FLY ASH REACTIVITY MODIFIED BY NITROGEN AND SULFUR COMPOUNDS

Soler A, Conesa JA, Ortuño N

Department of Chemical Engineering, University of Alicante, P.O. Box 99, E-03080 Alicante, Spain, email: ja.conesa@ua.es

Introduction

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.% $CuCl_2 \cdot 2H_2O$, pyrolyzed at 700 ºC and washed) was used as carbonaceous material. Adding $CuCl_2 \cdot 2H_2O$ 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 proof 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.

Materials and methods

An activated carbon (AC) with a very low chloride content was used in this study. Elemental analysis (98.72 wt.% C, 0.70 wt.% H and 0.58 wt.% O and ash) was carried out in a Thermo Finnigan Flash 1112 Series Elemental Analyser. The concentration of chlorine was 0.03 wt.%. AC was mixed with $CuCl_2 \cdot 2H_2O$ in a proportion $CuCl_2 \cdot 2H_2O$/activated carbon = 1 g·g^{-1}. This proportion was selected based on a previous study by Stieglitz [1], who analyzed the effect of several halides in different proportions.

This mixture was pyrolyzed in a tubular reactor, at 700 ºC for 17 min, in a similar way to that used in previous studies[2,3], and then washed with an acidified nitrate solution to remove $CuCl_2$ excess.

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 (Philips Magix Pro PW2400).

Three different inhibiting compounds were examined for their capacity to reduce PCDD/F formation: TUA, TSA and ASA; 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 ºC. 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.

Thermogravimetry (TGA) was performed on a Perkin Elmer thermogravimetric analyser (model STA6000). The samples were subjected to three different heating rates (5, 10 and 20 ºC min^{-1}) from room temperature up to 950 ºC 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.

To characterize the compounds evolved during TG runs, a Mettler Toledo thermobalance (model TGA/SDTA851e/LF/1600) coupled to a Pfeiffer Vacuum mass spectrometer (model Thermostar GSD301T) was used, operating in SIR mode and with electron impact ionization at 70 eV. Approximately 8 mg of sample was heated with a constant heating rate of 20 ºC min^{-1} from room temperature to 950 ºC in helium atmosphere.

Results and discussion

Prior to studying the effect of the inhibitors in the thermal decomposition of the activated carbon and model ash samples, TG runs were performed to study the evolution of weight according to temperature for pure TUA, ASA and TSA. Fig. 1 shows the results for the different heating rates tested (5, 10 and 20 ºC/min).

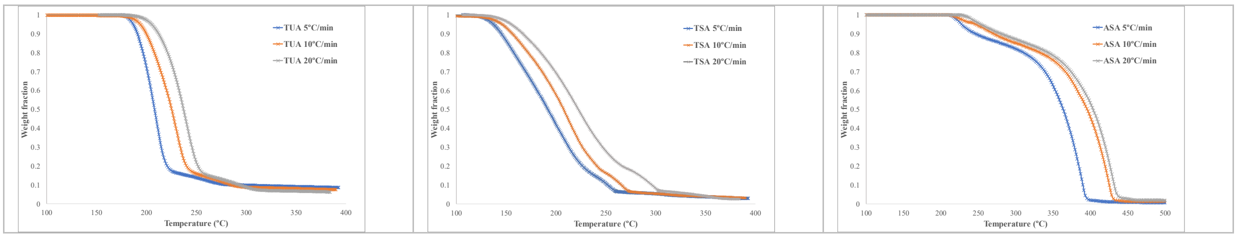


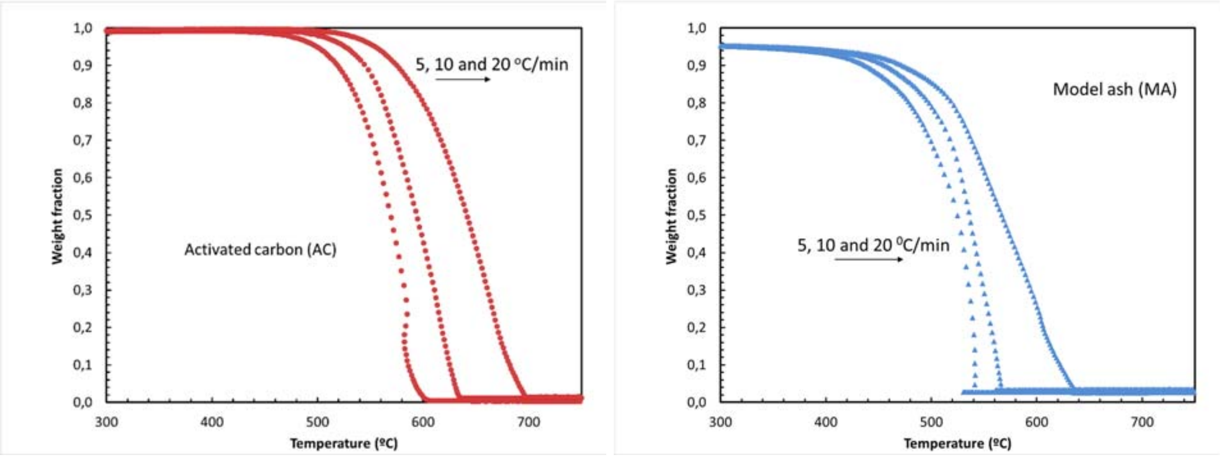
Figure 1. Thermal decomposition of the compounds used as inhibitors for PCDD/F formation: thiourea (TUA), ammonium thiosulfate (TSA) and amidosulfonic acid (ASA) at three different heating rates (5, 10 and 20 ºC min-1) in synthetic air.

All three compounds lost weight in the temperature range 150-450 ºC, but TSA and TUA lost weight much faster than ASA. Wang et al.[4] studied TUA decomposition and pointed out that TUA decomposed in carbon disulfide, isothiocyanic acid and ammonia at 187.5 - 246.2 ºC. Zhan et al.[5] confirmed that TUA decomposition set at temperatures of ca. 180 ºC and its residual weight declined fast between 200-250 ºC. Based on these studies, Fujimori et al.[6] concluded that thermal decomposition products from TUA showed a potential to inhibit chlorinated compound formation.

Based on the TG curves for TSA decomposition (see Fig. 1), it is possible to conclude that its decomposition takes place in two steps. TSA begins to decompose upon heating above 150 ºC, initially forming ammonium sulfate and resulting in ammonia, nitrogen, sulfur oxides and water when heating at higher temperatures (290 ºC approx.). Fu et al.[7] indicated that ammonium (NH^{4+}) contained in TSA tended to inhibit PCDD/F formation when released in the form of NH_3.

ASA, just like TSA, decomposes into oxidation products when heated, and thus the sulfur and nitrogen contained are converted into SO_2/SO_3 and ammonia, respectively. Samaras et al. (2000) concluded that the addition of 1 wt.% ASA to an artificial refuse derived fuel, before the combustion experiment, reduced the PCDD/F emissions by more than 95 % in combustion runs at 200 ºC.

Three dynamic experiments in synthetic air (4:1 N_2/O_2) were carried out at room temperature up to 950 ºC at different heating rates (5, 10 and 20 ºC min^{-1}) for each sample studied. Fig. 2 presents the experimental weight loss variation according to temperature in dynamic experiments. In all TG curves, the weight fraction is defined as the ratio between solid mass at any time and initial solid mass.



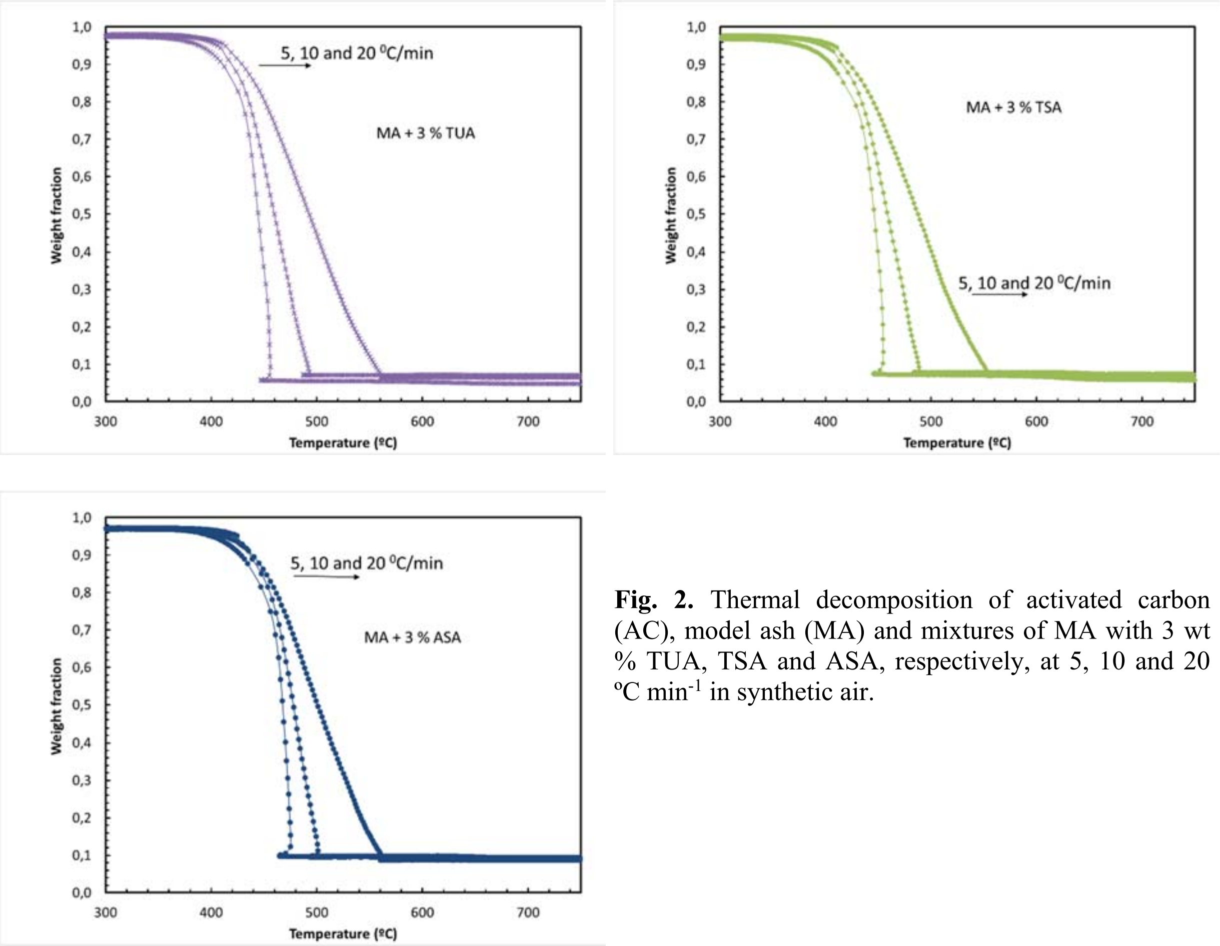


Fig. 2. Thermal decomposition of activated carbon (AC), model ash (MA) and mixtures of MA with 3 wt % TUA, TSA and ASA, respectively, at 5, 10 and 20 ºC min^{-1} in synthetic air.

A run mixing AC with TUA was also carried out (not shown in the Figures), to check whether there was a possible interaction; the decomposition of carbonaceous material was not influenced, however, by the presence of the inhibitor at any of the studied heating rates. This indicates that the interaction was mediated by the CuCl2 present in the MA or at least that the presence of C-Cl bonds was necessary.

For a better comparison, Fig. 3 shows the TG curves corresponding to the degradation runs at 5 ºC min^{-1}. The maximum mass loss rate -commonly used in the literature to characterize char reactivity- occurred at different temperatures for the different samples. The addition of $CuCl_2$ accelerated thermal decomposition (i.e. the MA curve was found to be at lower temperatures compared to the AC curve), in such a way that a temperature reduction of a maximum decomposition rate of almost 55 ºC was observed for MA. The presence of traces of copper and other metals has been found to catalyse the oxidative degradation process of materials such as AC. In this way, several authors [1,8,9] proved the accelerating effect of the presence of metal chlorides, acting as catalysts in the decomposition of AC.

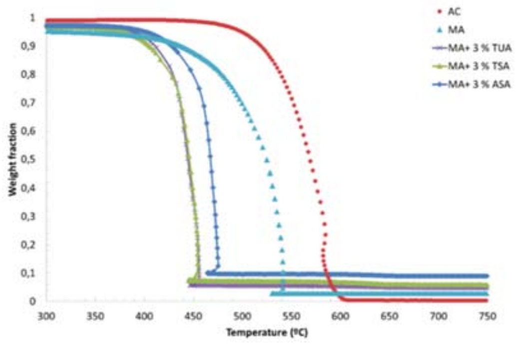


Fig. 3. Comparison of TG runs of the different materials performed at 5 ºC/min in synthetic air.

Fig. 3 also shows the results of the runs performed by mixing MA with 3 wt.% of TUA, TSA and ASA, respectively. Surprisingly, with these mixtures, decomposition greatly accelerates, displacing the temperature of the maximum decomposition rate at ca. 80-100 ºC. In this way, the main decomposition step is produced within the temperature range of 430-480 ºC. MA with 3 wt.% of TUA and MA with 3 wt.% of TSA present similar results, however ASA seems to have a less significant effect on decomposition. These results agree with the decomposition of pure inhibitor compounds shown in Fig. 1. TUA and TSA decompose within the temperature range of 200-300 ºC, but ASA decomposition takes place at a higher temperature, so this may be why ASA is less reactive.

Conclusions

After carrying out the thermal decomposition of all the samples in synthetic air in thermobalance, we can conclude that a potential reaction of the sulfur or the nitrogen to the carbonaceous matrix caused the acceleration of the thermal decomposition process, given that the decomposition of the mixtures (MA with 3 wt.% TUA, MA with 3 wt.% TSA and MA with 3 wt.% ASA) occurred at a surprisingly much faster rate than the decomposition of MA. In this way, the main decomposition step for the mixtures was produced within the temperature range 430-480 ºC, leading to a reduction in temperature of the maximum decomposition rate of almost 80-100 ºC. The inhibitor compounds accelerated the thermal decomposition of carbonaceous material in this order: ASA<TUA<TSA. Therefore, TSA and TUA can be better inhibitor compounds than ASA. The emission of HCN, H2S and SOx in the decomposition runs carried out in a TG-MS confirmed the possible reaction of the carbonaceous matrix with the N- and S- containing compounds, preventing the future production of chlorinated organic compounds.

Acknowledgements

This work was supported by the CTQ2016-76608-R project from the Ministry of Economy, Industry and Competitiveness (Spain), and the UAUSTI17-07 grant from University of Alicante (Spain).

References

1. Stieglitz L. (1998) *Environ Eng Sci* 15(1):5–18
2. Conesa JA, Fullana A, Font R. (2001) *J Anal Appl Pyrolysis* 58–59:553–68
3. Ortuño N, Conesa JA, Moltó J, Font R. (2014) *Environ Sci Technol* 48(14):7959–65
4. Wang S, Gao Q, Wang J (2005) *J. Phys. Chem. B*, 109 (36): 17281–17289
5. Wang SJ, He PJ, Lu WT, Shao LM, Zhang H. (2016) *Sci Rep* 6(March):1–11
6. Fujimori T, Nakamura M, Takaoka M, Shiota K, Kitajima Y. (2016) *J Hazard Mater* 311:43–50
7. Fu JY, Li XD, Chen T, Lin XQ, Buekens A, Lu SY. (2015) *Chemosphere* 123:9–16
8. Stieglitz L, Zwick G, Beck J, Bautz H, Roth W (1989) Chemosphere 19(1–6):283–90
9. Luijk R, Govers HAJ. (1992) *Chemosphere* 25(3):361–74