

Speciation of Hg retained in gasification biomass chars by temperature-programmed decomposition

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ABSTRACT

The development of elemental mercury (Hg^0) capture technology for coal-fired power plants is essential for achieving the goal of zero emissions from coal derived flue gas. Sorbents such as biomass gasification chars have proved to be effective for mercury capture and offer the added advantage of their low cost since they are sub-products of the thermal conversion process. However, the mercury species captured on the sorbents have not yet been characterized. In this study, a temperature programmed decomposition technique was used to identify the mercury species captured on the sorbents and to clarify the mechanisms responsible for mercury retention. The mercury species formed were observed to be dependent on char characteristics and flue gas composition. The results showed that mercury chloride was the most likely mercury species in a simulated coal combustion atmosphere from the chars obtained from poultry litter, sunflower husks and paper and plastic waste, the last two containing small amounts of mercury sulphate. The mercury compounds identified in the char from the gasification of wood waste were mainly sulphide and sulphate species.

Keywords: mercury; char; biomass; coal combustion

1. Introduction

The long-range transport of air pollution poses a considerable risk both to the ecosystem and to the human population, especially if this pollution contains an element as toxic as mercury. The global mercury emission in 2008 was about 8000 tons, 36% of which originated from anthropogenic activities [1-2]. The main anthropogenic source of mercury emissions is the combustion of fossil fuels. Several estimates for mercury emissions have been reported [3-5]. Accordingly the United States has developed a programme for reducing emissions of mercury from coal-fired power plants [6] and in 2005 the European Commission launched the EU's Mercury Strategy [7] which contains 20 measures for reducing mercury emissions.

Several methods have been studied for the reduction of mercury emissions from coal-fired power plants [8]. These include the use of activated carbons as sorbents which may reduce the emission of mercury with an efficiency of up to 90% or more. However, the injection of activated carbon upstream of the particulate control systems may have a negative impact on the quality of the by-products of flue gas cleaning and also entail high costs [9]. The results obtained from previous works [10-13] showed that some chars resulting from biomass gasification, mainly from plastic and paper waste, as well as from coal combustion, have mercury retention capacities similar to those of commercial activated carbons especially prepared for elemental mercury capture from flue gas from coal combustion. Such low-cost char sorbents could serve as a viable alternative to activated carbons for direct injection into power plants. However, it is necessary to identify the mercury species present in these sub-products to fully understand the behavior of mercury in biomass chars.

The mercury species in different types of samples can be identified by temperature programmed decomposition [14-16], a method which is highly sensitive and can identify different species of mercury even in samples with very low mercury contents such as the gypsum produced in flue gas desulphurization (FGD) systems [17-18]. An understanding of the speciation of mercury throughout the coal-combustion process is crucial for designing effective mercury removal technologies. By means of temperature-controlled decomposition technique it was possible for us to identify different modes of occurrence of mercury species in several gypsum samples. The species identified were mainly Hg-S compounds (insoluble mercury species) and HgCl_2 (water soluble species) [18], and thus determines the possibility that mercury might be retained in FGD facilities. The temperature programmed desorption technique can also be used as a tool for understanding mercury retention mechanisms in different types of sorbents such as fly ashes [19]. This work focuses on a little known technique for identification mercury species in sub-products of coal combustion, particularly in biomass gasification chars. The results of the evaluation of the retention capacities of each char and the influence of the gas composition have been presented in other works [10, 20].

2. Experimental

The chars employed in this study were obtained from a 500 kW pilot gasification plant with a circulated fluidized bed (CFB) gasifier BIVKIN in the Energy Research Centre of the Netherlands (ECN). The chars are sub-products of the gasification of sunflower husks, poultry litter, wood waste and a mixture of paper and plastic waste

labelled SH, PL, WW and PW, respectively. These biomass gasification chars had been previously characterized in a study carried out by Fuente-Cuesta et al. [10].

The experimental devices employed to retain the mercury and identify the mercury species in the char samples at laboratory scale have been described in previous works [10,14, 17-19]. The retention device consisted of a glass reactor in which the sorbent bed (20 mg of char with 60 mg of sand) was placed. The temperature of the sorbent bed was kept at 150 °C. Elemental mercury in gas phase was obtained from a permeation tube. An inert atmosphere (N₂) and a synthetic gas mixture containing species typically present in a coal combustion atmosphere (5% O₂, 1300 mg Nm⁻³ SO₂, 500 mg Nm⁻³ NO₂, 20.3 mg Nm⁻³ HCl) were passed through the reactor. The gas mixture carried the mercury in vapour phase through the sorbent bed at a flow rate of 0.5 L min⁻¹. The mercury concentration in gas phase was approximately 100 µg m⁻³. The mercury not retained in the sorbents was measured using a continuous mercury monitor (VM-3000). The experimental device used to decompose the sorbents after mercury retention and desorb the mercury species consists of a thermal dissociation rig (PS Analytical Thermogram model 50.042) coupled to a mercury analyser (PS Analytical Sir Galahad Mercury Analyser model 10.525). The commercial thermal dissociation unit was modified to improve the temperature distribution along the work-tube between the programmed dissociation zone (40-650°C max) and the “cracker” zone (operated at 800°C), where the volatilized mercury compounds are fully dissociated prior to detection as elemental mercury by the atomic fluorescence detector. The mercury compounds present in the solid sample were subjected to a programmed rise in temperature of 10°C

min⁻¹. Origin 6.0 professional software was used to deconvolute the overlapping peaks of the thermal decomposition curves.

3. Results and discussion

The mercury retention capacity of the chars in the inert and the simulated coal combustion atmospheres is presented in Table 1. Different mercury retentions were obtained depending on the characteristics of the biomass gasification chars and also on the gas compositions evaluated. A comparison of the results from both atmospheres shows that higher retention capacities are achieved in the simulated coal combustion atmosphere, but the increase varies significantly depending on the characteristics of each char. The char from paper and plastic waste (PW) showed the highest mercury retention capacity in the N₂ atmosphere, whereas the char from sunflower husks (SH) exhibited the highest mercury retention in simulated coal combustion conditions. The biggest difference in behaviour between both atmospheres corresponded to the SH char which showed a mercury retention capacity lower than 1 µg·g⁻¹ in the inert atmosphere and 120 µg·g⁻¹ in the coal combustion atmosphere. This difference was not so significant in the case of the PW char (65 and 78 µg·g⁻¹ in N₂ and simulated coal combustion, respectively) (Table 1). Therefore, different mercury species are formed in presence of certain reactive gases and the type of char.

According to previous studies [14, 17-18], the thermal decomposition test is a efficient method for identifying mercury species from coal combustion by-products due to the fact that individual mercury compounds have a characteristic temperature of desorption. Although the decomposition temperature may overlap for certain mercury

compounds, in general, the temperature rate of the mercury species can be arranged in increasing order as follows: $\text{HgBr}_2 < \text{HgCl}_2 < \text{Hg}_2\text{Cl}_2 < \text{HgS}(\text{black}) < \text{Hg}_2\text{SO}_4 < \text{HgS}(\text{red}) < \text{HgO} < \text{HgSO}_4$. The thermal dissociation temperature for mercury halogenated compounds ranges from 70 to 220°C. Mercury sulphur compounds decompose at higher temperatures (200-500°C) reaching 600°C in the case of HgSO_4 . The desorption of HgO presents a maximum peak at approximately 500°C [14]. The thermal decomposition profiles for the char samples after mercury retention are shown in Figures 1-3. The signal corresponding to mercury desorption in the SH and PL chars in an inert atmosphere is very low as might be expected from their mercury retention capacities (Table 1, Figure 1) making it impossible to identify the mercury species present in these samples. However, the char from wood waste (WW) shows two main peaks between approximately 150 to 400°C. To facilitate the identification of different peaks, the profile from the char WW was deconvoluted (Figure 2a). According to the decomposition temperatures for different mercury compounds [14], the mercury species present in WW in the N_2 atmosphere could be mercury sulphide and mercury sulphate. The sulphur content in the WW char was approximately 1% [10]. The highest signal due to mercury decomposition corresponded to char PW which also exhibited the highest mercury retention in the N_2 atmosphere. (Table 1, Figure 1). A sharp peak is observed at approximately 150°C suggesting that HgCl_2 is the main mercury compound in the PW char. This is consistent with the high chlorine content of this char (5-6%) resulting from the gasification of paper and plastic waste [10]. When comparing the results obtained from the simulated coal combustion (SCC) atmosphere for all the chars (Figure 1), different mercury desorption curves are observed. The WW char in SCC presents a similar behavior to that in the N_2 atmosphere,

the signal being higher in SCC as a consequence of the higher mercury retention capacity. Consequently the two peaks observed in the inert atmosphere now overlap in SCC (Figure 2b). Sulphide and sulphate compounds were also the main mercury species identified in the char from wood waste in the SCC atmosphere. These results corroborate those obtained in an X-ray photoemission spectroscopy (XPS) analysis in a previous work [10] which revealed two modes of occurrence for sulphur. Figure 2b suggests that HgCl_2 is not present in the WW char during mercury retention in the SCC atmosphere even though it has a content of 3% [10]. However, as can be seen in Figure 1, the mercury decomposition temperature for the char from poultry litter in the SCC atmosphere is close to that of HgCl_2 (~150°C). The chloride content of PL char was 1.8% [10]. With respect to the sunflower husk (SH) char, two peaks appear in the range of 100 and 350°C with maxima at 150 and 280°C, respectively. The deconvoluted profile (Figure 3a) suggests that the main mercury species present in SH is HgCl_2 with some mercury sulphate. The chloride and sulphur contents were 0.8 and 0.5 %, respectively [10]. Finally, the thermal decomposition of PW in SCC conditions, unlike the N_2 atmosphere, shows a broad signal between 100 and 400°C which sharpens and peaks at approximately 180 and 260°C, corresponding to halogenated and sulphate mercury compounds, respectively [14] (Figure 3b). As already mentioned, there were no major differences between the mercury retention capacity of PW in the N_2 and SCC atmospheres. This suggests that some of the mercury retained as mercury chloride in the inert atmosphere is now in the form of mercury sulfate in SCC due to oxidation in the presence of combustion gases. It should be noted that the peaks may be slightly shifted due to that

some component(s) of the char samples could be interfering in the thermal decomposition of some mercury compounds.

4. Conclusions

The thermal decomposition method enabled us to identify different mercury species using chars obtained from gasification of biomass as mercury sorbents. This study has demonstrated that, among other applications, thermal decomposition is a promising tool for understanding the mechanism involved in mercury capture in char sorbents. The results of this study also confirm the influence of both homogeneous and heterogeneous reactions on the sorbents and the important role of chlorine and sulfur species in these processes.

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Table 1. Mercury retention capacity of char samples in an inert (N₂) and simulated coal combustion atmosphere (SCC)

| Sample | Hg retained N₂ ($\mu\text{g}\cdot\text{g}^{-1}$) | Hg retained SCC ($\mu\text{g}\cdot\text{g}^{-1}$) |
|---------------|---|---|
| SH | <1 | 120 |
| PL | 1.1 | 36 |
| WW | 2.7 | 33 |
| PW | 65 | 78 |

(SH: sunflower husks; PL: poultry litter; WW: wood waste; PW: paper and plastic waste)

FIGURES CAPTIONS

Figure 1. Thermal decomposition profiles of char samples used as mercury sorbents in an inert (N_2) and simulated coal combustion (SCC) atmosphere.

Figure 2. Deconvoluted thermogram for WW (wood waste) char in (a) a nitrogen atmosphere and (b) a simulated coal combustion atmosphere.

Figure 3. Deconvoluted thermogram for (a) SH (sunflower husks) char and (b) PW (plastic and paper waste) char in a simulated coal combustion atmosphere.

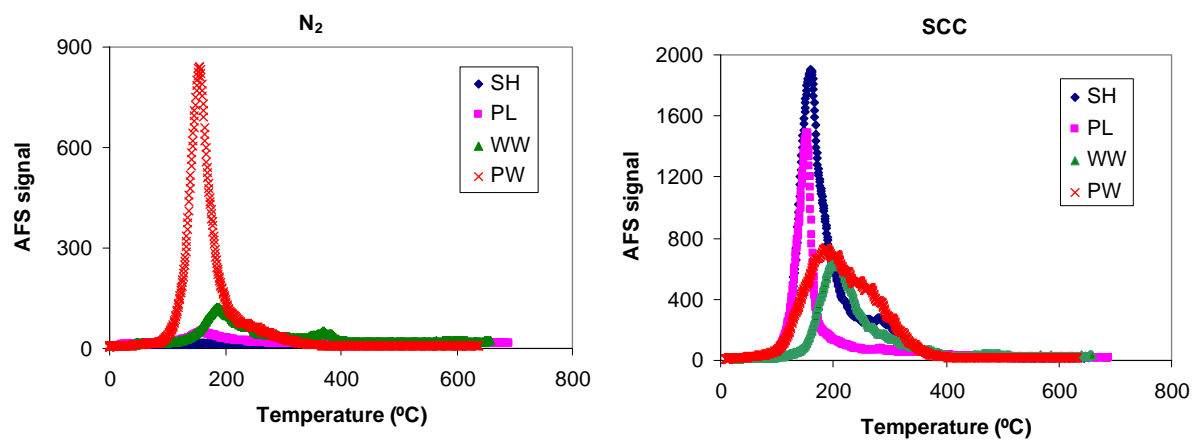


Figure 1

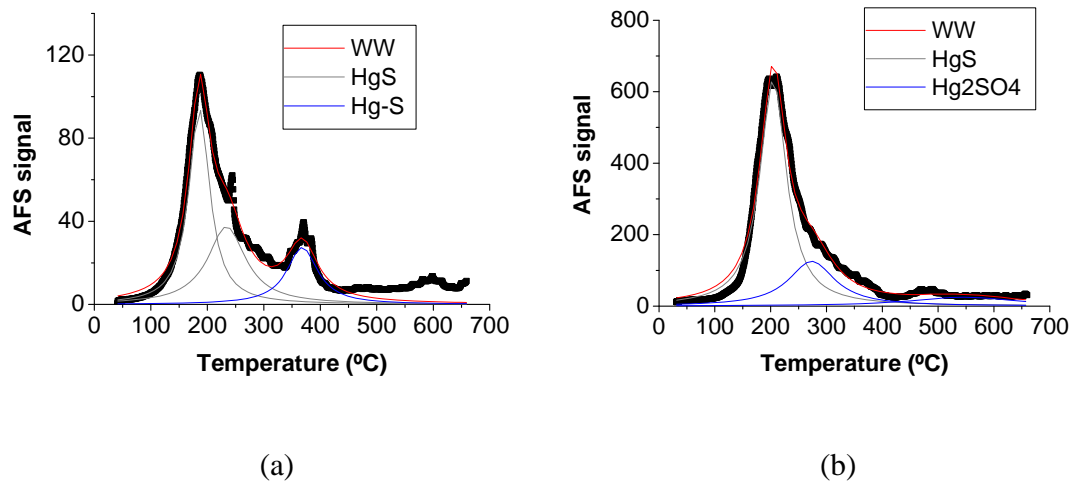
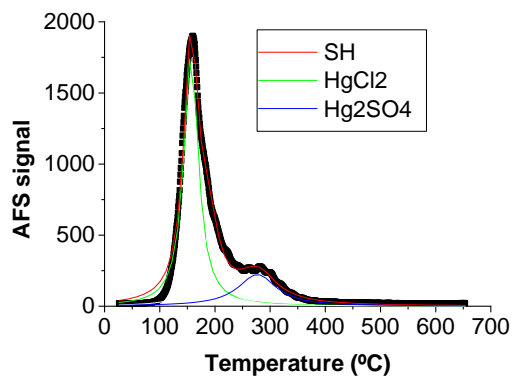
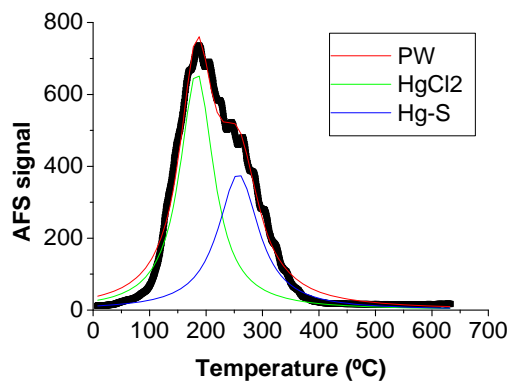


Figure 2



(a)



(b)

Figure 3