

Supporting Information

Table S1. Incremental ratios for PCDD and PCDF values, and initial formation rates.

The incremental ratios are calculated as

$$\frac{[\text{PCDD}/\text{F}]_{t_2} - [\text{PCDD}/\text{F}]_{t_1}}{t_2 - t_1} \text{ or } \frac{\sum [\text{PCDD}/\text{F}]_{t_2} - \sum [\text{PCDD}/\text{F}]_{t_1}}{t_2 - t_1}.$$

$\sum \text{PCDD}/\text{F}$ indicates the sum of PCDD and PCDF. For $t = 0$, PCDD/F were considered equal to zero.

The initial formation rate is analytically calculated from the model of eq. 10 in $\text{ng g}^{-1} \text{min}^{-1}$ using an average MW from each set of experiments at the same temperature.

t_2 (min)	T (°C)				
	280	320	350	380	415
PCDF (nmoles·g⁻¹ OXS_{oot} · min⁻¹)					
10	0.01	0.06	0.35	1.14	1.54
30	0.16	0.51	0.75	0.54	0.53
60	0.31	0.54	0.62	0.86	-0.05
120	nm	0.19	0.23	-0.09	nm
180	0.13	-0.05	0.12	0.12	nm
480	0.04	nm	nm	nm	nm
PCDD (nmoles·g⁻¹ OXS_{oot} · min⁻¹)					
10	nm	0.01	0.02	0.05	0.08
30	0.02	0.07	0.09	0.07	0.06
60	0.03	0.07	0.09	0.13	-0.01
120	nm	0.04	0.05	-0.01	nm
180	0.02	-0.01	0.01	0.02	nm
480	0.01	nm	nm	nm	nm
$\Sigma \text{PCDD}/\text{F}$ (ng·g⁻¹ OXS_{oot} · min⁻¹)					
10	5.9	23.8	106.9	322.8	491.7
30	75.9	214.0	332.1	246.8	232.5
60	138.8	251.0	276	389.7	-23.7
120	nm	95.2	110.0	-40.6	nm
180	59.3	-22.6	50.8	58.1	nm
480	20.4	nm	nm	nm	nm
Initial PCDD/F rate from eq. 10 (ng·g⁻¹ OXS_{oot} · min⁻¹)					
0	103	253	332	522	647

nm = not measured

Table S2 – PCDD/F concentrations at $t_{\max}$ and at crossing times, t_{cross} , calculated from eq. 10.

T	$t_{\max}$	[PCDD/F]_{max}	t_{cross}	[PCDD/F]_{cross}
°C	(min)	(nmol (PCDD/F)/g)	(min)	(nmol (PCDD/F)/g)
280	1672	51.9	910	51.4
320	546	49.7	241	47.7
350	533	75.1	254	72.1
380	241	53.5	118	51.8
415	153	40.2	67	37.6

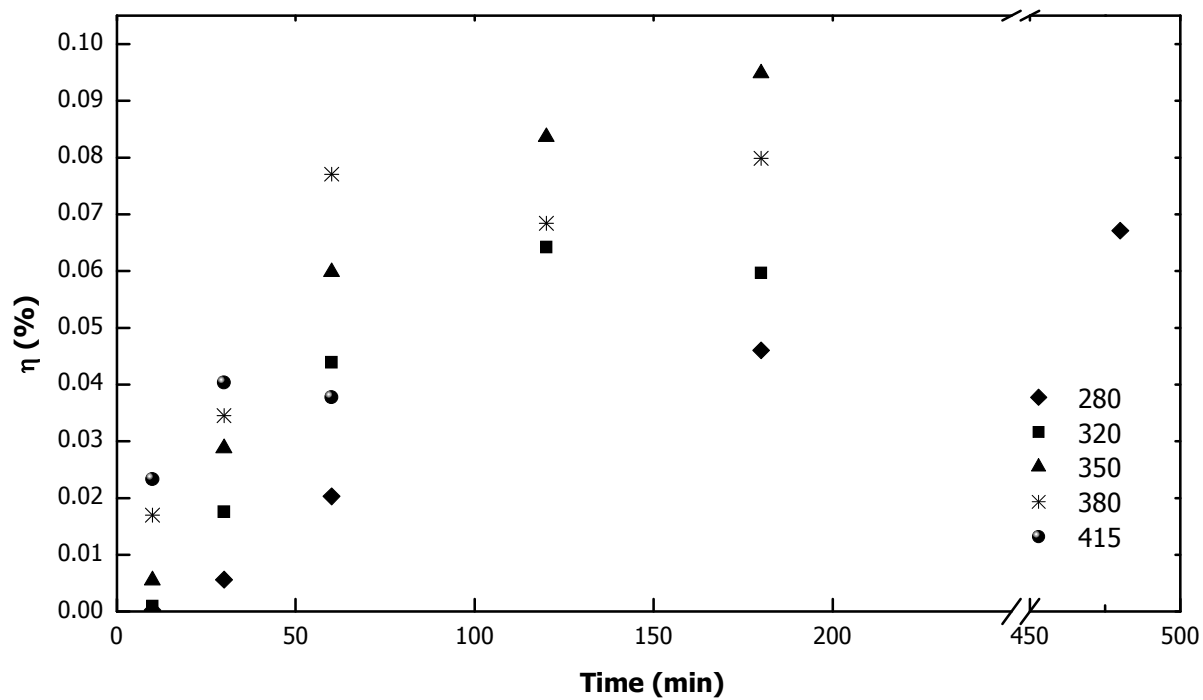


Figure S1. Carbon conversion efficiency, η , to Σ PCDD/F for experiments #1-23.

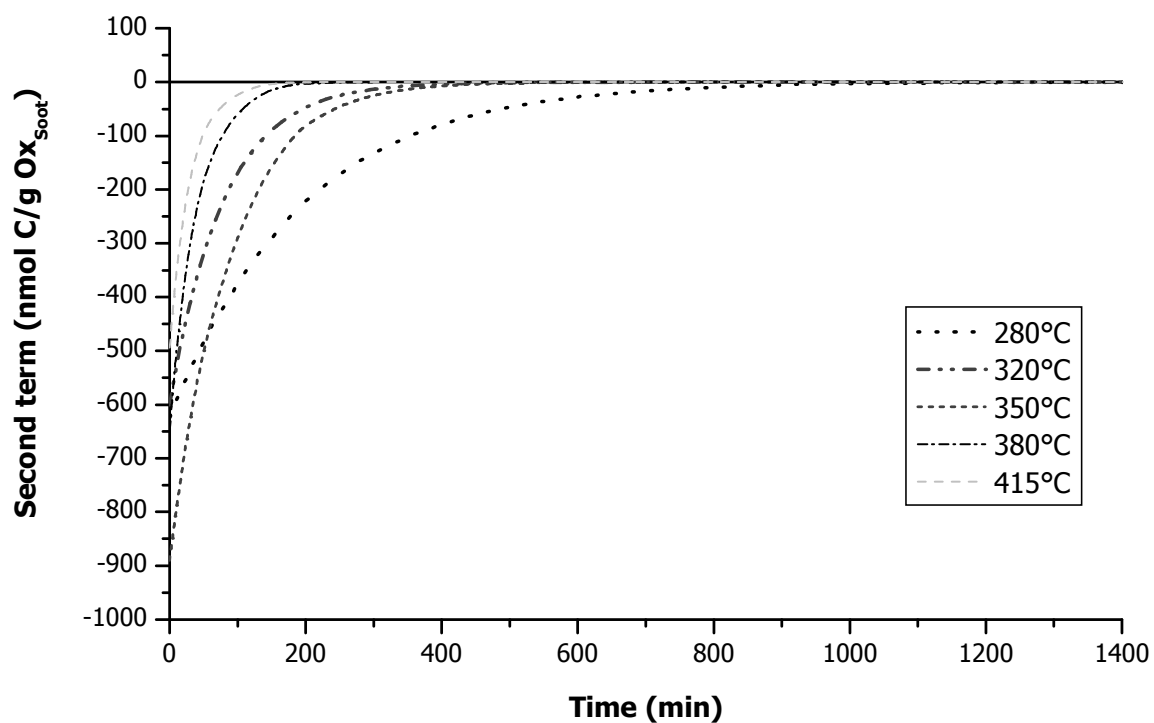


Figure S2. Calculated dependence on time of the second term in eq. 10, indicating the relative role of formation reactions.

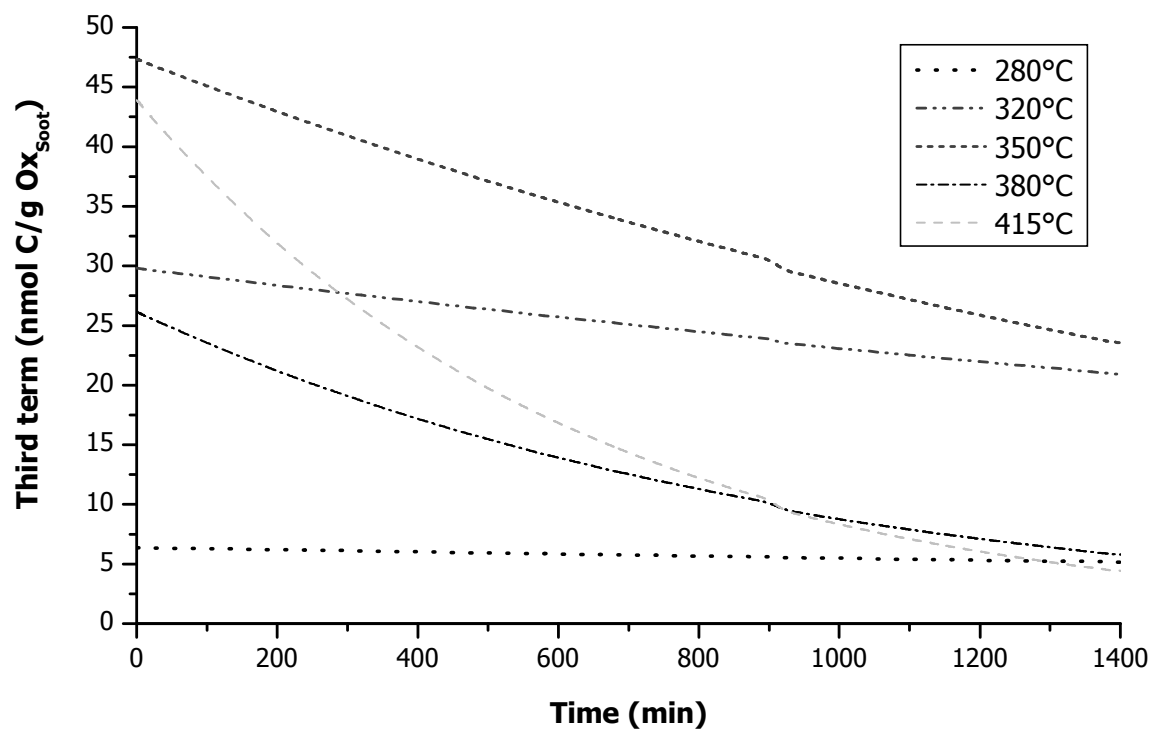


Figure S3. Calculated dependence on time of the third term in eq. 10, indicating the relative role of desorption and decomposition reactions.