INVESTIGATION OF CATALYTIC EFFECT SEWAGE SLUDGE COMBUSTION ASH IN THE FORMATION OF HAPS

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Introduction

Incineration is a very important technique in the treatment of sewage sludge. In 1998, approximately 1.5 million and 2.5 million dry tons of sewage sludge were incinerated in the United States and European Union (EU), respectively. In 1985, only 10 % of EU sludge was incinerated, but by 2005 approximately 40% of EU sludge is expected to be incinerated. Use of sewage sludge as agricultural fertilizer was considered the best application for sludge until it was discovered that the presence of heavy metals in sludge could contaminate farmland. The limitations facing landfills and recycling plants and the planned ban on sea disposal has led to the expectation that the role of incineration will increase in the future.

The expected increase in sludge incineration has also led to increased scrutiny of the main drawback to the incineration of sewage sludge: the formation of hazard air pollutants (HAP). Sewage sludge incineration has been identified as a very important source of HAPs such as chlorobenzenes, chlorophenols, and PCDD/Fs. One of the more important characteristics of sewage sludge incineration is the formation of large amounts of ash, which is rich in known HAP formation catalysts such as Cu and Fe. Thus, the sludge incineration ash is expected to play an important role in the formation of HAPs in the post-combustion zone of a sludge incinerator. In this paper, we present results of our investigation of the catalytic effect of sewage sludge ash on the formation of chlorobenzenes and chlorophenols. In this study, pyrolitic gas from sewage sludge was used as reaction gas instead of the synthetic organic mix that has been used in most previous HAPs formation studies.

Methods and Materials

Sewage sludge from a wastewater plant in South-eastern Spain was used in this study. This sludge had a high concentration of metals and thus was suitable for use as an agricultural fertilizer. The sewage sludge was dried and ground into fine particles before being used in this study.

All experiments were conducted using a dual chamber flow reactor assembly. A schematic diagram of the experimental apparatus used is given in Figure 1. The first chamber was operated at high temperature in pyrolytic conditions and the second chamber was operated at post-combustion zone conditions (temperatures ranged from 300 to 500 °C). During an experiment, a sludge sample was introduced in the first chamber and pyrolyzed in helium atmosphere by increasing the chamber temperature from ambient to 725 ºC. Figure 1b shows the temperature rise in the first chamber as a function of time. The effluent from the first chamber entered the second chamber (0.7 cm I.D. quartz reactor), where a 2 cm long fixed bed of sludge ash particles was held in place by quartz wool plugs. The second chamber was held at a fixed temperature to study the interaction between organic compounds generated by pyrolyzing sludge in the first furnace and sludge ash particles. The effluent from the second chamber was trapped in an adsorbent trap (Amberlite® XAD-2). All transfer lines in the reactor system were maintained at 250 ºC.

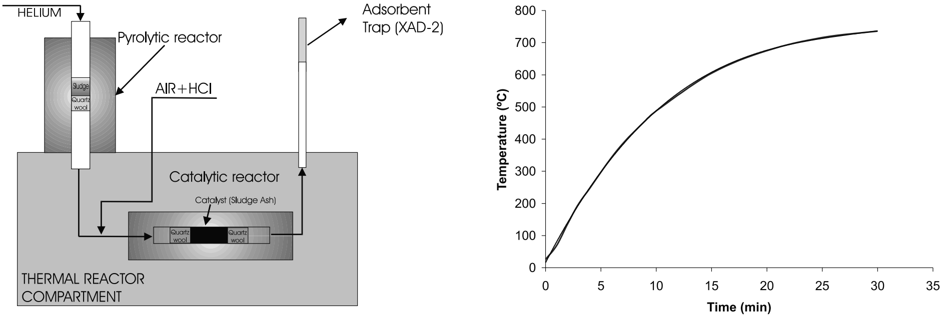

Figure 1. (a) Schematic of the dual chamber reactor system and (b) temperature profile in the pyrolytic reactor.

Interactions between sludge ash and sludge pyrolysis products were investigated at 300, 400, and 500 ºC using four different sludge ashes. In all experiments, approximately 150 mg of sewage sludge was pyrolyzed in the first chamber and the pyrolysis products were passed through a fixed bed with 50 mg of sludge ash in the second reactor chamber. The effluent from the first chamber was mixed with air to create 4 % O_2 in the reaction environment of the second reactor chamber. After each experiment, the fixed bed was removed and subjected to solvent extraction.

The sludge ash for each experiment was generated by combusting the sludge at 600 ºC for one hour. For the first series of experiments, the catalytic activity of this sludge ash was investigated in 4 %O_2 atmosphere. In the second series of experiments, the fixed bed was made of a combusted sludge ash sample to which 4% (by weight) $CuCl_2$ had been added. The reason for adding $CuCl_2$ was to increase the copper and chlorine content of the ash. For the third series of experiments, we investigated the catalytic activity of sludge ash in the presence of 1500 ppm of HCl in 4 %O_2 atmosphere. HCl as a source of chlorine was also included in the air stream of the fourth series experiments. In fourth series of experiments, the ash for the fixed bed was generated by combusting sewage sludge at 600 ºC for 12 hours with $Cu(NO_3)_2$ such that the resultant ash contained 4 % (by weight) CuO.

After each experiment, the adsorbent trap was extracted (Soxhlet Extraction) with methylene chloride for 18 hours, then concentrated and analyzed using a high-resolution GC-MS. Chlorophenols and chlorobenzenes were quantified using the selected ion mode. Analytical standard calibration curves for each congener were used to obtain quantitative response factors.

Results and Discussion

Chlorobenzenes, phenol, chlorophenols, naphthalene, polychloronaphthalenes, biphenyl and polychlorobiphenyls were observed in almost all experiments. Figure 2 shows the total yield of all chlorinated compounds. At 300 ºC, the total yield of chlorinated compounds is similar for experiments catalyzed with sludge ash and the ones conducted without any catalyst. This similarity in total chlorinated compound yield indicates that all the chlorine present in the sludge is already associated with organics and no chlorine is available to metals present in sludge ash to catalyze the chlorination reactions. Ash-catalyzed experiments also show that the total yield of chlorinated compounds is dependent on the temperature in the second chamber. This temperature dependence is perhaps to due to hydrocarbon (both chlorinated and non-chlorinated) oxidation and condensation reactions taking place in the sludge ash fixed bed. The second set of experiments, where $CuCl_2$ was added to the sludge ash, show a large increase in the yield of chlorinated compounds at 300 ºC. This increase in yield can be attributed to the addition of $CuCl_2$, as it provides both chlorine and a additional catalytic sites for condensation/chlorination reactions. As the temperature increases, the $CuCl_2$ quickly loses its chlorines and is oxidized to CuO. CuO thus formed acts as an oxidation catalyst, which results in a decrease in the total yield of chlorinated compounds at 400 and 500 ºC. The results of the second set of experiments showed that the addition of $CuCl_2$ increased the total yield of chlorinated compounds, but what it is not evident was whether this increase in yield was solely due to the availability of additional chlorine or the addition of copper.

To answer these questions, two more sets of experiments were conducted. In order to investigate the role of chlorine, a third set of experiments were conducted in which a catalytic bed was made of oxidized sludge ash, but this time 1500 ppm of HCl was introduced in the second chamber as a chlorine source. The results of these experiments showed a large increase in the total yield of chlorinated compounds at 400 and 500 ºC but a decrease in total yield of chlorinated compounds at 300 ºC. These results indicated that it took temperatures of 400 and 500 ºC for metal constituents of sludge ash to convert HCl to Cl_2 via the Deacon reaction. The Cl_2 thus generated then was able to chlorinate organics. The other possible explanation is that it took temperatures of 400 and 500 ºC to chlorinate sludge ash metals and these chlorinated metals then formed metal-organic complexes and thus chlorinated organics via ligand transfer mechanism. From the results of these experiments it was evident that in the presence of an additional chlorine source, the metals present in sludge ash were able to catalyze the formation of chlorinated compounds. However, the results were unable to elucidate the role of copper in the formation of chlorinated compounds. To elucidate the role of copper in sludge incineration, we conducted a fourth set of experiments in which an additional 4 % (by weight) CuO was added to the sludge ash and 1500 ppm of HCl was introduced as a chlorine source. The results of this set of experiments showed that the total yield of chlorinated compounds increased at 300 and 400 ºC, but the total yield decreased at 500 ºC. These results are consistent with the fact that at 300 and 400 ºC, CuO is chlorinated to $CuCl_2$, and $CuCl_2$ can then chlorinate organics via the mechanisms discussed above. However, at 500 ºC, it is not possible to chlorinate CuO efficiently and most of the copper at 500 ºC is present as CuO (oxidation catalyst) and not as $CuCl_2$/CuCl (oxychlorination catalyst). A comparison of Ash/HCl and Ash+CuO/HCl experiments (see Figure 2) shows that total yields of chlorinated compounds observed in Ash/HCl experiments is higher than those observed in Ash+CuO/HCl experiments at 400 and 500 ºC. A plausible explanation for these results is that copper is a more potent chlorinating agent at 300 ºC but at higher temperatures it starts acting more like an oxidation catalyst whereas other metals in sludge ash like iron are better chlorinating agents at higher temperatures.

To better understand the formation mechanism of chlorinated compounds, we also analyzed the isomer patterns of chlorobenzenes and chlorophenols. In all sets of experiments, the major yields were for chlorobenzenes with adjacent chlorine groups. Figure 3 shows a typical distribution for both chlorobenzenes and chlorophenols. The chlorobenzene and chlorophenol patterns observed in our experiments are very similar to those obtained by Froese and Hutzinger when they passed ethylene/HCl mix over fly ash [1,2]. This is consistent with the hypothesis that sludge organics that are evolved during pyrolysis are mainly small aliphatic compounds like ethylene, and in presence of HCl and sludge ash in the second chamber these aliphatic compounds chlorinate and condense to form chlorinated pollutants. The chlorobenzene pattern obtained by Milligan and Altwicker for denovo synthesis is different than the ones observed in our experiments [3]. In de novo synthesis, low concentration of hexaclorobenzene and pentachlorobenzene was obtained, whereas in our experiment the major chlorobenzene product is hexachlorobenzene. Zimmerman, et al. have also observed similar patterns of chlorobenzenes in incinerator flue gas after the incinerator was operated in fuel-rich conditions [4].

Based on the experimental results of this study, we can conclude that in presence of a chlorine source the metals present in sludge ash are able to chlorinate and condense the aliphatic compounds from sludge pyrolysis to form chlorinated pollutants.

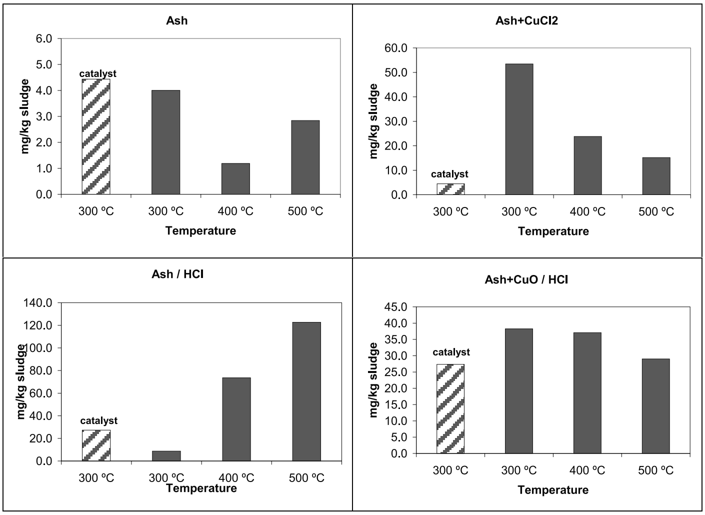

Figure 2. Total yield of chlorobenzenes, chlorophenols, chloronaphthalenes and chlorobiphenyls in four experimental series.

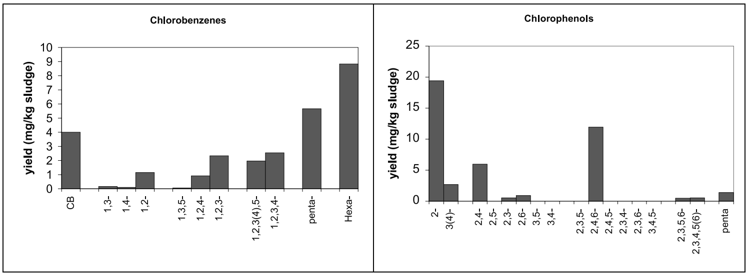

Figure 3. Isomers patterns for the Ash/HCl experiments at 400 ºC. a) chlorobenzenes b)chlorophenols

Ackowledgments

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