

## KINETICS OF MSWI FLY ASH THERMAL DEGRADATION. MECHANISM OF NATIVE CARBON GASIFICATION

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### Introduction

Present data clearly indicate that polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) are formed after the combustion zones of MSWIs, involving low temperatures and probably two mechanisms on fly ash surface: (i) formation from precursors, *i.e.* chloroaromatic molecules such as polychlorobenzenes and polychlorophenols; (ii) *de novo* synthesis, starting from more or less complex non-chlorinated molecules, native carbon included, and a source such as chlorine, hydrochloric acid or inorganic chlorides. In both cases, fly ash can act as a catalyst and oxygen is essential. In nitrogen, no PCDD or PCDF forms whereas, already with 1% oxygen, their formation is observed [1, 2].

In a previous work [3], the native carbon thermal degradation of four fly ash samples from ESP hoppers was studied in batch experiments in air. The fly ash were taken from three MSWIs in Denmark and Italy. A lump parameter, Total Organic Carbon (TOC), was used to measure the decrease of reagent concentration in time [4]. The TOC vs time data were well fitted by deconvolution treatment with a sum of two first-order reactions, Ri and Rj:

$$\text{TOC} = E_i \exp(-k_i t) + E_j \exp(-k_j t)$$

At time  $t = 0$ ,  $E_i + E_j = \text{TOC}^0$ ;  $k_i$  and  $k_j$  are the rate constants of Ri and Rj reactions; conventionally, the higher rate constant is called  $k_j$ . Both Ri and Rj were carbon oxidation reactions to CO<sub>2</sub>, the oxidized carbon being not from adsorbed organic compounds but from the native carbon matrix of MSWI fly ash. The presence of two combustion reactions was also shown in a previous study performed by Differential Scanning Calorimetry [5].

The key experimental information for the formulation of a reaction scheme is the temperature dependence of the pre-exponential  $E_i$  and  $E_j$  parameters.  $E_i$ , related to the slower Ri process, decreased, while  $E_j$ , related to Rj, increased with increasing temperature; moreover, at each temperature, their sum is almost coincident with the initial TOC value,  $\text{TOC}^0$ .

On these bases, a generalized kinetic model for fly ash native carbon oxidation was developed. The final reaction scheme was then validated on raw fly ash from the hoppers of the Italian MSWI.

### Materials and Methods

The thermal treatment of fly ashes from different MSWIs was performed in batch experiments in air. The samples were thermally treated in a closed muffle furnace, internal volume 9 L, temperature determined to  $\pm 5^\circ\text{C}$ , with oxygen present in great excess. The reaction temperature ranged from 150 to 700°C. The reaction times varied from 5 to 1440 minutes. At each kinetic time, the residual TOC content of the sample was determined [4].

## Results and Discussion

Carbon gasification can result from both of the two following processes or their combination [6]. One possible process is the direct impingement of oxygen onto vacant carbon active sites, leading to some immediate carbon gasification. In the second process, molecular oxygen is first chemisorbed on carbon (uncatalyzed adsorption) or metallic (catalyzed adsorption) sites and then the oxygenated complexes are oxidized mainly to gaseous products CO and CO<sub>2</sub>.

As the TOC loss, as a function of time and temperature, is the result of two uncatalyzed simultaneous processes [3], the proposed generalized reaction scheme is:



Equations 1 and 3 describe the activated oxygen chemisorption with intermediate surface oxygen complexes formation and their subsequent desorption as gaseous CO<sub>2</sub>. Equation 2 is the direct impingement of oxygen onto active carbon sites and involves adsorption.

The rate equations for C and C(O) are expressed by equations 4 and 5 (excess oxygen is used)

$$d[\text{C}]/dt = -(k_1 + k_2) [\text{C}] + k_{-1} [\text{C(O)}] \quad (4)$$

$$d[\text{C(O)}]/dt = k_1 [\text{C}] - (k_{-1} + k_3) [\text{C(O)}] \quad (5)$$

where:

$$k_1 = k_1^0 [\text{O}_2]^{n_1}, k_2 = k_2^0 [\text{O}_2]^{n_2}, k_3 = k_3^0 [\text{O}_2]^{n_3}.$$

The system of differential equations 4 and 5 is solved analytically with the boundary condition [C(O)] = 0 at t=0; thus [C]<sub>0</sub>, i.e. [C] at t=0, is equal to TOC<sup>0</sup>. Moreover, k<sub>-1</sub> = 0, if reaction 1 is assumed to be the dissociative oxygen chemisorption. Thus, the TOC decrease with time is:

$$\frac{\text{TOC}}{\text{TOC}^0} = \frac{[\text{C}] + [\text{C(O)}]}{[\text{C}]_0} = \frac{k_1}{(k_1 + k_2 - k_3)} \exp(-k_3 t) + \frac{(k_2 - k_3)}{(k_1 + k_2 - k_3)} \exp[-(k_1 + k_2) t]$$

For the four fly ashes, the rate constants, k<sub>1</sub>, k<sub>2</sub>, and k<sub>3</sub> together with activation and thermodynamic parameters are calculated. In Table 1 thermodynamic parameters are reported.

Table 1 - Thermodynamic (Eyring Equation) Parameters for Elementary Reactions.

	- ΔS* (kJ K <sup>-1</sup> mol <sup>-1</sup> )			ΔH* (kJ mol <sup>-1</sup> )		
	k <sub>1</sub>	k <sub>2</sub>	k <sub>3</sub>	k <sub>1</sub>	k <sub>2</sub>	k <sub>3</sub>
<b>FA1</b>		0.285 ± 0.008	0.30 ± 0.01		26 ± 5	26 ± 8
<b>R<sup>2</sup></b>		0.87	0.73			
<b>FA2a</b>	0.284 ± 0.009	0.225 ± 0.002	0.30 ± 0.01	22 ± 5	60 ± 1	29 ± 7

$R^2$	0.66	0.99	0.70			
<b>FA2b</b>		0.288 ±0.007	0.26 ±0.08	27 ±5	67 ±12	
$R^2$		0.92	0.91			
<b>FA3E</b>	0.272 ±0.006	0.218 ±0.005	0.291 ±0.004	30 ±4	61 ±3	39 ±3
$R^2$	0.93	0.99	0.98			
<b>FA3O</b>	0.26 ±0.02	0.21 ±0.01	0.28 ±0.01	40 ±10	65 ±8	47 ±9
$R^2$	0.95	0.99	0.96			
<b>FA3E</b>	0.27 ±0.02	0.21 ±0.02	0.28 ±0.01	33 ±13	65 ±10	44 ±8
$R^2$	0.68	0.93	0.91			

Figure 1 shows the experimental and the calculated dependence on time of the C and C(O) concentrations as well as of their sum, all expressed as TOC, at two selected temperatures. It can be seen that also at lower temperatures both the formation of intermediate complexes, equation 1, and the direct CO<sub>2</sub> formation, equation 2, are practically complete in about 8 hrs. At the highest times and the lowest temperature the residual TOC content is entirely due to the complex concentration. At the highest temperature the residual TOC is the result of the balance between C(O) formation and oxidation. So, the intermediate C(O) oxidation is the rate-determining step of the overall process. Finally, it can be observed that the complex oxidation is almost completed in 24 hrs at 600°C.

To deepen the validation and to obtain useful information on the whole thermal process the kinetic model was applied to fly ash collected from a modern waste incinerator hoppers in Milan. The sampling points were: a) first boiler hopper; b) second boiler hopper; c) third boiler hopper; d) fourth boiler hopper; e) heat exchanger hopper; f) economizer hopper; g) first ESP hopper; h) second ESP hopper. The sampling was performed in 5 days.

We conclude that the nature of the interaction between native carbon and the fly ash surface is the key factor for C(O) complex formation and gasification. We are investigating the hypothesis that a molecular event involving oxygen and a metallic-like site takes place on the fly ash surface.

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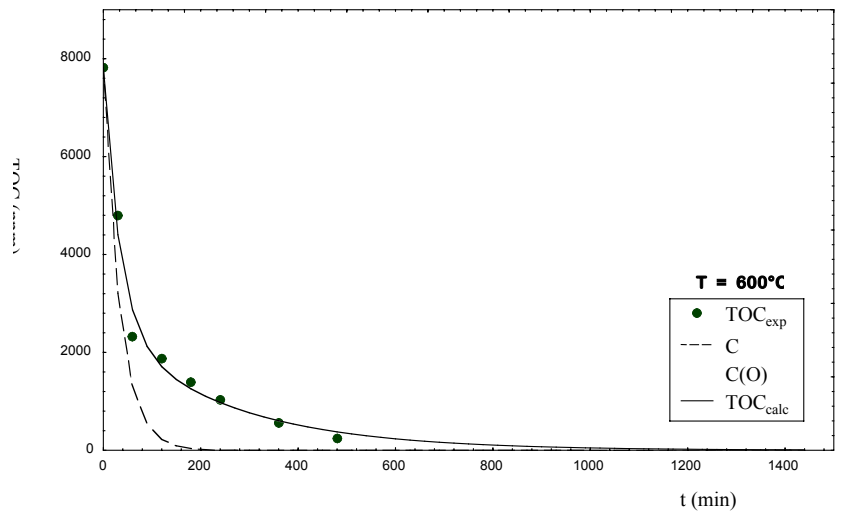


Figure 1 - Experimental and calculated TOC along with the dependence on time of C and C(O) at 250°C and 600°C for FA2b.

