STUDY OF THE INFLUENCE OF IRON PARTICLES IN THE COMBUSTION OF PVC

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Introduction

Poly(vinyl chloride) (PVC) is the single largest chlorine source in municipal waste, and has a significant role in the formation of dioxin and other toxic polychlorinated hydrocarbons in many countries. It has been reported that the emission of dioxins can be reduced by using secondary measures such as catalytic combustion, photocatalytic decomposition, and photolysis. Combining the combustion method with a catalytic process in the treatment of toxic pollutants has several advantages, because it only requires low temperatures and is energy efficient[1]. On the other hand, PVC wastes can be mixed with different metals, so the knowledge of possible interactions is very important to valuate the formation of dioxins.

Iron has been used to enhance dechlorination of PCBs present in water[2] and soils[3] by reducing the chlorinated compounds to their dechlorinated form. As the dechlorination is a surface reaction, the surface area of iron particles needs to be maximized.

According to some authors [4 - 6], PVC thermal degradation consists of two main steps: hydrogen chloride is firstly released and then, aromatic hydrocarbons are subsequently formed from cyclation reactions of the remaining polyene chain and also a residual char is generated. The presence of oxygen in the atmosphere instead of an inert gas allows the char to volatilize completely. In this work PVC and a PVC + iron nanoparticles mixture were burnt in two states, first the sample was introduced in a laboratory reactor at 375 ºC and after the combustion the char obtained was cooled and weighted and next this char was burnt at 850 ºC. The main aim of present work is to study the influence of the presence of the iron nanoparticles in the PCCD/F emission in the combustion of PVC in fuel rich conditions.

Materials and Methods

Experiments were carried out with white powdery PVC resin Etinox-450 free of additives obtained by emulsion polymerization. It has a medium molecular weight (104,000 and 40,000 for M_w and M_n, respectively) and a very small particle size, ranging between 1.4 and 24.4 μm. Table 1 shows the chemical composition of PVC analyzed by two complementary techniques: elemental analysis with a Perkin-Elmer 2400 CHN (for C, H, N and S) and X-ray fluorescence with an automatic sequential spectrometer model PW1480 (semiquantitative analysis for elements with an atomic weight higher than that of Mg).

The nano particles were prepared according Varanasi, Fullana and Sidhu[3] by reducing a ferric chloride solution:

$$Fe(H_2O)_6^{3+} + 3BH^{4-} + 3\ H_2O \longrightarrow Fe^0 + 3B(OH)_3 + 10.5\ H_2$$

1.6M sodium borohydride was added drop wise into 0.2 M of ferric chloride solution, to produce iron. The nanoparticles were then rinsed with water three times and water and nanoparticles were separated using the magnetic properties of nano iron and stored in a nitrogen atmosphere. Iron particles obtained have an area of 84.1 m^2/g and a radio of 4.5 nm.

A batch laboratory scale horizontal tubular reactor[7] was used for the combustion at fuel-rich conditions of PVC and PVC and iron nanoparticles mixture. Basically, the sample placed in a quartz crucible is introduced into the reactor at constant speed (1 mm/s) when the furnace is already at the final temperature. The synthetic air was

introduced parallel to the solid, with constant gas flowing at around 300 mL/min. After collecting the exit gas for 5 minutes, the holder was removed from the furnace. The reactor gas was colleted in an adsorptive trap containing XAD-2 resin. After each experiment, the resin was extracted with toluene and the extract was analyzed by HRGC/HRMS for the PCDD/F analysis, ^{13}C-labeled compounds included in the EPA 1613 method were used.

The bulk air ratio (λ) parameter was defined as the ratio between the actual air flow and the stoichiometric air flow necessary for complete combustion, assuming that the combustion of the solid occurs at the same rate that being introduced. The expression to calculate λ is:

$$\lambda = \frac{(m_{air})_{actual}}{(m_{air})_{stoichiometric}} = \frac{m_{air}\,23}{\frac{w_{sample}\,\nu}{L}(\%H - \frac{\%Cl}{35.5})\frac{1}{4} + \frac{\%S}{32} - \frac{\%O}{32})32}$$

In the previous expression, m_{air} is the air flow introduced (mg/s), w_{sample} the total sample mass (mg), ν the rate of sample inlet (mm/s), L the length of the boat (mm) and %C, %H, %Cl, %S and %O are, respectively, the weight percentages of carbon, hydrogen, chlorine, sulphur and oxygen in the sample. In this work for the experiments at 375 ºC, λ=0.46 was selected. For the runs with the carbonaceous residue obtained previously, the value of λ is close to the unity.

Results and Discussion

In this work, two different samples were used: 41 mg of PVC and a PVC iron nano particles mixture (41 mg PVC + 33 mg iron nano particles). Each sample was burnt in two states, first the sample was introduced in a reactor at 375 ºC and after the combustion the char obtained was cooled and weighted and next this char was burnt at 850 ºC. The nomenclature used for each experiment is: PVC375: combustion of PVC at 375 ºC, PVC850: combustion of PVC at 850 ºC, PVCFe375: combustion of PVC and iron nano particles mixture at 375 ºC and PVCFe850: combustion of PVC iron nano particles mixture at 850 ºC.

Table 2 shows the different PCDD/F emissions, the distribution of the toxic congeners, their contribution to the TEQ and the total yields corresponding to the isomers. Figure 1 and 2 show the corresponding distributions as percentages. In view of Table 2, it can be concluded that the formation of PCDD/Fs in the run carried out with PVC and iron nano particles in presence of oxygen at 375 ºC (although without formation of carbon oxides) is very high in comparison with the other cases. This probably can due to the Deacon process, catalyzed by the iron or oxidized iron particles, that favour the formation of chlorine, increasing the formation of chlorinated precursor that lead to the formation of dioxin/furans. Significant PCDD/F concentrations are obtained in all cases. Concerning the distribution shown in Figures 1 and 2, it can be deduced that the formation of furans and their contribution to the total toxicity is greater than that corresponding to the dioxins.

Acknowledgements

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Table 1. Chemical composition of PVC resin

Element	wt.%	Element	wt.%
Cl	55.2	Zn	0.034
C	38.4	K	0.018
H	4.80	Ca	0.017
S	1.40	Si	0.0095
Na	0.12	Al	0.0057
O	0.076		

Table 2. Different PCDD/F emission obtained for each experiment

	PVC375	**PVC850**	**PVCFe375**	**PVCFe850**
	pg i-TEQ/g initial PVC	**pg i-TEQ/g initial PVC**	**pg i-TEQ/g initial PVC**	**pg i-TEQ/g initial PVC**
2378-TCDF	1	8867	23244	14
12378-PeCDF	32	784	72273	60
23478-PeCDF	57	84682	1439673	1867
123478-HxCDF	18	19474	2276215	1175
123678-HxCDF	13	10710	1067311	543
234678-HxCDF	4	19911	598437	300
123789-HxCDF	5	12885	646958	290
1234678-HpCDF	30	9036	1018465	563
1234789-HpCDF	8	1677	251968	132
OCDF	9	803	372904	179
2378-TCDD	nd	9552	7284	0
12378-PeCDD	nd	11612	51336	1048
123478-HxCDD	nd	5520	41207	81
123678-HxCDD	nd	11051	98730	57
123789-HxCDD	nd	7341	63866	40
1234678-HpCDD	4	9267	139222	68
OCDD	2	1087	47913	25
Total PCDD/Fs	183	224259	8217005	6441
	pg/g	pg/g	pg/g	pg/g
Total-TCDF	4906	1295063	8686765	679
Total-PeCDF	4032	1514803	25672978	23299
Total-HxCDF	1922	2002259	94242128	53598
Total-HpCDF	3952	1879788	177475756	106383
OCDF	8632	802871	372904126	178506
Total-TCDD	nd	253331	0	346
Total-PCDD	nd	1347856	860077	2096
Total-HxCDD	nd	2063001	6841738	1778
Total-HpCDD	nd	1857483	23201096	11427
OCDD	1621	1086799	47913202	25242

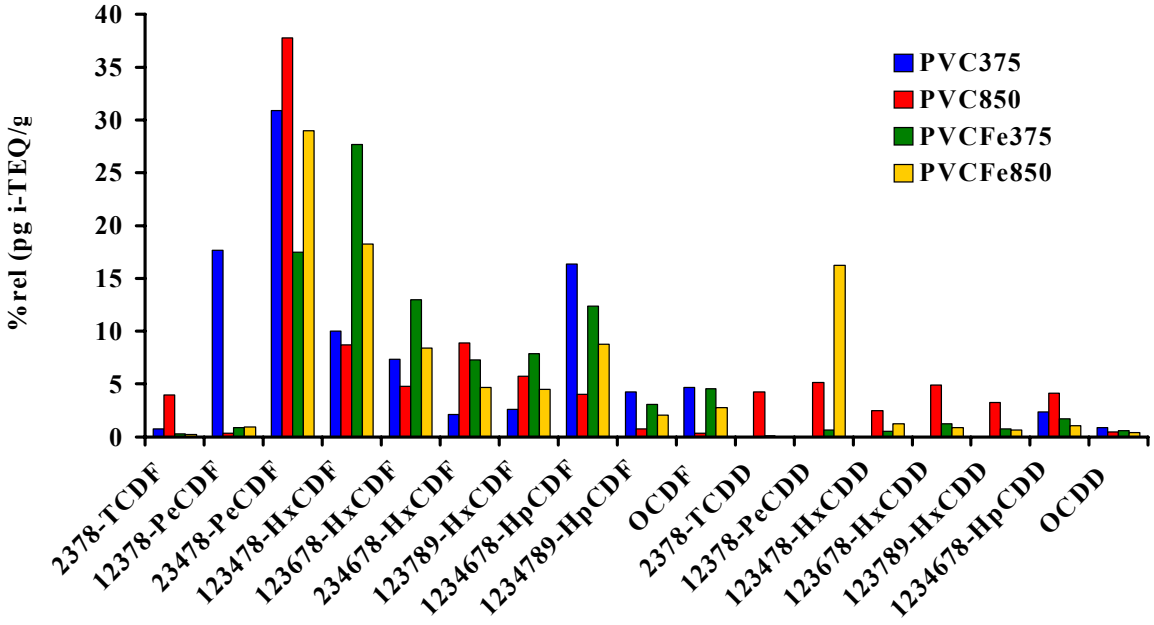

Figure 1. Congener specific 2,3,7,8 PCDD/F distribution

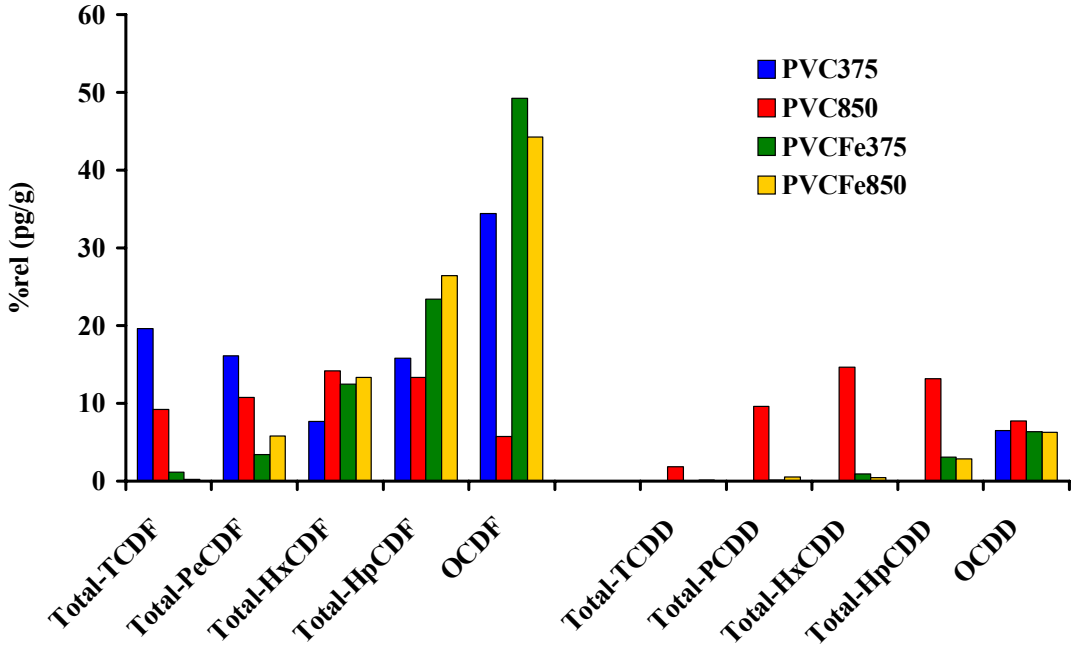

Figure 2. PCDD/F homolog profile of the experiments