MERCURY, SO$_2$ AND NO REMOVAL FROM FLUE GAS BY ADSORPTION ON ACTIVATED CARBONS

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Introduction

The high volatility of mercury makes control of this metal particularly difficult. To date, no commercial technology is available for mercury removal from combustion flue gas. This project addresses the problem of removal and recovery of mercury from combustion/incineration flue gas with concurrent control of SO$_2$ and NO$_x$. The approach is based on regenerative adsorption on activated carbon. In this paper, preliminary results of packed-bed experiments are presented, with an emphasis on the effect of NO, SO$_2$, and O$_2$ on mercury sorption on the carbon surface. Since the simultaneous SO$_2$ and NO$_x$ control by adsorption on carbon is a commercial technology (see, e.g., reference [1]), only mercury sorption is addressed here.

Mercury is known to readily react with sulfur-containing species, and special types of sulfur-impregnated carbons have been successfully used for mercury capture [2,3]. The high cost of such carbons (~\$5/lb) is prohibitive, however, and low-cost alternatives are sought. The use of scrap tires is proposed in this work as an activated-carbon precursor. In the process of tire manufacturing, sulfur is commonly used as a vulcanization agent, and the waste-tire material contains about 1.5 wt.% sulfur. If proved effective, inexpensive tire-derived carbons would provide good economic leverage for the process, and may themselves become a value-added product of the waste-tire pyrolysis plant.

Materials and Experimental

A commercial activated carbon, CBC103X, and a tire-derived carbon, TDC101, were used in this project. TDC101 was prepared by pyrolysis of scrap tires in a large-scale auger-type facility that was operated at 660–720 °C, with a carbon residence time of approximately 2.5–10 minutes. TDC101 carbon was activated by CO$_2$ gasification in a tube furnace at ~900 °C. (The activated TDC carbon is denoted TDC101-AC, in contrast to the non-activated material TDC101.) Nitrogen BET surface areas of the CBC103X, TDC101, and TDC101-AC carbons were found to be 655 m^2/g, 56.2 m^2/g, and 563 m^2/g,

respectively. The corresponding values on a dry, ash-free basis are 701 m^2/g, 67.0 m^2/g and 749 m^2/g.

There was a concern that tire pyrolysis and char activation processes might lead to the depletion of sulfur in the final product. This was demonstrated not to be the case. The initial sulfur content of ~1.5% in the tire material increased to 3.2% upon pyrolysis, and to 5.1% upon activation (daf basis).

A quartz packed-bed reactor (ID = 3/4 in.) was used in this work. Approximately 0.25 g of sorbent (0.025 g in some runs) was mixed with 12 g of quartz sand prior to each run. The sorbents were sieved to a particle size less than 38 μm, and the flow rate of the carrier gas was 1000 ml/min (STP). Bed temperature was monitored by means of a quartz-sheathed thermocouple, and the sorption temperature was 100 °C. The mercury concentration at the reactor inlet was ~100 μg/Nm^3.

Results and Discussion

The percentage of mercury captured by different sorbents, X_{Hg}, is plotted as a function of time in Figure 1. It can be seen that the TDC101–AC carbon exhibits a mercury-sorption capacity appreciably higher than that of the control carbon CBC103X.

The effect of SO$_2$, NO, and O$_2$ on mercury sorption is illustrated in Figure 2 and Figure 3. In Figure 2, a transient response of the system to a step change in gas composition is shown. A dramatic increase in the mercury-sorption capacity from 40% to 85% is observed when NO and SO$_2$ are introduced. A pseudo-steady state is established in which mercury is effectively adsorbed for more than 30 hours. This result is impressive when compared with the data of Figure 1, especially when the difference in sample weight is taken into account (25 mg versus 250 mg). The comparison of Figure 1 and Figure 2 also shows that the presence of oxygen alone enhances mercury sorption.

The data in Figure 2 point to the importance of surface condition in terms of the inventory of surface oxides present at any given moment. When SO$_2$ and NO were added to the gas mixture, the carbon surface

had already been oxidized due to the prior exposure to oxygen. However, new types of reactive surface species were formed due to the presence of NO and SO_2. As a result, mercury sorption was enhanced to a final value of $X_{Hg} \approx 85\%$. It is expected that this value would eventually have started declining (due to surface saturation with mercury) if the experiment had continued long enough. The long time scale of surface reconstitution is noteworthy (Figure 2). This points to the effect of surface preoxidation, or "aging," which we observed in several runs. This effect was not quantified, however, and a more systematic study is warranted.

The results of Figure 2 do not show whether the enhanced mercury sorption upon SO_2/NO addition is due to the presence of SO_2 or NO. The two effects are separated in Figure 3. The data show that both NO and O_2 enhance mercury sorption, with NO having a stronger influence. The presence of SO_2 has only a weak effect. In separate experiments, it was shown that adding NO and SO_2 without the presence of oxygen does not enhance mercury sorption.

Conclusions

Activated carbons from scrap tires show good potential for mercury-sorption applications. Mercury sorption is enhanced by oxidizing environments: O_2 and NO, with NO having a stronger effect. Both NO and O_2 must be present for NO to augment mercury sorption. The effect of SO_2 on mercury sorption was found to be weak. Adsorbed mercury forms surface complexes with adsorbed O_2, NO, and SO_2. The state of carbon surface, in particular the inventory of surface species, is critical for good mercury sorption.

Acknowledgments

References

1. Knoblauch, K., Richter, E. and Jüntgen, H., *Fuel*, 1981, 60, 832.
2. Sinha, R.K. and Walker, P.L., Jr., *Carbon*, 1972, 10, 754.
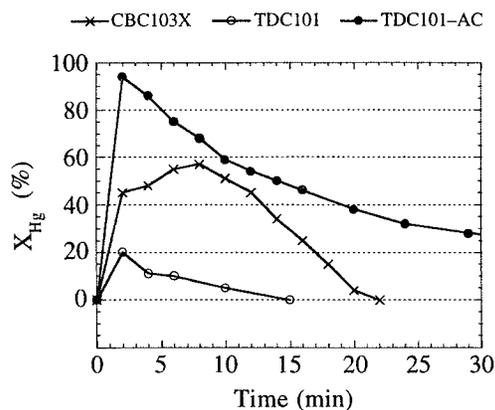3. Livengood, C.D., Huang, H.S., Mendelsohn, M.H. and Wu, J.M., *ACS Div. of Fuel Chem. Prepr.*, 1995, 40(4), 848-852.

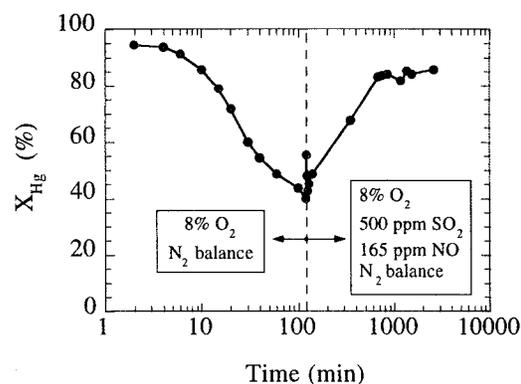**Figure 1.** Mercury retention, X_{Hg}, vs. time (100 μm Hg/N_2 balance; 250 mg sorbent).

Figure 2. Mercury retention for TDC101-AC in a gas mixture containing Hg, O_2, SO_2, NO, and balance N_2 (25 mg sorbent).
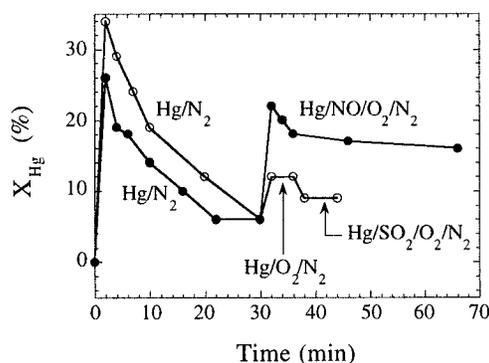

Figure 3. A transient response to a change from a non-oxidizing atmosphere (Hg/N_2) to atmospheres containing (a) Hg, 50 ppm NO, 6% O_2, N_2; and (b) Hg, 6% O_2, N_2, and then to Hg, 50 ppm SO_2, 6% O_2, N_2 (250 mg TDC101-AC sorbent).

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