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Isocyanate emissions from pyrolysis of mattresses containing polyurethane foam

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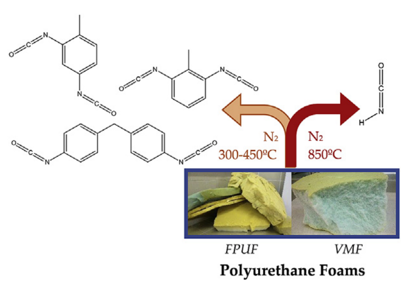
HIGHLIGHTS

- Pyrolysis of flexible and viscoelastic memory foams was performed.
- At 350-450 °C, diisocyanates are formed (around 0.1 μg/g_{sample}).
- At 850 °C, the emission factors of ICA and PHI 1 and 0.01 μg/g_{sample}, respectively.
- Isocyanate profiles observed agree with kinetic models proposed previously.
- Six new aminoisocyanates have been found in the evolved gases from FPUF pyrolysis.

GRAPHICAL ABSTRACT



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ABSTRACT

This study examined the emissions of powerful asthmatic agents called isocyanates from small-scale pyrolysis experiments of two common foams employed in mattress production such as flexible polyurethane foam (FPUF) and viscoelastic memory foam (VMF). A nitrogen atmosphere and five different temperatures, 300, 350, 400, 450 and 850 °C, were selected to carry out the experiments in order to evaluate the worst possible conditions for thermal degradation.

A similar trend for both materials was found. At lower temperatures, diisocyanates were the most important products whereas at 850 °C monoisocyanates, and mainly isocyanic acid released mainly from the thermal cracking of diisocyanates evolved directly from the polymer chains.

The total yields of isocyanates were in the range of 1.43–11.95 mg/m^3 for FPUF at 300-850 °C and 0.05–6.13 mg/m^3 for VMF, 300-850 °C. This difference could be a consequence of the lower amount of isocyanates employed in the VMF production which was confirmed by the nitrogen content of the foams, 5.95% FPUF vs. 3.34% in VMF.

Additionally, a qualitative search for so far unknown isocyanates was performed in samples from the pyrolysis of FPUF at 300, 400 and 850 °C. It was confirmed that six different aminoisocyanates at 300 °C were evolved, whereas at 400 and 850 °C only five of them were detected. The general trend observed was a decrease of the aminoisocyanate levels with increasing pyrolysis temperature.

1. Introduction

Organic isocyanates are reactive compounds which contain one

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Abbreviations

2,4-TDI	Toluene-2,4-diisocyanate
2,6-TDI	Toluene-2,6-diisocyanate
4,4′-MDI	Methylenediphenyl-4,4'-diisocyanate
DBA	Di-*n*-butylamine
EIC	Ethyl isocyanate
HCN	Hydrogen cyanide
HDI	Hexamethylene isocyanate
HPLC-QQQ-MS	High-performance liquid chromatography coupled to triple quadrupole mass spectrometry
HPLC-QTOF-MS	High-performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry
ICA	Isocyanic acid
IDPI	Isophorone diisocyanate
MIC	Methyl isocyanate
NCO	Weight of equivalent NCO groups
PFUF	Flexible polyurethane foam
VMF	Viscoelastic memory foam
PHI	Phenyl isocyanate
PIC	Propyl isocyanate

or more isocyanate functional groups (R–N=C=O) joined to aliphatic or aromatic residues (R). The most common isocyanates, their names and abbreviations used herein are shown in Fig. S1, Supporting Information.

Monomeric diisocyanates and organic diamines are the main raw materials for manufacturing polyurethane products widely used in paints, glues and foams.

Isocyanates are extremely toxic compounds (Alves et al., 2016). Consequently, workplace exposure is regulated in most occupational health legislations, e. g. in Spain a Threshold Limit Value (TLV) has been adopted for some of the isocyanates shown in Fig. S1 as an 8-h-time-weighted average (TWA) (INSHT, 2016). The limit value that nearly all workers can be exposed to without an adverse health effect can be found in Table S1, Supporting Information.

Exposure to isocyanates is associated with irritation of skin, eyes and the respiratory system (Henneken et al., 2007). In fact, between 5 and 13% of workers exposed to relatively small amounts of isocyanates of 0.02 ppm (Lefkowitz et al., 2015) develop a disease called isocyanate asthma (Krone and Klingner, 2005). Higher concentrations can even induce pulmonary oedema and death (Dhara and Dhara, 2002).

The relationship between work exposure and health problems has triggered studies on the emissions of these compounds during synthesis of polyurethane products and during thermal or mechanical treatment of the final products, analysing the airborne isocyanates at different workplace atmospheres. In this way, Rosenberg (1984) analysed the workplace environment during the production of polyurethane-coated wire employing two different polyurethane varnishes and a horizontal and a vertical coating machine. Karlsson et al. (2000) studied airborne isocyanates emitted during grinding, cutting and welding operations in a car repair shop. An extensive study by Karlsson et al. (2001) also included aminoisocyanates and amines alongside isocyanates from the thermal degradation of polyurethane during welding in district heating pipes and PUR-coated metal sheets. The highest concentrations were obtained in the welding operation and isocyanates were the most abundant in both processes.

Boutin et al. (2004) employed a laboratory-scale furnace to identify the isocyanates emitted during the thermal degradation of polyurethane car paint under inert and oxidative atmospheres at 473 °C. Boutin et al. (2006) also determined airborne isocyanates generated during the thermal degradation of car paint in body repair shops. Thereby, they focussed on abrasive processes such as cutting, grinding and sanding, where sufficient heat is generated to emit isocyanates to the air.

Polyurethane products are also used in everyday life products such as mattresses, sofas or carpets and the emission of isocyanates from burning these products has also been studied. Blomqvist et al. (2003) performed a series of small-scale combustion experiments in a cone calorimeter of different building materials such as flexible and rigid polyurethane foams. The highest isocyanate concentrations were obtained from the degradation of rigid polyurethane foam. The authors also performed full scale experiments to study emissions from a polyurethane mattress and a sofa in the case of fire. Considerable amounts of isocyanates were produced from the sofa.

Another study developed by Blomqvist et al. (2014) analysed the distribution patterns of isocyanates under different firing conditions such as oxidative pyrolysis, well-ventilated flaming fires and under-ventilated flaming post-flashover fires in a steady-state tube furnace where a low polyurethane content PVC carpet was degraded.

In Europe, 30 million mattresses reach their end of life annually (Turner, 2014). About 60% are dumped in landfill sites; the remaining 40% are incinerated. In order to decrease the amount of waste sent to landfills, the European Commission modified Directive 1999/31/EC on the landfill of waste in 2014. After January 1st, 2015, only 25% of the total amount of municipal waste generated in the previous year was to be accepted in landfills; whereas, from January 1st, 2030, this rate will be finally reduced by up to 5%. This new legislation requires a substantial reduction of mattresses sent to landfill sites and a respective increase of mattresses being incinerated.

This paper presents isocyanate emission data obtained from small-scale pyrolysis experiments of two different types of mattress foams, flexible polyurethane foam (FPUF) and viscoelastic memory foam (VMF). Pyrolysis experiments were performed at five different temperatures in a laboratory furnace under nitrogen atmosphere to replicate the worst conditions that could appear in big furnaces, such as cement kilns which are the main destination for these wastes due to the high volume to be incinerated. The quantification of respective isocyanates was performed by HPLC-QQQ-MS and a qualitative search for so far unknown isocyanates was performed with a HPLC-QTOF-MS system.

2. Experimental

2.1. Materials

Flexible polyurethane foam (FPUF) and viscoelastic memory foam (VMF) were used as they are the most frequently used materials for mattress production. These foams were collected from a landfill in Alicante (Spain) as waste material and their composition was unknown. For the characterization, elemental analyses were performed with a Flash EA 1112 Elemental Analyzer. The respective results are given in Table S2 together with the ash contents obtained by calcination of the samples in a muffle furnace at 950 °C for 8 h.

2.2. Thermal degradation of polyurethane foams

A tubular quartz reactor located inside a horizontal laboratory furnace (Fig. S2) described previously (Aracil et al., 2005) was