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Destruction of Organic Compounds on Fly Ash: A Kinetic Study Using TOC as Indicator Parameter

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1. Introduction

Since the detection of PCDDs and PCDFs in the emissions of municipal solid waste incinerators, the formation and destruction reactions of these compounds have been intensively studied[1]. It seems that especially the cold zones of the incineration plants are involved in this kind of reactions. The kinetic study of PCDDs' and PCDFs' formation and destruction reactions requires a big analytical effort, as there are 75 PCDD and 135 PCDF isomers, and several experimental data are needed to compute the kinetic parameters. Moreover, apart from PCDDs and PCDFs, a great number of organic compounds is present on fly ash and their qualitative and quantitative determination is a very difficult task.

In the present study we report the results of batch experiments on the combustion rate of organic compounds at different temperatures. The reagents' concentrations are measured as Total Organic Carbon (TOC), which is a sum-parameter. This is possible as we recently set up a methodology for a quick determination of TOC directly on the solid matrix[2]. Experiments are performed on fly ash from MSW incinerators and synthetic mixtures of pure compounds on silica gel as a model support. For cost reasons, for the preliminary studies we chose the unchlorinated parent compounds of PCDFs and PCBs, dibenzofuran and biphenyl, together with activated carbon.

2. Experimental and results

Silica gel (Merck, grade 60, 230-400 Mesh ASTM), dibenzofuran and biphenyl (Janssen, purity 99+% and 99% respectively) are used without treatment.

Total organic carbon is measured using a Dorhmann instrument assembled with the Standard Module, DC-90, the Purgeable Organics Module, PRG-1, and the Sludge Sediment Sampler Accessory, S/SS. Details of the analytical method are already reported[2,3].

Fly ash was collected from the hopper of the ESP of a modern waste incinerator and used for the experiments without further treatment.

The synthetic mixtures with known weighting fractions are prepared by mixing the organic compound directly with the model support. The mixture is homogenized using a ball mill (Retsch, Model S1) operating with five balls (3 with ϕ = 10 mm and 2 with ϕ = 20 mm) at 80 rpm for 25 min.

The thermal treatment of the samples is performed in a closed muffle furnace, internal

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volume 9 1, temperature determined to ±5°C, with oxygen being present in great excess. The results of the tests performed on fly ash and synthetic mixtures are reported in Tables 1-3 as the variation of TOC as a function of time at different temperatures.

Table 1. Oxidation of fly ash: TOC (ppm) - time data at different T.
At t=0, TOC = 2230 ppm.

t(min) T(°C)	30	60	120	180	240	360	480
150	2210	2230	2225	2215	2210	2220	2210
200	2180	2160	2120	2100	2085	2060	2055
225	2160	2085	2020	1940	1890	1890	1870
250	2120	2045	1915	1855	1700	1630	1600
275	2105	1955	1815	1710	1655	1605	1575
300	2035	1860	1695	1500	1370	1215	1110
325	2005	1785	1600	1405	1140	1015	910
350	1960	1710	1400	1165	1005	775	695
375	1505	1100	760	565	490	450	460
400	1200	765	355	250	155	110	105
500	1075	650	300	185	135	105	105
600	985	580	310	175	130	105	100

Table 2. Oxidation of mixtures of dibenzofuran (DBF) and biphenyl (BPh) with silica: TOC (ppm) - time data at different T.
At t = 0, TOC_{DBF} = 2030 ppm, TOC_{BPh} = 2030 ppm

t(min) T(°C)	30	60	120 D	180 B	240 F	360	480	30	60	120 B	180 P	240 h	360	480
50		2030	2045	2025	2000	1965	1980	1760	1755	1740	1740	1730	1700	1700
68		1970	1950	1750	1685	1675	1640							
75		1860	1725	1600	1465	1230	1045	1730	1650	1545	1435	1345	1265	1050
100		1760	1495	1285	1110	815	595	1650	1555	1340	1170	1015	760	555
125		1640	1310	1050	840	580	370	1505	1360	895	560	455	205	
150		1270	790	505	315			1385	1050	650	355	210		
200	1505	910	425					955	395	115				

3. Discussion

The interpretation of the experimental data for fly ash is quite difficult, as the plot of TOC vs time at a given temperature isn't of immediate comprehension.
Therefore the oxidation of mixtures of pure organic compounds with silica as model support is studied to help in finding a reasonable interpretation for the fly ash behavior. The actual results show that the oxidation reactions of dibenzofuran, DBF,

biphenyl, BPh, and carbon are pseudo first order reactions. The rate constants (min^{-1}) are shown in Figure 1a-b, as Arrhenius plots.

Table 3. Oxidation of mixtures of activated carbon with silica:
TOC (ppm) - time data at different T. At t = 0, TOC = 1800 ppm

t(min) T(°C)	30	60	90	120	150	180	240	360	480
325	1805	1785		1780		1780	1800	1770	1765
350	1785	1725		1705		1685	1605	1505	1480
375	1680	1580		1390		1190	1170	790	625
400	1660	1535		1320		1095	960	655	490
500	1600	1400		1100		860	650	405	270
550	1500	1370		780		580	265		
600	1290	935	615	380	260	240			

The DBF and BPh reactivity is almost the same. In any case, two mechanisms seem to work. According to the calculated apparent activation energies (Table 4), at lower temperatures a surface reaction, i.e. the chemical step, seems to be the rate-limiting one whereas at higher temperatures the reaction seems to be diffusion controlled.
Bearing in mind that TOC is a sum-parameter, i.e. every organic compound present on fly ash contributes to its value, these results on pure compounds suggest that the plot of TOC vs time for fly ash may be interpreted as the sum of first order curves.
To test this hypothesis, the oxidation reaction of a dibenzofuran-biphenyl mixture on silica is performed at different temperatures. The deconvolution of the TOC vs time curves leads to a sum of two exponentials. The parameters of the two exponentials are in a very good agreement with the kinetic parameters obtained for the pure compounds on silica. Results are not reported here.
The procedure is successfully applied to the fly ash curves. Also in these cases, a good fitting is achieved with two exponentials for every temperature. The initial concentrations and the pseudo first order rate constants for two unknown reactions (R1 and R2) are obtained. Arrhenius plots for both constants are reported in Figure 1c, showing a fairly good linear correlation. Apparent activation energies for the two pseudo-first order reactions (Table 4) are of the same order of magnitude as those for pure compounds in the temperature range where diffusion is the rate-limiting step.

4. Conclusions

Experiments carried out show that TOC is a good and quick parameter for the measure of carbon content variations on fly ash during the reaction with oxygen. It has been demonstrated[3] that the inorganic carbon content of fly ash is lower than 5% of the total carbon present. The observed carbon content variations are therefore TOC variations.
On the basis of the kinetic parameters obtained for pure compounds, fly ash reactions seem to be diffusion controlled. For a deeper understanding of the mechanism, runs on a continuous flow apparatus will be performed.

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Table 4. Activation parameters: $\Delta E^{\ddagger}$ (cal mol^{-1}) and ln A.

	DBF		BPh		Carbon		Fly Ash	
	50-75°C	75-200°C	50-100°C	100-200°C	325-375°C	375-600°C	R1	R2
$\Delta E^{\ddagger}$	25000	6060	16200	7650	61900	7960	11100	3130
sd	2760	475	3910	636	5290	1300	2840	1190
ln A	29.4	8.76	16.0	4.39	42.0	-8.69 E-3	1.35	-1.69
sd	4.12	0.602	5.67	0.775	4.28	0.877E-3	2.31	0.972

Figure 1. Arrhenius plots for: (a) DBF, BPh; (b) carbon; (c) fly ash.
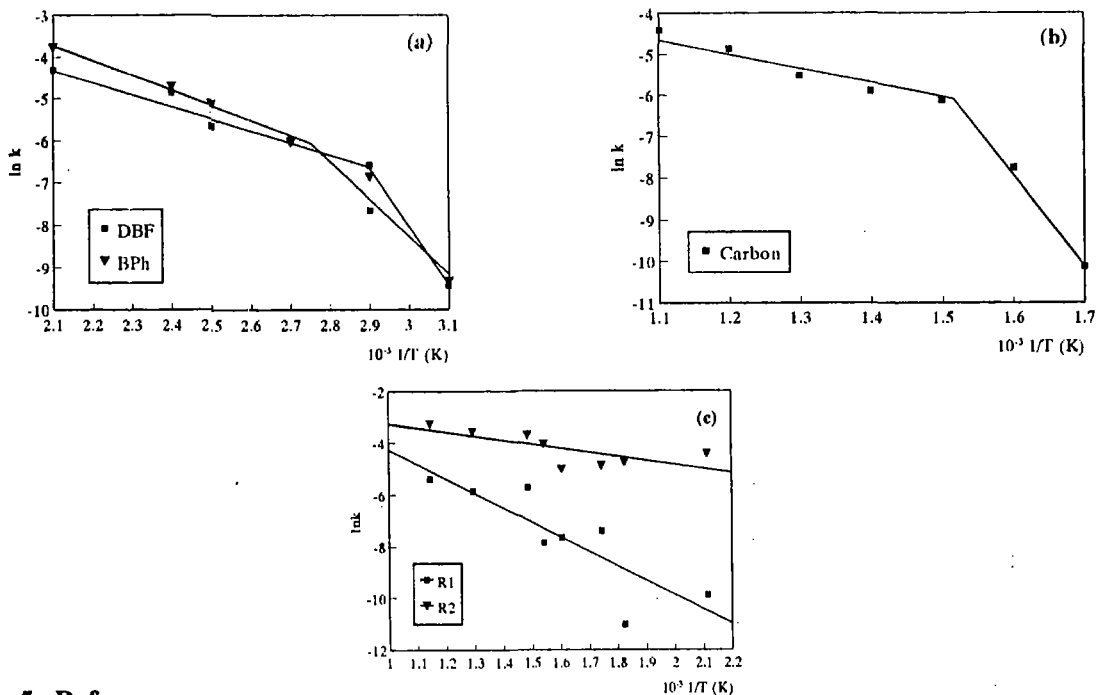
5. References

1 For a short review of general references, see: Lasagni M, Moro G, Pitea G, Stieglitz L. *Chemosphere* 1991;23:1245-53.
2 Lasagni M, Cosentino U, Moro G, Pitea D. In: Bonati L, Cosentino U, Lasagni M, Moro G, Pitea D, Schiraldi A, eds. *Trends in Ecological Physical Chemistry*. Amsterdam: Elsevier, 1993:253-74.
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