used for adsorption experiments. Experimental conditions were altered for a few adsorption experiments to determine their effect on H₂S adsorption. The inlet gas stream was modified to include only H₂S and N₂ in two experiments (Char F & G) and the reactor temperature was lowered from 550 to 400°C for one experiment (Char I). The characteristics and total added sulfur (initial sulfur in the sorbents was about 1 wt. %) for adsorption experiments run with the stainless steel reactor are shown in Table 1. The sulfur content of the chars before and after H₂S adsorption was measured.

A comparison of the sulfur contents of different chars produced several interesting results. As displayed in Table 1, char E had the highest sulfur content after adsorption experiments. Char E was oxidized with nitric acid and impregnated by ion exchange with zinc. The nitric acid oxidized chars (A and B) adsorbed 10.2 to 11.3 wt. % sulfur. A char desorbed of oxygen (char C) adsorbed a significant amount of sulfur (6.5 wt. %), but did not perform as well as the oxidized or metal impregnated chars. This suggests that while carbon sites will adsorb H₂S, oxygen and metal content are also important to achieve optimal adsorption. Char B and C differ in oxygen content only. The oxidized char (B) adsorbed about 50% more sulfur than the desorbed char (C) for comparable adsorption times. It may be concluded from Table 1 that the presence of chemisorbed oxygen enhances H₂S adsorption on activated char. Based upon our measurements to date, we propose three possible routes for H₂S adsorption on carbon:



The total sulfur results in Table 1 suggest the importance of the inlet gas stream. The inlet gas was modified to include only H₂S and N₂ for adsorption experiments with chars F and G. Without CO₂ present in the influent gas stream, the measured adsorption capacities were significantly lower with CO₂. This occurrence can be seen when chars F and G are compared to A and J, respectively. Char A adsorbed about 50% more sulfur than char F for comparable adsorption times and char J adsorbed about 50% more sulfur than char G for a shorter adsorption time. The only difference between these experiments was the presence of CO₂. This occurrence suggests

some interaction between the carbon surface and CO_2 , but it is known that carbon should not gasify in a reducing environment below 700°C . The importance of CO_2 in H_2S adsorption continues to be studied and more research is necessary before any type of conclusion can be suggested.

The total sulfur results in Table 1 indicate the importance of char surface area and reactor temperature. By comparing the surface areas of metal impregnated chars (E, H, N, and O), it can be seen that incipient wetness (IW) reduces surface area to a greater extent than ion exchange (IE). The reduced surface area appears to slightly lower adsorption capacity for similar chars (H and O). The influence of reactor temperature can be seen by comparing chars I and J in Table 1. Char J (550°C) adsorbed significantly more sulfur than char I (400°C) during a shorter run time.

Table 1 also displays total sulfur content of chars after adsorption experiments with the quartz reactor. Chars impregnated with metals (N and O) adsorbed about 10.5 wt. % sulfur before the effluent H_2S concentration reached 500 ppmv (350-390 min). An oxidized char (K) that was run for a longer time (610 min) attained a added sulfur content of 12.7 wt. %. A steam activated char (M), with no nitric acid oxidation, achieved a added sulfur content of 6.1 wt. %. The results show that significant amounts of sulfur (6.1-10.6 wt. %) can be added to carbon in fairly short adsorption times (<400 min). The sulfur contents for chars K-O (quartz reactor) are comparable and slightly better than those of chars A-J (stainless steel reactor). The improvements in adsorption capacities and breakthrough times are most likely due to improved char preparation methods.

Figure 1 displays breakthrough curves for four adsorption experiments with the quartz reactor. Breakthrough times to 200 ppmv outlet H_2S concentration for chars K, M, N, and O ranged from 4-6.5 hours. These breakthrough times were performed at 550°C , a space velocity (SV) of $1700\text{-}2000\text{ hr}^{-1}$ ($200\text{ cm}^3/\text{min}$), and an influent concentration of 5000 ppmv H_2S . The oxidized char impregnated with zinc by ion exchange performed the best, followed by the copper impregnated char. The oxidized char (K) displayed a leveling off of outlet concentration at 1300-1500 ppmv H_2S which is similar to previous adsorption experiments. This may indicate that a catalytic reaction might be occurring which converts H_2S to another compound or it may mean that H_2S adsorption on carbon exhibits a two-stage breakthrough curve. An interesting discovery of the adsorption experiments was that the steam activated char (M) had a breakthrough time (200 ppmv) that was very similar to that of the oxidized char (K).

SUMMARY AND CONCLUSIONS

Results of this project to date have shown that carbon-based sorbents are still adsorbing H_2S at sulfur loadings of 6 to 13 wt. % sulfur from a gas stream containing 0.5% hydrogen sulfide (H_2S) in CO_2 and N_2 at 550°C . Fixed-bed breakthrough curves have been obtained for several chars using a simulated coal gas stream containing 0.5% H_2S at a space velocity of 2000 hr^{-1} ($200\text{ cm}^3/\text{min}$). Breakthrough times to 200 ppmv effluent H_2S concentration ranged from 2 to 6.5 hours, depending on the char used. These breakthrough times are comparable to some metal-based sorbents. Results of adsorption properties are encouraging and show that carbon may be a viable hot gas cleanup sorbent. With further research, we believe that we can increase both the sulfidation capacity and breakthrough time of carbon-based sorbents. It remains to be determined how the pore structure and surface chemistry of the char can be modified to maximize H_2S adsorption capacity. The mechanism of H_2S removal by carbon is also not well understood, and any research to optimize the H_2S removal capabilities of carbon will inevitably lead to new insights into H_2S adsorption and conversion to elemental sulfur on the carbon surface. One distinct advantage carbon has over metal-based is that carbon, itself, adsorbs large quantities of H_2S , meaning that it could be used as an active support for metals such as copper and zinc which also adsorb H_2S . Most metal-based sorbents have an inert support matrix, sometimes constituting up to 60% of the mass of the sorbent. Metal-based sorbents, such as zinc titanate and Phillips Z-Sorb have an inert support matrix that does not participate in the H_2S adsorption reaction.

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Table 1: Carbon-Based Sorbents Analyzed for H₂S Adsorption.

Sorbent ID	Inlet Gas Composition	Oxygen on Sorbent [wt %]	BET Surface Area [m ² /g]	Char Description	Sulfur Added [wt %]	Adsorption Time [min]
Stainless Steel Reactor						
A	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	12-15	567	HNO ₃ oxidized	10.2	750
B	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	12-15	567	HNO ₃ oxidized	11.3	1200
C	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	~0	-	desorbed of oxygen	7.55	1350
D	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	12-15	465	HNO ₃ oxidized	11.6	1100
E	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	12-15	509	HNO ₃ oxidized + Zn by IE	13.2	1100
F	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	12-15	465	HNO ₃ oxidized	6.54	830
G	0.5% H ₂ S, 99.5% N ₂	~0	-	desorbed of oxygen	3.12	460
H	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	12-15	130	HNO ₃ oxidized + Cu by IW	10.0	1060
I	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	12-15	465	HNO ₃ oxidized, 400°C	2.41	410
J	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	12-15	465	HNO ₃ oxidized	4.78	180
Quartz Reactor						
K	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	10-15	567	HNO ₃ oxidized	12.7	610
L	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	10-15	-	HNO ₃ oxidized + Ca by IW	10.7	640
M	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	-	520	steam activated	6.1	300
N	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	10-15	509	HNO ₃ oxidized + Zn by IE	10.4	390
O	0.5% H ₂ S, 49.5% N ₂ , 50% CO ₂	10-15	250	HNO ₃ oxidized + Cu by IE	10.6	350

Table 1 Notes:

- All chars were preoxidized, pyrolyzed and steam activated.
- Reactor temperature = 550°C, inlet gas flow rate = 200 cm³/min, and space velocity = 1700 to 2000 hr⁻¹.
- IE = ion exchange method, and IW = incipient wetness method.

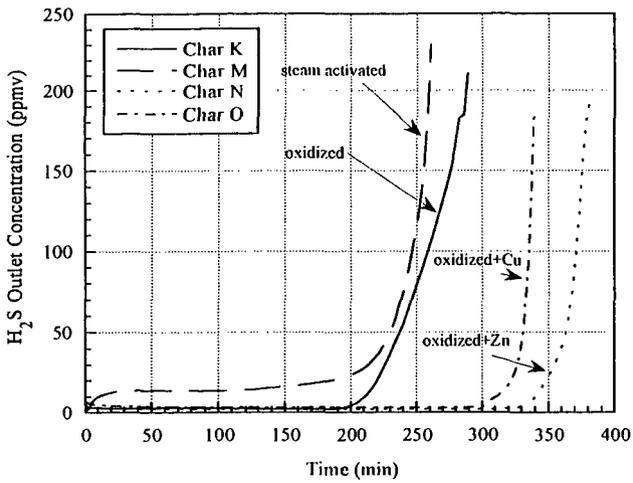


Figure 1. H₂S Breakthrough Curves for Carbon-Based Sorbents using Quartz Reactor

Conditions: SV = 1700-2000 hr⁻¹, 0.5% H₂S, 49.5% N₂, 50% CO₂, 550°C, 1 atm.