

# MERCURY OXIDATION AND CAPTURE BY COAL CHARs

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## 1. Introduction

The estimated annual cost of mercury control at a level of 90%, using technologies based on injection of commercial activated carbons, is estimated to be in the range \$1–\$15 billion [1], where a large excess of carbon sorbent is needed to be injected to ensure the required level of mercury removal. Moreover, there is a lack of understanding of the interaction between mercury and the carbon sorbent, and therefore, it is very difficult to predict the amount of carbon sorbent needed for a specific plant configuration. Accordingly, there is a clear need to find novel sorbents that can compete with expensive commercial sorbents and optimize their current performance. Due to its inherent porosity and adsorption properties, as well as on-site availability, the authors have previously shown that chars from coal-fired combustors or gasifiers are potential mercury sorbent candidates.

Mercury can be both elemental and oxidized in the flue gas system. The former is more difficult to be removed, while the latter is more easily captured by current flue gas cleanup systems, such as particulate control devices and scrubbers. The oxidation of mercury occurs in the post-combustion system during cooling of the flue gas. The authors' previous studies have shown that coal chars can oxidize and capture mercury. However, the mercury capacity changed significantly across the different char samples studied, from 0.2ppm for a char sample collected from a combustor to 0.01ppm for a char sample collected from a gasifier. Accordingly, in this work, the char properties are correlated with their mercury uptake capacity, including porous texture and surface chemistry.

## 2. Experimental

Nine char samples were collected from different facilities, including four are biomass (wood) based and five are coal based (three from Powder River Basin coals and two from bituminous coal). Three of the chars samples were generated

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from gasifiers and six were generated from boilers. The mercury content of these char samples were tested using CVAA according to the EPA 7470 method. The loss-on-ignition (LOI) contents or total carbon content of the char samples were determined according to the ASTM C311 procedure. The porous texture of the chars and activated char samples was characterized by conducting N<sub>2</sub> adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT, as described elsewhere [2].

It is known that the mercury capacity of the inorganic fraction is very low compared to the carbon present in a char [3]. Accordingly, a cleanability study of one of the chars was conducted to generate an enriched carbon sample that can be used to produce mercury sorbents and to study the effect of the carbon content in their mercury capture capacity. The de-ashed process was conducted by acid digestion using HCl/HNO<sub>3</sub>/HF at 65°C. The de-ashed char sample and a commercial activated carbon, Darco Insul, were tested for mercury adsorption using a fixed-bed with a simulated flue gas at 138°C. A detailed description of the mercury capacity test protocol used in this work can be found elsewhere [4]. The simulated flue gas used in the study contains 16% CO<sub>2</sub>, 5% O<sub>2</sub>, 2000ppm SO<sub>2</sub>, 270ppm Hg and balance nitrogen, and the length of exposure is 350 minutes.

### 3. Results and Discussion

#### 3.1 LOI of the study samples

Table 1 presents the chars studied, including their LOI and ash values.

Table 1. Summary of the char samples studied.

Sample	Feed	System	LOI, wt%	Ash, %
CPC-Filter	Wood	Gasifier	70.6	29.4
CPC-Knockout	Wood	Gasifier	89.6	10.4
FA1	Bituminous	Boiler	62.7	37.3
FA2	Bibuminous	Boiler	28.0	72.0
Woodchar	Wood	Gasifier	85.4	14.6
Tra-WoodFA	Wood	Boiler	22.0	78.0
F9830	PRB	Boiler	1.0	99.0
DarkAsh99	PRB	Boiler	0.7	99.3
DarkAsh00	PRB	Boiler	0.8	99.2

The LOI of the collected samples are widely distributed. Some samples contain more than 50% LOI. For instance, CPC-Knockout, which is a biomass-based sample collected from a gasifier, has a LOI as high as 89.6%, and contains only

10.4% ash. The other sample collected from the same facility, CPC-Filter, also has a high LOI, 70.6%. Another wood-based char sample, collected from the GTI gasifier, contains very small aluminum beads; however, they were separated from the char sample by sieving. The separated char sample, Woodchar, also has a high LOI (85.4%), as presented in Table 1. The other wood-based sample Tra-WoodFA, has a relatively low LOI, 22%, compared to the other wood-based samples. Some of the coal-based samples also have high LOI, such as FA1 (62.7%). However, there are some coal-based samples that have very low LOI, such as the samples collected from a boiler, DarkAsh99, DarkAsh00 and F9830, that have an LOI value as low as ~1%. The sample DarkAsh99 has the lowest LOI, 0.66%. Generally, the biomass-based char samples collected have higher LOI than the coal-based samples.

### 3.2 Porosity studies of the char samples

The surface area and pore volume of the char samples were calculated from N<sub>2</sub>-77K isotherms and are listed in Table 2. Corresponding to its high LOI and adsorption capability, CPC-Knockout has the highest surface area and pore volume, 243.2 m<sup>2</sup>/g and 0.238 ml/g, respectively. This confirms the authors' previous observation that the remaining carbon in fly ash has generated a certain porosity during the combustion/gasification process [2]. The sample CPC-Knockout can be expected to have sorbent properties prior to any further treatment. Another sample collected from the sample facility, CPC-Filter, also has a high surface area and pore volume, 119.6 m<sup>2</sup>/g and 0.196 ml/g, respectively. The three low LOI samples collected from a boiler, F9830, DarkAsh99 and DarkAsh00, have surface areas as low as 1~2 m<sup>2</sup>/g, as expected from their low LOI.

Table 2. Porosity analysis results of the samples.

Sample	S <sub>BET</sub> , m <sup>2</sup> /g	V <sub>t</sub> , ml/g
CPC filter	119.6	0.196
CPC Knockout	243.2	0.238
FA1	53.1	0.040
FA2	25.5	0.020
Tra-WoodFA	77.4	0.072
F9830	2.1	0.003
DarkAsh99	0.9	0.002
DarkAsh00	1.1	0.002

### 3.3 Inherent mercury content of the char samples

The inherent mercury content of the char samples was analyzed by CVAA and the data is presented in Table 3. The mercury contents are low, mainly below ~0.3 ppm, except for the samples F9830 and Woodchar, which have mercury contents of 0.81 and 2.84, respectively

Table 3. Mercury content of the samples collected.

Sample	Coal Used	LOI, wt%	Mercury, ppm
CPC-Filter	Wood	70.6	0.03
CPC-Knockout	Wood	89.6	0.02
Darkash00	PRB	0.8	0.31
Darkash99	PRB	0.7	0.27
FA1	Bit.	62.7	0.20
FA2	Bit.	28.0	0.36
F9830	PRB	1.0	0.81
Woodchar	Wood	85.4	2.84

### 3.4 Mercury capacity adsorption tests

The sample FA1 was collected from a pulverized coal (PC) unit and has a carbon content around 58%, which is higher than those reported in previous studies that are typically ~15%. However, this work focuses on the utilization of high carbon chars, and therefore, this high carbon content sample was intentionally selected. As previously described, the carbon is the active component in chars to capture mercury [3]. Therefore, the sample was subjected to separation and de-ashing treatment prior to further investigation. The de-ashed sample was labeled as FA1-Dem. The ash content, total surface area, pore volume and the average pore size (based on the cylinder pore model) of the studied samples are presented in Table 4.

The de-ashing process used here can effectively remove the ash from the char sample down to 3.6% for FA1-Dem vs. 37.3% for the parent sample. The sample, FA1-Dem, has a surface area and pore volume of 53 m<sup>2</sup>/g and 0.04 ml/g, respectively. This again confirms that the some porosity was generated while in the PC combustor, where the pores generated are mainly in the mesopore range, with an average pore size about 3nm.

Table 4. Porosity and mercury capacity of the de-ashed char sample FA1-Dem and Darco Insul.

Sample	Ash Content %	S <sub>BET</sub> m <sup>2</sup> /g	V <sub>0.95</sub> ml/g	D <sub>a</sub> nm	Mercury Capacity <sup>2</sup> mg/g
FA1-Dem	3.6	53	0.040	3.0	1.85
Darco Insul <sup>1</sup> .	-	700	-	-	2.77

Note: 1. Darco Insul is a commercial activated carbon used as benchmark for mercury capture tests.

2. Mercury capacity tested using a fixed bed at 138°C and simulated flue gas.

The mercury adsorption tests results are also listed in Table 2, where the data obtained under the same conditions for the commercial activated carbon Darco Insul are also presented. The sample FA1-Dem has a mercury capacity as high as 1.85mg/g, which is comparable to the commercial activated carbon Darco Insul, whose mercury capacity is 2.77mg/g. Previous studies on a Thief sorbent, which is a semi-combusted coal extracted from a combustion chamber, have also shown that sorbents with modest surface areas exhibit good capacities for mercury capture from flue gas [4]. Micropores (< 2nm) are the major active sites for most adsorbates, while mesopores (2-50nm) act as adsorption sites especially for larger molecules, and also as transportation routes for small adsorbates. In certain cases, the transportation function is more important than the adsorption site function. For instance, in carbon sorbent injection technology to control mercury emissions, the retention time of carbon in flue gas is very short, and therefore, at most conditions, mass transfer rate is the determining factor and the adsorption of the mercury onto the carbon surface is mass-transfer limited. Therefore, a carbon sorbent selected for mercury capture should have good mass transfer properties.

Furthermore, previous studies have shown that mercury capture using carbon sorbents occurs at approximately 140°C and the surface properties of the carbon sorbent plays a very important role. The char sample studied here, FA1-Dem, has surprisingly high mercury capacity compared to its low porosity. This may be due to its specific surface chemistry properties, where F, Cl, and oxygen functional groups were probably introduced during the de-ashing process [5].

Previous studies conducted by the authors have focused on different adsorbents for mercury, including activated carbon, and also investigated the effect of several elements including F, Cl, I, S and O on mercury adsorption [4]. EPA studies on the effect of activated carbon surface moisture on low temperature mercury adsorption indicated that surface oxygen complexes provide the active sites for mercury bonding [6], where possibly lacton and carbonyl groups, are the active sites for Hg<sup>0</sup> capture [7]. However, other published work on the impact of surface heterogeneity on mercury uptake by carbonaceous sorbents under ultra high vacuum and atmospheric pressure concluded that in physisorption regime,

oxygen functional groups decrease mercury adsorption due to their blocking of access for mercury to micropores, while in chemisorption regime, no significant impact of oxygen functionalities was observed [8]. The data discussed here indicates that the surface functionality of chars may play an important role during mercury adsorption, while their surface area does not seem to have a significant impact on its mercury capacity (Table 4). Based on the above data, chars have the potential to capture mercury if they have certain porous structure and surface functionality. Further studies on the modification of the surface properties of chars and their mercury adsorption properties are under way.

#### 4. Conclusions

Following the demand for mercury emission control and utilization of chars, this paper focuses on developing sorbents from chars for mercury capture and to determine their mercury capacity under typical flue gas compositions. For this work, nine char samples, including six samples from boiler systems and three samples from gasifiers were collected and analyzed. Of the samples collected, the wood-based samples have higher LOI than the coal-based samples. Corresponding to its high LOI and adsorption amount, CPC-Knockout has the highest surface area and pore volume, 243.2 m<sup>2</sup>/g and 0.238 ml/g, respectively.

In addition, a cleanability study of one of the chars was conducted to generate an enriched carbon sample, FA1-Dem, to study the effect of the carbon content on their mercury capture capacity. The enriched carbon sample has an ash content of around 3.6% and its surface area and pore volume are 53 m<sup>2</sup>/g and 0.04 ml/g, respectively. This suggests that the some porosity was generated while in the PC combustor, where the pores generated are mainly in the mesopore range, with an average pore size about 3nm.

The samples prior to the mercury adsorption tests were analyzed by a CVAA for inherent mercury content. The mercury contents were generally low. In addition, selected chars were tested for mercury capacity using a simulated flue gas. The char sample FA1-Dem has a mercury capacity as high as 1.85mg/g, which is comparable to the commercial activated carbon Darco Insul, whose mercury capacity is 2.77mg/g. However, the very different mercury capacity of the samples studied here cannot only be ascribed to differences in their porous structures. The de-ashing process using HCl/HNO<sub>3</sub>/HF not only removed most of ash from the sample, but it also changed the surface chemistry of the sample, leaving F, Cl elements and oxygen functional group on the surface of fly ash char. The data in the present paper suggests that the oxygen functionality of carbon sorbent plays an important role during mercury adsorption, while the porosity of the carbon sorbent does not seem to have a significant impact on its mercury capacity.

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