



Inhibiting fly ash reactivity by adding N- and S- containing compounds

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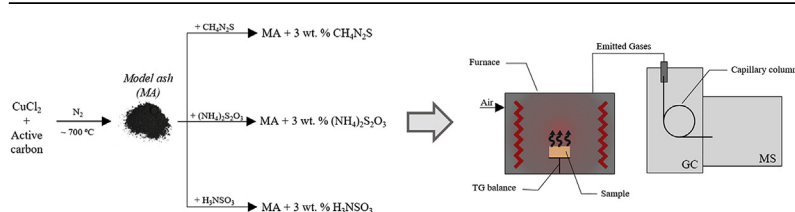
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HIGHLIGHTS

- Inhibiting fly ash reactivity by N- and S- compounds was studied in a thermobalance.
- The presence of N- and S- compounds accelerated the decomposition of the fly ash.
- The compounds evolved during TG runs was monitored by TG-MS.
- A kinetic model of a single reaction with nth order was proposed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 April 2018

Received in revised form

23 July 2018

Accepted 29 July 2018

Available online 31 July 2018

Handling Editor: Hyunook Kim

Keywords:

Inhibition

Thiourea

Ammonium thiosulfate

Amidosulfonic acid

Model ash

Thermogravimetry

ABSTRACT

The inhibitory effect of thiourea (TUA), ammonium thiosulfate (TSA) and amidosulfonic acid (ASA) on the reactivity of fly ash air was investigated using a thermobalance at different heating rates (5, 10 and 20 K min^{-1}). A model fly ash (activated carbon + 50 wt% $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, pyrolyzed at 700°C and washed) was used as carbonaceous material. Adding $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to the activated carbon led to an increased rate of decomposition with the air's oxygen. TUA and TSA behaved in a similar way, accelerating the decomposition of the model fly ash. ASA also accelerated the decomposition but to a lower extent. We postulate that the increase in decomposition rate is caused by a reaction between carbonaceous material and N- and S-containing compounds. The formation of nitrogenated and sulphured compounds was confirmed by TG-MS. A kinetic model based on a single reaction of order 0.6 showed very good correlations with all the heating rates tested in oxidant atmosphere.

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1. Introduction

Municipal solid waste (MSW) – more commonly known as garbage – consists of every item humans use in their homes, hospitals, schools and businesses, and then throw away. MSW represents around 10% of total waste generated worldwide (Eurostat, 2018).

Despite the fact that MSW generation in Europe has slowed down and stabilized at about 520 kg per capita since 2002 (Blumenthal, 2011), the volume of landfilled MSW continues to grow. Waste disposal can cause different impacts on the environment, including pollution of air, surface and water; moreover, it can present a risk to public health (Eurostat, 2010). Therefore, sound waste management is needed to protect the environment and public health, as well as to reduce demand for natural resources. In recent years, processes with low impacts on the environment and based on thermochemical methods, allowing to produce energy from waste, have developed and played a major role (Conesa et al., 2001).

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Conventional processes consist in MSW incineration, generating three potential sources of exposure to different pollutants: solid residues (bottom and fly ashes), cooling water and atmospheric emissions (fine particles and toxic pollutants). Fine particles generated in the combustion can have negative effects on human health due to their size and composition (Laden et al., 2000; Morawska and Zhang, 2002). In combustion processes, chlorinated organic pollutants, including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), can be released into the atmosphere (Baker and Hites, 2000; Ricketts et al., 2002; Jedynska et al., 2014) because residual organic carbon and high-molecular-weight compounds from incomplete combustion can result in precursor materials for *de novo synthesis*.

As reported by Vogg and Stieglitz (1986), PCDD/Fs were directly formed outside the combustion zone from carbonaceous materials, such as soot and chlorine, in the presence of volatile metals contained in the ash, which catalysed the process (e.g. copper, zinc and aluminium) at temperatures ranging from 200 to 400 °C. Based on a previous study by Stieglitz et al. (1989b), two consecutive reactions occurred: (1) The metal-ion catalysed transfer of chloride (halide) to the macromolecular structure of carbon with the formation of carbon-halide bonds and (2) the degradation of the macromolecular structure of the carbon in presence of oxygen and metal-ions as catalyst of CO₂ and volatile chlorinated aromatic compounds.

Therefore, thermal facilities require technologies that inhibit the formation of chlorinated aromatic compounds so as to reduce their emission and thus prevent toxic and detrimental environmental effects. Numerous reduction methods have been tested, e.g. photocatalytic decomposition, catalytic and as well as ozone oxidation, etc. (Lu et al., 2011, 2012; Ji et al., 2013). However, chemical inhibition is the most promising method to prevent the formation of chlorinated aromatic compounds. The inhibiting compounds used in the reaction must be efficient, non-toxic, inexpensive and environment-friendly; they must also remain active for as long as required to suppress the formation of chlorinated aromatic compounds (Ruokojärvi et al., 2001).

The ability to reduce PCDD/F formation of various inhibitors has been object of extensive research. Pandelova et al. (2005) and Wielgosinski et al. (2016) studied the suppression of PCDD/F formation using different inhibitors divided into four subgroups: metal oxides, N-compounds, S-compounds and N- and S-compounds, the latter being the most effective inhibitors. Fu et al. (2015) and Zhan et al. (2016) tested the inhibitory capacity of thiourea (TUA), amidosulfonic acid (ASA) as well as ammonium thiosulfate (TSA) and concluded that TUA had the highest inhibition efficiency. Fujimori et al. (2016) investigated the inhibitory effects and mechanisms of TUA during the formation of chloroaromatic compounds in MSW fly ash. Samaras et al. (2000) obtained that a 1 wt% of ASA was sufficient to prevent 96% of PCDD/F emission. Kuzuhara et al. (2005) found that formation of PCDD/F decreased significantly upon addition of ammonia or urea, suggesting that this suppression was caused by the competing reaction between organic compounds with NH₂· and CN₂· radicals. Nitrogen and sulfur contain free pairs of electrons making them capable of forming stable catalytic complexes with metals, delaying catalyst activity, while the ammonia compound decreases the concentration of hydrogen chloride, which is involved in the formation of PCDD/Fs (Ooi et al., 2011).

Despite the large number of studies on the reduction of PCDD/F formation using inhibiting compounds, no research was found in the literature on the inhibitory effect of N- and S-containing compounds on reactivity of fly ash in thermobalance. Therefore, the aim of this study was to examine the effect of TUA, TSA and ASA on the oxidative decomposition of model fly ash and to propose a valid kinetic model. Evolved gas products were also examined.

2. Materials and methods

2.1. Materials

In this study, an activated carbon (AC) with a very low chloride content was supplied by Merck KGaA, Darmstadt, Germany. Elemental analysis (98.72 wt% C, 0.70 wt% H and 0.58 wt% O and ash) was carried out in a Flash 1112 Series Elemental Analyser (ThermoFisher Scientific, Waltham, MA, USA). The concentration of chlorine was measured using the US EPA Methods 5050 (US EPA, 1994) and 9056A (US EPA, 2000) by oxygen combustion bomb-ion chromatography model Dionex DX-500 (ThermoFisher Scientific, Waltham, MA, USA), the average value of two duplicates being 0.03 wt%.

AC was mixed with CuCl₂·2H₂O (ThermoFisher Scientific, Waltham, MA, USA) in a proportion CuCl₂·2H₂O/activated carbon = 1 g g⁻¹. This proportion was selected based on a previous study by Stieglitz (1998), who analysed the effect of several halides in different proportions.

This mixture was pyrolyzed in a tubular reactor, which consisted in a quartz tube (80 mm internal diameter) located inside a horizontal furnace, at 700 °C for 17 min (1000 s), in a similar way to that used in previous studies (Conesa et al., 2001, 2002; Ortuño et al., 2014), and then washed with an acidified nitrate solution to remove CuCl₂ excess. To do this, 2 g of the material was mixed with 1 L of nitrate solution (0.2 mol/L NaNO₃ acidified with HNO₃) and agitated for 1 h using a mechanical shaker. Later, the suspension was filtered, giving rise to a filter cake which was subsequently washed with a dilute nitrate solution (0.01 mol/L NaNO₃ acidified with HNO₃) and was left to dry at room temperature. This procedure yields a material that presents copper chloride chemically bonded to the structure of the carbon, as was already pointed out in a previous study (Conesa et al., 2001).

The resulting material (model ash 'MA') was characterized, and the results of its composition were 89.69 wt% C, 0.87 wt% H and 9.44 wt% O and ash. The concentration of other elements (2.21 wt% O, 0.18 wt% Si, 0.18 wt% Cl and 6.50 wt% Cu) was measured using a sequential X-ray fluorescence spectrometer model Magix Pro PW2400 (PANalytical, Almelo, the Netherlands). In addition, this material was characterized in the thermobalance, and no interferences were found from the decomposition of CuCl₂.

Three different inhibiting compounds were examined for their capacity to reduce PCDD/F formation: TUA (VWR, Radnor, PA, USA), TSA (Alfa Aesar, Haverhill, MA, USA) and ASA (VWR, Radnor, PA, USA); all of them were applied in a concentration of 3 wt% of the total sample amount. These inhibiting compounds were added to the MA by adding an aqueous solution of the corresponding inhibitor at room temperature, followed by a drying stage with stirring at 70 °C. Worthy of note, the addition of inhibitors in the solid phase was also tested but it was discarded because it did not give rise to sufficiently homogeneous samples.

2.2. Thermogravimetric analysis (TGA)

The TGA was performed on a thermogravimetric analyser model STA6000 (PerkinElmer, Waltham, MA, USA). The samples were subjected to three different heating rates (5, 10 and 20 °C min⁻¹) from room temperature up to 950 °C in an oxidizing atmosphere. The flow rate of the carrier gas (synthetic air) was set at 100 mL min⁻¹. For each run, approximately 8 mg of sample was weighed.

Prior to each experiment, a blank run was performed under the same experimental conditions but using an empty crucible. Subsequently, for baseline correction, the weight values recorded for

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