CHLOROPHENOLS, CHLOROBENZENES AND PAHs DURING THERMAL DEGRADATION OF FLEXIBLE POLYURETHANE FOAM.

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Introduction

Polyurethanes are polymers obtained from the reaction between polyfunctional isocyanates, as the toluene diisocyanate, and polyfunctional alcohols like polyethers and polyesters. Due to the wide range of possible composition, polyurethanes have been found in different commercial applications being the flexible polyurethane foams (FPUF) the largest market for polyurethanes[1]. These foams are employed mainly in the furniture, concretely in mattresses, and interior industry and the most common route for end-of-life mattresses appears to be sent to landfill. However, mattresses account for a large proportion of the total waste sent to landfill for their small density and this represents a large quantity of material which is not recovered. Waste mattresses can be used to obtaining energy by thermal decomposition, so it is important to study the evolved products obtained in this recovery method.

In spite of the polyurethane is widely used in different applications, limited data regarding semivolatile compound from the thermal decomposition of polyurethane was found.

Font et al. [2] studied the main volatile and semivolatile organic compounds produced during the pyrolysis of polyurethane by GC-MS at two different temperatures 600 and 850ºC. Herrera et al.[3] also identified the evolved products from the pyrolysis of polyurethane at 800 and 950ºC, but in this case they compared the these gases with the obtained in the combustion at the same temperatures.

Watanabe et al.[4] investigated the semivolatile compounds emitted during heating of different plastics being polyurethane one of them at low temperature.

Materials and methods

Polyurethane foam

The flexible polyurethane foam studied was obtained from the mattresses disposed in a landfill of Alicante. The moisture and density of the polyurethane foam used were 1.2% and 19.62 kg/m^3 respectively, being the last value inside the range of density proposed by Polyurethane Foam Association for to mattress topper pads and upholstery [5].

Elemental analysis and the net calorific value of the flexible polyurethane foam are shown in **Table 1.**. The final CHNS analysis was carried out in a Perkin Elmer 2400 apparatus. The ash content was obtained by calcination at 850ºC and the oxygen by difference. The calorific value was obtained using an AC-350 calorific bomb.

Table 1. Elemental analysis and net calorific value of flexible polyurethane foam.

Composition on dry basis	
C (%)	57.79
H (%)	7.36
N (%)	5.95
S (%)	0
Ash (%)	5.47
O (%)(by difference)	23.43
Net calorific value	5786.3 kcal kg^{-1}

The content of chlorine was carried out following the US EPA Method 5050. Hydrogen chloride evolved from chlorine in combustion was collected over 10 mL of $NaHCO_3/Na_2CO_3$ solution which was analyzed by ion chromatography employing the Dionex DX-500 instrument with an AS9HC (Dionex) column. The value obtained in this analysis was 315 mg Cl^- kg^{-1} dry mass.

Experimental system

Experiments were performed in a horizontal tubular-quartz reactor showed in the Figure 1, where the sample, which is introduced inside a crucible, is moved through it at a velocity of 0.8 mm s^{-1}. This reactor is situated inside an electric furnace consisting of two independent heating zones and hence the reactor is uniformly heated.

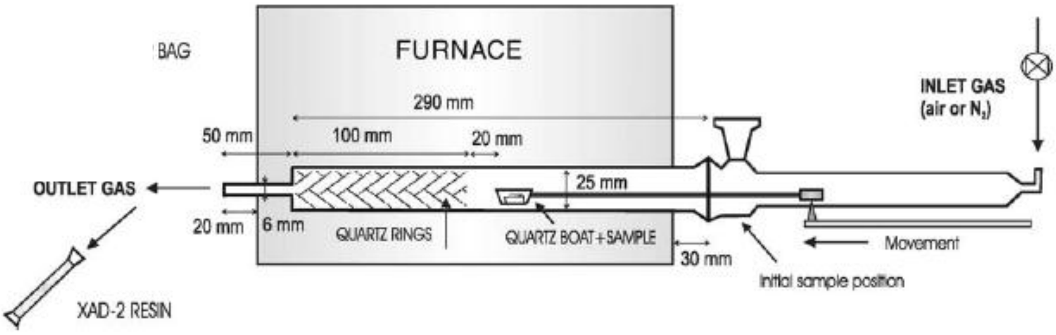

Figure 1. Scheme of the reactor inside the furnace.

Both pyrolysis and combustion experiments were performed at 550 and 850ºC with about 50 mg of FPUF. Synthetic air or nitrogen gas was used in combustion or pyrolysis, respectively, with a flow of 300 mL/min (measured at 1 atm and 20ºC).

The outlet gas stream was sampled to analyze semivolatile compounds (boiling point above 130 ºC) such as polycyclic aromatic hydrocarbons (PAHs), chlorophenols (ClPhs) or chlorobenzenes (ClBzs). The emitted gases were collected in a tube at the outlet of the reactor filled with XAD-2 resin, in which this kind of compounds were adsorbed or condensed.

The XAD-2 resin was extracted in a mixture of dichloromethane-acetone (1:1) by Accelerated Solvent Extraction (ASE-100,Dionex-Thermo Fisher Scientific Inc., California, USA) and previously to the extraction, 5 µl of the following deuterated standards, with an individual concentration 4000 µg mL^{-1}, were added to analyze PAHs (US-EPA 8270D method): 1,4-dichlorobenzene-D4, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12. Also, were added prior to extraction 10 µl of ^{13}C-labelled ClPh and 10 µl ^{13}C-labelled ClBz internal standards. The extract was concentrated in a rotavapor and with a gentle stream of nitrogen up to 1.5 mL. Finally, 10 µL of a solution 2000 µg/mL anthracene-d10 was spiked to the vials as a recovery standard.

Semivolatile compounds collected in XAD-2 resin were analyzed using Agilent 6890 Gas Chromatograph (GC) coupled with an Agilent 5973 MS. The GC column was HP-5MS, 5% Phenyl Methyl Siloxane (30.0 m × 250 µm × 0.25 µm).

Results and discussion

Table 2 shows the results on the emission of PAHs for the pyrolysis and combustion of FPUF performed in the tubular reactor. Great differences in the total levels of the PAHs have been obtained in the experiments performed at 850ºC and 550ºC, being higher the yields in the highest temperature. The variation of the PAHs with the temperature has been already reported[6] finding that the yields of these compounds show a maximum at temperatures between 750ºC and 850ºC, as consequence of the thermal cracking of heavier products. In the experiments performed at 550ºC, only naphthalene has been detected in two different atmospheres which agrees with the results obtained in a previous paper[2] where the pyrolysis of polyurethane was performed at 600ºC and 850ºC.The atmosphere has an important impact in the PAHs obtained in the runs at 850ºC where the total level detected in the pyrolysis experiment is almost three times as much as obtained in the combustion run. As it is known, the rise of temperature in pyrolysis involves both thermal cracking and pyroshynthesis reactions; therefore, the highest value of the total yield obtained in the pyrolysis experiment at 850ºC can be explained for the effect of these reactions. The profiles recovered in the experiments at 850ºC under the two different atmospheres show a similar distribution of PAHs where the most abundant compounds are the lightest PAHs like naphthalene and acenaphthylene. This behavior agrees with the theory proposed in a previous study[7] which establishes that initially, the first aromatic ring (benzene) is formed and then begins growing to heavier PAHs. For this reason, the concentration of naphthalene is higher than acenaphthylene, whose concentration is higher than phenanthrene.

Table 2. Yields of PAHs in Pyrolysis and Combustion Experiments.

Compound	PYROLYSIS		COMBUSTION	
	550ºC	850ºC	550ºC	850ºC
	mg compound/kg sample (ppm)			
naphthalene	40	4250	40	1660
acenaphthylene	0	920	0	360
acenaphthene	10	60	0	10
fluorene	0	300	0	90
phenanthrene	0	480	nd	200
anthracene	0	200	0	70
fluoranthene	0	110	0	0
pyrene	0	320	0	0
benzo(a)anthracene	nd	140	nd	30
chrysene	nd	60	nd	20
benzo(b)fluoranthene	nd	20	0	10
benzo(k)fluoranthene	nd	20	0	10
benzo(a)pyrene	nd	44	0	10
indeno(1,2,3-cd)pyrene	nd	20	nd	0
dibenzo(a,h)anthracene	nd	10	0	0
benzo(g,h,i)perylene	nd	10	0	0
TOTAL	**50**	**6960**	**40**	**2470**

It is important to remark that no references have been found which studied the formation of ClBzs and ClPhs in the thermal degradation of polyurethane.

Table 3. Yields of Chlorobenzenes in Pyrolysis and Combustion Experiments.

Compound	PYROLYSIS		COMBUSTION	
	550ºC	850ºC	550ºC	850ºC
	mg compound/kg sample (ppm)			
monoClBz	35	1858	3,1	27
1,3-diClBz	0,15	nd	0,07	nd
1,4-diClBz	1,0	0,1	0,2	0,02
1,2-diClBz	nd	1,0	nd	3,6
1,3,5-triClBz	nd	0,004	nd	nd
1,2,4-triClBz	nd	0,007	0,004	0,01
1,2,3-triClBz	0,007	0,004	0,005	0,03
1,2,3,5-+1,2,4,5-tetraClBz	0,006	nd	nd	0,009
1,2,3,4-tetraClBz	0,02	0,0004	nd	0,02
pentaClBz	0,49	0,003	0,31	0,03
hexaClBz	0,018	nd	0,01	0,004
TOTAL	37	1859	4	30

Table 3 shows the yields of the ClBzs obtained in pyrolysis and combustion of FPUF. In general, the effect of the temperature was the same in pyrolysis and combustion because there was an increase of the total yields of ClBzs when the temperature rose, being higher the variation in pyrolysis, from 37 to 1859 ppm, than in combustion, from 4 to 30 ppm. The total yields of ClBzs increased from combustion to pyrolysis both at 550ºC and 850ºC, but no important difference was detected in the profiles obtained being the monochlorobenzene the predominant congener in all cases. A great rise in the yield of this congener was detected at 850ºC from combustion to pyrolysis which produced an increase more than 90% in the total yields.

The results obtained in the ClBzs agree with the previous theory for the formation of PAHs which supposes that the lightest PAHs are formed initially. It can be extrapolated to the formation of ClBzs taking into account that the concentration of Cl^- in the foam was small, 315 ppm. For that, in pyrolysis the benzene can react with the Cl^- to obtain monochlorobenzene majority; while in combustion this aromatic ring is oxidized to more volatiles compounds avoiding the formation of ClBzs.

Table 4. Yields of Chlorobenzenes in Pyrolysis and Combustion Experiments.

Compound	**PYROLYSIS**		**COMBUSTION**	
	550ºC	**850ºC**	**550ºC**	**850ºC**
	mg compound/kg sample (ppm)			
monochlorophenols	12	22	7	14
dichlorophenols	3	0	0	0
trichlorophenols	2	0	2	0
tetrachlorophenols	0	0	0	0
pentachlorophenols	0	0	0	0
TOTAL	**17**	**22**	**9**	**14**

Table 4 shows the concentration of chlorophenols and the total yields obtained in pyrolysis and combustion at 550ºC and 850ºC. The most important effect in this case is the atmosphere employed because the total levels of chlorophenols detected in pyrolysis were almost the double that obtained under an oxidative atmosphere, from 9 to 17 ppm and from 14 to 22 pmm. The increase of temperature does not produce a great variation in the levels of chlorophenols neither pyrolysis nor combustion. However, the yields of di- and tri-chlorophenols, which are emitted at 550ºC, decrease when the temperature increases obtaining that at 850ºC only monochlorophenols are detected.

Acknowledgements
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