

FTIR analysis of gases produced by the thermal decomposition of polyurethane foams

FTIR is an ideal on-line analysis technique for determining the nature and quantity of toxic gases emitted by burning materials

Authors

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Introduction

A foam pit is an essential element of trampoline parks as it allows you to safely perform a variety of acrobatic moves. The foam blocks are placed in a disordered way and, along with the air pockets between them, create a shock-absorbing surface that can safely cushion a fall from several meters high. The air pockets are an essential part of the surface, which is why the blocks must be regularly stirred and decompressed so that they do not create a compact mattress. The foam blocks are typically cubes with 20-cm sides and they are largely made of soft polyurethane materials that might have a variety of densities.

Polyurethanes are a family of synthetic polymers produced by the reaction of an isocyanate and an alcohol. They can be tailored to have a wide variety of textures and hardnesses by varying the monomers and different functional groups that are used.^[1]

Standard non-flame-retardant polyurethane foams do not have sufficient fire resistance and they ignite and burn rapidly, with a high rate of heat release. They also produce a large quantity of smoke and toxic gas, in particular carbon monoxide (CO), nitric oxides (NOx), and hydrogen cyanide (HCN). Although they can be covered with an M1-class fireproof coating, a large portion of trampoline parks use uncoated foams.

Currently, there are no explicit requirements for the fire resistance of foams. However, the global use of polyurethanes is likely to keep increasing each year and it is therefore urgent that the fire science community has a clear understanding of the fire toxicity risks of these materials. Considering the volume of combustible load as well as the difficulty that people could experience to extract themselves from foam pits, the evaluation of the potential risk was tested in semi-real conditions. The experiments were carried out under a calorimetric hood coupled with a Fourier-transform infrared (FTIR) spectroscopy analyzer to check the gaseous effluents that escape during combustion. FTIR is the method of choice since it allows direct on-line analysis of multiple different compounds from percent levels to parts-per-billion in a single measurement. Analysis is fast, precise, and non-destructive and requires minimal maintenance and recalibration.^[2]

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Materials and methods

Combustion-modified polyurethane foams were supplied by Efectis France. Two densities were studied: 17 kg/m³ and 23 kg/m³. Both foams have an M4 fire rating with ignited drops according to NF P 92-507. Two size conditions were tested for the 23 kg/m³ density foams: uniform cubes with 200-mm sides and a mixture of differently sized cubes.

The foams were placed in a steel tray (2,000 x 500 x 600 mm) that was lined with 10-mm-thick calcium silicate plates to avoid possible deformations due to combustion heat.

The characteristics and quantity of tested foams are shown in Table 1.

Trial	Density (kg/m³)	Dimension (mm)	Quantity	Total mass (kg)
1	17	200 x 200 x 200	35	4.8
2	23	200 x 200 x 200	35	6.4
		280 x 205 x 200	6	
3	23	307 x 280 x 200	6	6.3
		307 x 280 x 280	6	

Table 1. Description of the foams used in the combustion tests.

The tray was installed under a calorimetric hood in accordance with ISO 9705-1^[3] and ISO 24473. A spigot on the exhaust duct was connected to a heated sampling probe, which in turn was connected to the FTIR analyzer.



Figure 1. Photo of the Thermo Scientific Modular Gas Sampling System.

A Thermo Scientific Modular Gas Sampling System (Figure 1), which complies with ISO 19702^[4]; the sampling complies with ISO 16405^[5]. The system consists of a Thermo Scientific[™] Nicolet[™] iG50 FTIR Spectrometer, a DTGS detector, and a 10 meter (2 L) gas cell, working at 180°C and 650 torr, with pressure regulated at ±10 torr.^[6] Temperature and pressure are read directly by sensors to correct deviations from calibration measurements. The pressure can vary significantly during the experiment for a variety of reasons, causing linear or non-linear effects on the gas spectra that can lead to prediction errors ^[6]. The spectral range is 4,000 to 650 cm⁻¹ with a resolution of 0.5 cm⁻¹. The time resolution is on the order of 5 seconds. The quantitative analysis is performed using a classical least square (CLS) algorithm, allowing for the simultaneous measurement of a large number of species and a limit of quantification on the order of 10 to 20 ppm. The quantified gases were H₂O, CO₂, CO, SO₂, NO, NO₂, N₂O, HCI, HBr, HCN, HF, formaldehyde, CH₄, C₂H₂, C₂H₄, and NH₃. This list of gases is exhaustive as they may be analyzed quantitatively for their direct toxic impact or for data correction as they may potentially interfere with the compound results. Calibration is achieved using recommendations from References 2, 7, and 8.

The ignition was carried out with a match, represented by a 35-mm-high flame obtained from a 6-mm-diameter stainless steel tube; the fuel was 99% purity propane gas. The flame was applied for 20 seconds to the top of a horizontally placed cube, halfway to the edges of the short side of the tank, in order to minimize the speed of propagation at the start of the test. The ignition is carried out at one end to measure the speed of propagation of the flame front over the 2 m length of the tray. Figure 2 illustrates ignition at different times during combustion.



Figure 2. Photos of the foam tray a) at the beginning of ignition (t = 0), b) at t = 3 min, and c) at t = 5 min.

Results and discussion

For all three tests, the maximum heat release value is in the order of 1 MW with a similar combustion efficiency. The combustion is both very fast and efficient. However, the heat release kinetics and propagation rate are greatly influenced by the density of the foam and very little by the size of the blocks. They are faster for test 1 and comparable for tests 2 and 3. Lower density cubes burn faster but shorter.

For all tests, the gases observed are mainly carbon dioxide and water, with small amounts of nitric oxide and carbon monoxide. The masses produced for each of the gases are given in Table 2.



Figure 3. Concentration of the main gases detected as a function of time.

Trial	CO₂ mass produced (kg)	CO mass produced (kg)	NO mass produced (kg)
1	7.87	0.09	0.0007
2	10.2	0.09	0.043
3	11.1	0.11	0.0443

Table 2. Smoke analysis.

Figure 3 represents the kinetics obtained for the first trial, which are shown to be identical to those of the heat output. There was a maximum CO_2 concentration of about 14,000 ppm after 5 minutes, and small amounts of CO and NO are observed with a maximum concentration of about 50 ppm. The other two trials show similar results. The density and size of the cubes, therefore, have little influence on the quantity and kinetics of the gases released.

These results reflect a very widely ventilated combustion. The intensity of the combustion limits the formation of unburnt species. No trace of hydrocyanic acid was detected.

Conclusions

The results of this study demonstrate the advantages of FTIR for determining, in real time, the nature and quantity of toxic gases emitted during the combustion of materials. CO₂ is the main gas produced during the combustion of polyurethane foams in the specific test conditions of this study. In particular, ventilation conditions can have a critical effect on the gas yields and these results are not generalizable without determining how representative these samples and tests are.

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