

Inhibition effect of polyurethane waste in PCDD/F formation

Moreno A.I., Font R., Conesa, J.A., Gómez-Rico, M.F.

Department of Chemical Engineering, University of Alicante, P.O. Box 99, E-03080 Alicante, Spain

Introduction

It has been tested that the addition of inorganic sulphur and nitrogen compounds to the fuel prior to the combustion is an effective and low cost prevention technique of PCDD/F formation¹. On the other hand, gaseous NH₃ has been also found as an effective inhibitor of PCDD/F formation²⁻³. The first stage of combustion is a pyrolysis process, in which the ammonia formation is high if the nitrogen content of the fuel is significant⁴. The objective of the present work is the study of the inhibition effect of polyurethane waste addition into the fuel and the injection of polyurethane pyrolysis gases (containing high ammonia content and other N-compounds), in the formation of toxic compounds (mainly PCDD/Fs) during combustion of a mixture of sawdust and PVC.

Materials and methods

Three different experiments were carried out in a laboratory-scale horizontal tubular quartz reactor to compare the effect of different inhibitors. The fuel used was sawdust with an addition of 5 wt.% of PVC (*M0 experiment*). The first inhibitor studied was the addition of 5 wt.% of polyurethane foam (material with high N content) to the mixed fuel (*M1 experiment*). The second inhibitor studied was the addition of polyurethane pyrolysis gases (*M2 experiment*). Pyrolysis of polyurethane foam was carried out to obtain the gaseous NH₃ and other compounds, and these pyrolysis gases were mixed with air for the combustion, in a proportion of approximately 24% of pyrolysis gases and 76% air.

The experimental apparatus has previously been described in detail by Font et al⁵. A small sample (around 60 mg for analysis of volatile, semivolatile compounds, chlorobenzenes and chlorophenols) was introduced inside a reactor with controlled temperature, and in the latter part of the reactor some quartz rasching rings are placed, which promote the secondary cracking reactions. These set-ups were carried out under substoichiometric conditions to promote the formation of products of incomplete combustion.

The sampling of gases and volatile compounds was carried out with a Tedlar® bag. The gas stream passed through an adsorptive trap containing XAD-2 resin to retain the semivolatile compounds, chlorobenzenes, chlorophenols and PCDD/Fs. For analysis of PCDD/Fs, between 6-20 continuous combustions were carried out (being retained their emissions by the same XAD-2 resin), in order to amplify the signal in the analysis.

Methodologies of analysis:

The gases collected in the Tedlar® bags were analysed by gas chromatography: CO and CO₂ were analysed by GC-TCD and aliphatic hydrocarbons C₁-C₆ (with low boiling points) were analysed by GC-FID.

The extractions of different compounds retained in the resin were carried out with an Accelerated Solvent Extraction (ASE) according to U.S. EPA Method 3545.

The analysis of PAHs was carried out by GC-MS according to U.S. EPA 8270D method and the analysis of PCDD/Fs were performed by HRGC-HRMS according to U.S. EPA Method 1613

Results and discussion

Table 1 shows the results corresponding to the formation of carbon oxides and the main light hydrocarbons. It can be observed that the CO/(CO + CO₂) ratio is lower in the experiment M2, carried out with the gases of pyrolysis (higher amount of gaseous NH₃). It is noteworthy the decrease of the yield of some main light hydrocarbons in the experiments with inhibitors, although the greatest decrease was in experiment M2 (combustion with an amount of pyrolysis gases).

Table 1: Main volatile gases evolved in combustion experiments

COMPOUND	mg compound/kg dry sample		
	M0 (wood/PVC) (n = 4)	M1 (wood/PVC/PU) (n = 4)	M2 (wood/PVC/PU pyrolysis gases) (n = 7)
CO ₂	1607000 ± 48000	1655000 ± 249000	2076000 ± 200000
CO	200000 ± 49000	187000 ± 21000	19000 ± 18000
Ratio CO/(CO + CO ₂)	0.11 ± 0.02	0.10 ± 0.01	0.009 ± 0.008
<i>Main light hydrocarbons:</i>	M0 (wood/PVC) (n = 3)	M1 (wood/PVC/PU) (n = 3)	M2 (wood/PVC/PU pyrolysis gases) (n = 3)
Methane	18400 ± 1300	14600 ± 3400	1900 ± 1800
Ethene	1800 ± 900	500 ± 100	300 ± 600
Acetylene	2300 ± 200	20 ± 40	400 ± 100
Benzene	5900 ± 600	1500 ± 1000	700 ± 500

Table 2 shows the emission concentrations of the PAHs obtained. Emissions of the PAHs studied were also lower in the experiments carried with the inhibitors. Naphthalene, acenaphthylene, phenanthrene and fluoranthene were the majority PAHs obtained in all cases. Moreover, a decrease of their formation is observed in M1 (wood/PVC/PU) and M2 (wood/PVC/PU pyrolysis gases) experiments.

Table 2: 16 EPA priority PAHs evolved in combustion experiments

COMPOUND	mg compound/kg dry sample		
	M0 (wood/PVC) (n = 3)	M1 (wood/PVC/PU) (n = 3)	M2 (wood/PVC/PU pyrolysis gases) (n = 3)
Naphthalene	193.8 ± 94.6	67.8 ± 26.0	83.9 ± 53.0
Acenaphthylene	99.1 ± 66.6	21.7 ± 13.5	26.0 ± 19.6
Acenaphthene	0.4 ± 0.4	nd	nd
Fluorene	1.0 ± 0.5	nd	nd
Phenanthrene	134.5 ± 79.8	31.3 ± 15.7	26.2 ± 19.6
Anthracene	14.5 ± 7.4	2.2 ± 0.6	1.6 ± 1.2
Fluoranthene	43.1 ± 29.7	9.0 ± 4.2	8.5 ± 7.6
Pyrene	28.6 ± 13.0	3.5 ± 1.7	6.0 ± 5.4
Benzo(a)anthracene	8.9 ± 5.1	1.1 ± 0.6	0.3 ± 0.1
Chrysene	22.6 ± 10.8	3.3 ± 1.7	1.1 ± 0.3
Benzo(b)fluoranthene	9.1 ± 3.1	1.8 ± 0.5	2.6 ± 1.7
Benzo(k)fluoranthene	4.4 ± 1.6	0.7 ± 0.6	0.9 ± 0.7

COMPOUND	mg compound/kg dry sample		
	M0 (wood/PVC) (n = 3)	M1 (wood/PVC/PU) (n = 3)	M2 (wood/PVC/PU pyrolysis gases) (n = 3)
Benzo(a)pyrene	4.0 ± 1.4	0.41 ± 0.04	0.6 ± 0.5
Indeno(1,2,3-cd)pyrene	3.4 ± 2.8	0.04 ± 0.07	0.3 ± 0.4
Dibenz(a,h)anthracene	0.4 ± 0.5	nd	nd
Benzo(g,h,i)perylene	1.6 ± 0.9	0.06 ± 0.06	0.2 ± 0.4
Total 16 PAHs	569.5	142.9	158.0

Table 3 shows the emission concentrations of PCBzs and PCPhs. A slightly decrease of formation of chlorobenzenes was observed in experiment M1 (with addition of polyurethane foam to the fuel). However, comparing M0 (combustion of wood with 5 wt.% of PVC) and M2 (combustion of wood with 5 wt.% of PVC and with PU pyrolysis gases) experiments, the yields obtained were very similar. On the other hand, chlorophenols evolved were also almost analogous in all the experiments.

Table 3: Chlorobenzenes and chlorophenols evolved in combustion experiments

COMPOUND	µg compound/kg dry sample		
	M0 (wood/PVC) (n = 3)	M1 (wood/PVC/PU) (n = 3)	M2 (wood/PVC/PU pyrolysis gases) (n = 3)
<i>Chlorobenzenes (µg/kg dry basis)</i>			
MONO-	35900 ± 8700	15400 ± 5700	27700 ± 8700
DI-	2800 ± 500	1500 ± 500	3900 ± 1700
TRI-	66 ± 27	36 ± 11	103 ± 56
TETRA-	7 ± 2	7 ± 1	6 ± 4
PENTA-	2 ± 1	10 ± 3	nd
HEXA-	40 ± 30	22 ± 2	20.0 ± 0.4
TOTAL	38845	16918	31722
<i>Chlorophenols (µg/kg dry basis)</i>			
MONO-	1850 ± 520	1550 ± 430	1350 ± 590
DI-	750 ± 440	440 ± 150	780 ± 290
TRI-	43 ± 24	25 ± 4	15 ± 7
TETRA-	2.3 ± 0.4	14.9 ± 2.6	1.7 ± 2.1
PENTA-	26 ± 11	19 ± 3	17 ± 3
TOTAL	2676	2043	2156

Table 4 shows the WHO-TEQ of PCDD/Fs evolved. The results suggest that the addition of polyurethane foam to the fuel and the addition of the pyrolysis gases reduce the PCDD/F formation. The yields of PCDFs is much higher than that corresponding to PCDDs, this tendency is mainly observed in experiment M0 (combustion of wood with 5 wt.% of PVC) and this was also the tendency during the combustion of PVC⁶. The congeners with the most important contribution to toxicity were: 23478-PeCDF, 234678-HxCDF and 123789-HxCDF.

Table 4: WHO-TEQ of 17 PCDD/Fs (ng TEQ / kg dry sample) in experimental combustions

COMPOUND	ng WHO-TEQ/kg dry sample			
	M0 (wood/PVC) (n = 2)	M1(wood/PVC/PU) (n = 2)	M2 (wood/PVC/PU pyrolysis gases) (n = 2)	LOD
2378-TCDF	0.7 ± 0.9	0.2 ± 0.3	nd	0.05
12378-PeCDF	0.9 ± 1.3	0.2 ± 0.3	0.05 ± 0.08	0.01
23478-PeCDF	118 ± 49	24 ± 12	nd	0.1
123478-HxCDF	52 ± 34	5.6 ± 2.0	nd	0.07
123678-HxCDF	74 ± 47	10.0 ± 0.4	nd	0.07
234678-HxCDF	146 ± 66	19 ± 3	1.2 ± 1.7	0.08
123789-HxCDF	112 ± 82	16 ± 1	nd	0.1
1234678-HpCDF	51 ± 32	4.9 ± 0.3	0.9 ± 1.2	0.01
1234789-HpCDF	13 ± 10	0.6 ± 0.8	nd	0.01
OCDF	0.7 ± 0.5	0.05 ± 0.07	0.03 ± 0.05	0.001
2378-TCDD	nd	nd	nd	0.4
12378-PeCDD	nd	0.6 ± 0.8	nd	0.4
123478-HxCDD	0.2 ± 0.3	nd	nd	0.1
123678-HxCDD	2.2 ± 3.0	0.2 ± 0.3	nd	0.1
123789-HxCDD	0.1 ± 0.2	nd	nd	0.1
1234678-HpCDD	1.1 ± 1.6	0.2 ± 0.3	nd	0.02
OCDD	nd	nd	nd	0.002
Total PCDFs	569.3	81.7	2.1	
Total PCDDs	3.6	0.9	nd	
Total PCDD/Fs	572.9	82.6	2.1	

nd < LOD

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