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Isocyanate emissions from pyrolysis of mattresses containing polyurethane foam

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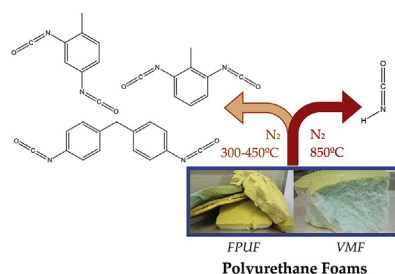
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HIGHLIGHTS

- 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/m³ for FPUF at 300–850 °C and 0.05–6.13 mg/m³ 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.

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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- <i>n</i> -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

employed to study the evolution of isocyanates from the pyrolysis of FPUF and VMF at 300, 350, 400, 450 and 850 °C. About 50 mg of the sample were placed in the quartz boat and 150 mL/min of N₂ was fed parallel to the sample. The residence times of the gas along the reactor zone at nominal temperatures were calculated obtaining 17 s at 300 °C, 15.5 s at 350 °C, 14 s at 400 °C, 12.7 s at 450 °C and 7.1 s at 850 °C.

When the furnace reached the nominal temperature the crucible was introduced inside the reactor with a constant velocity of 2.50 mm/s and the exhaust gases were collected for 30 min in two impinger flasks containing a solution of di-*n*-butylamine (DBA) 0.01 mol/L in toluene. Previously, it was tested that the retention on the first impinger flask was higher than 99%.

Triplicate experiments and blank samples were taken for both foams at five different temperatures.

2.3. Exhaust analysis

2.3.1. Sampling procedure

Isocyanates are highly electrophilic reacting with nucleophiles such as amines, alcohols and even water. To prevent uncontrolled reactions with nucleophiles during sampling and work-up, isocyanate groups are derivatized. In addition, the derivatization can also improve the sensitivity and selectivity of the analytical method (Streicher et al., 2000). Primary and secondary amines such as 9-(*N*-methylaminomethyl) anthracene (MAMA) (Karlsson et al., 1998), 1-(2-methoxyphenyl) piperazine (MOPIP) (Henriks-Eckerman et al., 2000; Boutin et al., 2004) or di-*n*-butylamine (DBA) (Spanne et al., 1996; Blomqvist et al., 2003, 2014) are often used. In this study, DBA was used according to the ISO norm 17734-1:2013 (ISO 17734-1, 2013) which describes sampling and analysis of airborne isocyanates in workplace air. Therein, gas and particle phases were collected by impinger flasks containing DBA solutions and DBA-coated glass fibre filters in series. However, bearing in mind the low amounts of isocyanates collected in the particle fraction, as shown in previous studies (Blomqvist et al., 2003; Dahlin et al., 2008), only 100 mL impinger flasks were employed in this study containing 50 mL of 0.01 mol/L DBA in toluene. Before collecting the exhaust gases, the sampling solutions were spiked with 1 mL of a solution containing 100 µg of 4,4'-methylenediphenyl diisocyanate derivatized with di-*n*-ethylamine (DEA) (4,4'-MDI-DEA) and 100 µg of 2,4-toluene diisocyanate derivatized with di-*n*-ethylamine (2,4-TDI-DEA) which were employed to calculate losses during the experimental procedure.

2.3.2. Work-up procedure

Impinger flask samples were diluted with toluene up to a final volume of 100 mL and 10 mL of these solutions were concentrated in a rotary evaporator to about 1 mL and finally concentrated to dryness with a moderate stream of nitrogen. The residues were solved in 1 mL acetonitrile (ACN).

Before analysis, 100 µL of the sample solutions were spiked with 10 µL of a diluted commercial mix of D18-DBA labelled isocyanates (1 µg/mL, Supelco, USA) as the internal standard.

2.3.3. HPLC-QQQ-MS analysis

2.3.3.1. Calibration. A commercial mix of isocyanate concentrated DBA derivatives (Supelco, USA) was employed to prepare seven solutions covering a specific concentration range for different isocyanate DBA derivatives (see Table S3, Supporting Information). These standard solutions were also spiked with the same amount of D18-DBA isocyanates (Supelco, USA).

The limit of detection (LOD) for 11 different isocyanate derivatives was set at the lowest concentration in the calibration curves.

2.3.3.2. Analysis conditions. Samples were analysed with an Agilent 6460 Triple Quadrupole (QQQ) LC/MS system (San Jose, CA, USA). For analysis, 2 µL of the samples were injected and passed through a reversed phase column Zorbax Bonus-RP, 2.1 × 150 mm, 5 µm, at a flow rate of 0.25 mL/min at 40 °C. Mobile phases were A: buffer solution of 5 mM ammonium acetate (pH = 6) and B: acetonitrile with a gradient: 0–8 min from 50% to 95% B; 1 min 95% B; 2 min from 95% to 50% B; 1 min 50% B. Electrospray ionization was performed monitoring positive ions using N₂ as nebulizing gas at 45 psi with a flow rate of 8 L/min at 325 °C. The temperature in the ion source was 325 °C, the desolvation temperature 340 °C.

Ions were monitored in the multiple-reaction monitoring (MRM) mode with individually optimized collision energies, ranging from 8 to 45 V. Monoisocyanates (ICA-DBA, MIC-DBA, EIC-DBA, PIC-DBA, PHI-DBA) were monitored as $m/z = 130$ amu [DBA + H] and $m/z = 57$ amu [C₄H₉]⁺, which are both typical fragment ions of isocyanate-DBA derivatives (Karlsson et al., 2000) together with the protonated molecular ions [DBA-M + H]. Diisocyanate derivatives (HDI-DBA, 2,6-TDI-DBA, 2,4-TDI-DBA, IPDI-1-DBA, IPDI-2-DBA, 4,4'-MDI-DBA) were in addition to the previous ions, also studied as respective fragment ions [M + H-129] in order to increase the selectivity. These ions are fragments for the corresponding diisocyanates (Karlsson et al., 2005).

2.3.4. HPLC-QTOF-MS

A search for other isocyanates present in the pyrolysis samples of FPUF (300, 400, 850 °C) was performed with an Agilent 6530 Accurate-Mass Q-TOF LC/MS system (San Jose, CA, USA). The mass spectrometer was operated in the positive electrospray mode. The nebuliser flow gas was set to 10 L/min at 300 °C. HPLC column and gradient conditions were identical to the HPLC-QQQ-MS measurements.

First, precursor ions scan was performed in the QTOF-MS to assess the main ions found in the samples along with their retention times. Secondly, for each ion detected, product ion scans were acquired for two minutes, applying four different collision energies.

3. Results and discussion

3.1. Isocyanate emissions from FPUF

The results obtained from thermal degradation of flexible polyurethane foam (FPUF) under an inert atmosphere at 300, 350, 400, 450 and 850 °C are shown in Fig. 1 (note the logarithm scale). The recoveries obtained in the FPUF samples were 63–85%.

ICA, MIC, 2,6-TDI, 2,4-TDI and 4,4'-MDI were the most abundant isocyanates obtained at all temperatures. In addition, PHI emissions exhibited 100 times higher levels at 850 °C than those found at lower temperatures.

Similar low temperature profiles were reported previously by Blomqvist et al. (2003). They analysed isocyanates, amino-isocyanates and amines generated during the combustion of FPUF. High levels of ICA, 2,4-TDI, 2,6-TDI and MDI emissions were detected in those small-scale tests as well.

Fig. 2A–F (note the logarithm scale) display the observed temperature profiles together with the weight loss curve calculated with the kinetic model of Garrido and Font (2015) for the thermal degradation of FPUF under an inert atmosphere. They postulated that the pyrolysis of FPUF occurs in two consecutive reactions, the first at about 280 °C and the second at 370 °C. The kinetic model was based on TGA measurements with accurate temperature measure, whereas the horizontal furnace employed in this study exhibits a parabolic temperature distribution with the highest values in the middle of the furnace and the lowest at the edge (Aracil et al., 2005). Thus, when moving the sample inside the

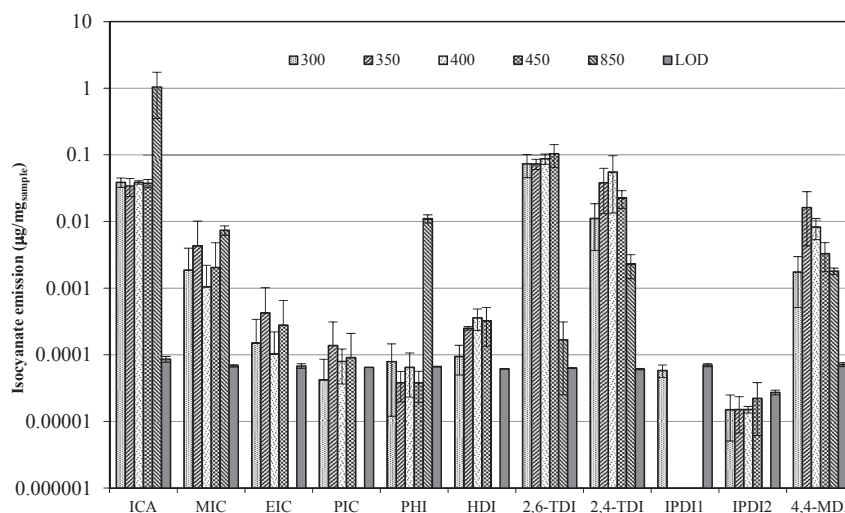


Fig. 1. Emissions of isocyanates from thermal degradation of FPUF under inert atmosphere at different temperatures. The concentrations were calculated as average values of three different samples analysed for each temperature, standard deviations are also presented.

furnace, it is on average exposed at lower than nominal temperatures. Experiments at the lowest selected temperatures (300–450 °C) are expected to induce the first degradation step when the urethane bonds are broken resulting in the emission of isocyanate monomers, such as 2,6 and 2,4-TDI and 4,4'-MDI. The formation of longer chains of polyol segments are expected in the second step (Garrido and Font, 2015). In the second step, not only the chains of polyols but also the released isocyanate monomers decomposed to more simple products such as ICA, MIC and PHI, resulting in increased emissions at 850 °C.

Variations of isocyanate concentration with the temperature have been reported previously. Rosenberg (1984) analysed the amount of TDI obtained from the combustion of polyurethane varnishes in a laboratory oven at 220 and 370 °C observing that the TDI concentration decreased when the combustion temperature was raised. Karlsson et al. (2000) undertook an intensive study of isocyanates released (from MIC to IPDI) from polyurethane coatings heated from 100 to 500 °C in a tube furnace employing an impinger-filter system with DBA as the derivatization agent. In spite of employing air as the carrier gas, they observed a similar isocyanate profile as obtained in this study. At temperatures lower than 350 °C, diisocyanate monomers such as TDI dominated, whereas at higher temperatures than 350 °C monoisocyanates exhibited the highest concentrations in the exhaust gas.

The most simple isocyanate, isocyanic acid (ICA), showed increased emissions at 850 °C (Fig. 2A). This behaviour can be explained by the conclusion of Blomqvist et al. (2003) in their study of isocyanates, aminoisocyanates and amines from combustion of buildings materials including FPUF. They observed that ICA was the main product from the degradation of FPUF and postulated that ICA is the “final” breakdown product of the polyurethane structure. Karlsson et al. (2001) analysed ICA and MIC emissions from the combustion of polyurethane lacquers from car metal sheets in a tube furnace at temperatures between 100 and 700 °C. Thereby, they observed the largest emissions at 600 °C and a decrease at temperatures higher than 600 °C. The presence of oxygen might explain the difference in the results of our study. These hypotheses agree with the results obtained by Blomqvist et al. (2014) in their study of the effects of the combustion atmosphere on isocyanate emissions from polyvinyl chloride carpet and wood board employing the ISO/TS 19700 steady-state tube furnace. They showed that tests performed under well-ventilated conditions

exhibited a more efficient degradation than the oxidative pyrolysis and under-ventilated conditions. In other words, these tests produced more degradation products compared with tests under well-ventilated conditions. They postulated that the reason for this difference must be a lack of oxygen to achieve complete oxidation of the material.

The diisocyanate monomers, 2,6-TDI and 2,4-TDI, were the predominant species at lower temperatures as they originate from the polymer chain without further thermal breakdown (Fig. 2D and E).

To improve the structural properties of FPUF, a blend of 80% TDI and 20% MDI (Chanda and Roy, 2008) is employed to produce these foams, which can be confirmed observing the high concentration of TDI compared to MDI which was mainly released at lower temperatures (Knaub et al., 1997) (Fig. 2F).

At 850 °C, monoisocyanates such as ICA, MIC and PHI exhibited a higher concentration than diisocyanates. As has been said, ICA and MIC are the final breakdown products from the thermal cracking of larger compounds, which explains their increase with temperature. The increased PHI emissions (Fig. 2C) could be the consequence of two different processes. Firstly, it is known that PHI is an intermediate product from the thermal breakdown of technical MDI (Blomqvist et al., 2003). But observing the low decreased in the MDI concentration, this cannot be single reason for the increased PHI emissions at 850 °C. Secondly, the high amount of naphthalene obtained by Garrido et al. (2016b) from the pyrolysis of FPUF at 850 °C, performed in the same horizontal laboratory reactor, could be responsible for the PHI formation at this temperature. This fact can be explained by the hypothesis of Parker et al. (2012) who suggested that the formation of naphthalene is via a reaction between phenyl radical and vinylacetylene. This means that with an increase of temperature, naphthalene could break down to produce the phenyl radical which will react with isocyanate groups present in the urethane structure to produce PHI.

The total NCO concentration can be found in Table S4 with highest values was obtained at 850 °C (1.032 µg NCO/mg_{sample}). Those at 450, 400, 350 and 300 °C were all similar levels of 0.100, 0.110, 0.096 and 0.081 µg NCO/mg_{sample}, respectively. ICA and 2,6-TDI varied from 34 to 47% and from 37 to 50% respectively, between 300 and 450 °C in the NCO contribution. At the highest temperature, ICA clearly dominated the emission with 99% of the total NCO concentration detected.

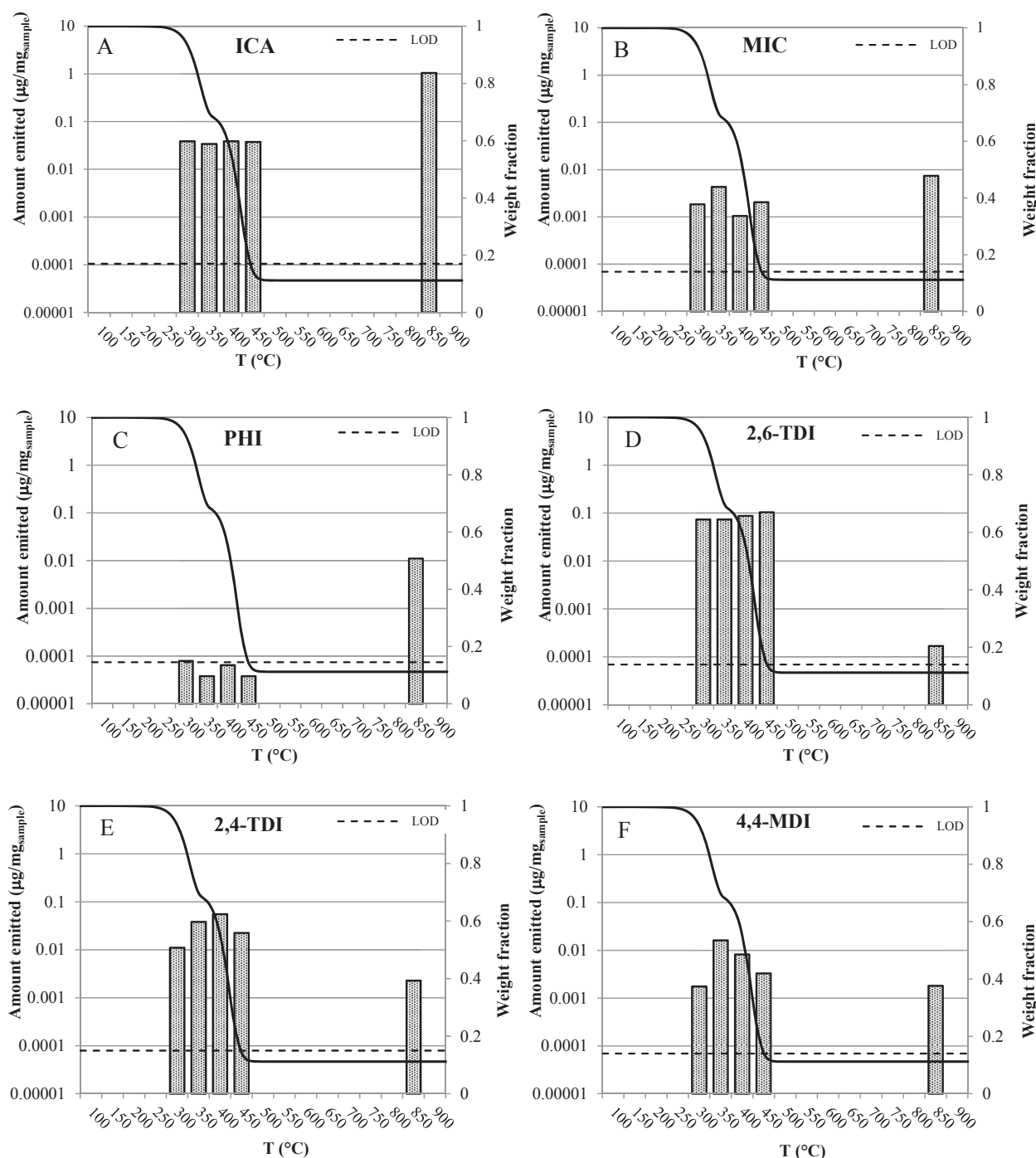


Fig. 2. Comparison of proportions weight loss (—) in the FPUF pyrolysis process and the amount of ICA (A), MIC (B); PHI (C), 2,6-TDI (D), 2,4-TDI (E) and 4,4'-MDI (F) obtained at each temperature (▒).

Considering a nitrogen content of 5.95% in FPUF (Table S2), the recovery of the initial N as NCO was 0.1% for experiments performed at 300, 350, 400 and 450 °C, whereas at 850 °C this value increased up to 0.6% due to the highest ICA emissions.

Total emission of isocyanates at 850 °C was ten times higher than those at lower temperatures. Blomqvist et al. (2003) performed a series of small-scale combustion experiments in a cone calorimeter analysing isocyanate emissions during the combustion of 24 different materials: flexible polyurethane foam being one of them. They reported a yield of total isocyanates of 0.869 μg/mg

sample. This value is close to those observed here at 850 °C, which is the expected result bearing in mind that in flexible polyurethane mattress fires temperatures are around 600–800 °C (Commision, 2006).

Other nitrogen compounds were detected by Garrido et al. (2016b) from the pyrolysis of FPUF at 550 and 850 °C. In addition to ammonia, 22 volatile nitrogen containing compounds were detected. Hydrogen cyanide, acetonitrile and acrylonitrile were the most abundant of them. The N recovery for ammonia was 34% and 20% at 550 °C and 850 °C, respectively, whereas for the other 22

compounds N recoveries were: 4% at 550 °C and 70% at 850 °C. Also, more than 75 different nitrogen containing semivolatile products were detected in the pyrolysis runs. The most important were: benzonitrile, aniline, indole, isoquinoline, indene, 4-methyl-benzonitrile and quinolone. The N recovery for these semivolatile compounds were 0.8 and 3.9% at 550 °C and 850 °C, respectively. In conclusion, the release of nitrogen containing compounds reported by Garrido et al. (2016b) agrees with the results presented in this study. With increasing temperatures, the thermal cracking resulted in an increased emission of ICA (the simplest isocyanate) and nitrogen-containing aromatic compounds. A similar product distribution was obtained by Marks and Metcalfe (1996) in a pyrolysis study of *para*-toluene isocyanate.

3.2. Isocyanate emissions from VMF

Fig. 3 (logarithm scale) displays the results from the thermal degradation of viscoelastic memory foam (VMF) under an inert atmosphere at 300, 350, 400, 450 and 850 °C.

Viscoelastic memory foams are produced with the addition of MDI, to obtain the elastic properties. The isocyanate profiles obtained are similar to those of FPUF pyrolysis. The experiments performed between 300 °C and 450 °C presented the same isocyanate profiles with TDI and MDI monomers dominating, in this case, 2,4-TDI and 4,4'-MDI. The recoveries obtained in the VMF sample were in the range 71–80%.

The clear differences between 2,4- and 2,6-TDI isomers, agrees with the commercial blend used to produce more flexible polyurethane foams. Typically, an 80/20% 2,4- and 2,6-TDI mixture is used (Chanda and Roy, 2008). The MDI emission at lower temperatures also confirms the use of this isocyanate in the respective foam formulation in order to achieve the desired mechanical properties.

No diisocyanates have been detected at 850 °C. However, the substantial increase of ICA and PHI should again be the consequence of thermal cracking of the diisocyanates and the radical reaction between phenyl radicals and isocyanates groups, respectively. The absence of these diisocyanates could be the result of subsequent reactions with some of the additives that are usually employed in the production of VMF foams, but are not used in the formulation of FPUF.

Fig. S4A–Fig. S4D show the calculated curve with the kinetic model proposed by Garrido et al. (2016a) for the pyrolysis of VMF.

This also consists of two consecutive reactions; the first located around 372 °C and the second at 412 °C where the most important weight loss was obtained. 2,4-TDI and 4,4'-MDI (Fig. S4C and Fig. S4D) levels at 400 °C were higher than those at the other temperatures and coincided with the highest weight loss. Thus, in the experiments performed between 300 °C to 450 °C, only the break of urethane chains occurred whereas at 850 °C the monomers released were terminally degraded to monoisocyanates (Fig. S4A and Fig. S4B), mainly ICA.

No previous studies on isocyanate emissions of viscoelastic memory foams have been found.

The thermal degradation of VMFs (Table S5) showed lower yields on isocyanates than FPUFs, being often near the LOD, especially at lower temperatures. This corresponds to the fact that the amount of isocyanates that are used in the formulation of VMF are lower than for FPUF production, as can be confirmed with the nitrogen content of this foam which was 3.34% (Table S2). In fact, not only the total isocyanate concentration but also the total NCO concentrations emitted from the pyrolysis of VMF were in some cases negligible compared with those from the FPUF degradation (Table S5). 2,4-TDI and 4,4'-MDI were the monomers contributing 36–68% and 26–48% of the total NCO concentration for all experiments except those at the highest temperature, where once again ICA provided 98% of the total NCO detected.

The N recoveries achieved in the VMF samples were of the same order of magnitude as those obtained from the FPUF pyrolysis, 0.002% at 300 °C, 0.01% at 350 and 450 °C, 0.02% at 400 °C and 0.52% at 850 °C. These values suggested that in the same way as FPUF, it is expected that the main nitrogen-containing compounds will be detected in volatile and semivolatile compounds.

3.3. Estimation of potential health hazard

It is known that isocyanates are strong skin and respiratory irritants which are able to induce isocyanate asthma. Furthermore, the European Commission (EC) considers monomer toluene diisocyanate (TDI) as a possible carcinogen to humans (Roberge et al., 2013). In order to prevent harmful health effects and these diseases, it is important to evaluate the exposure of workers employing occupational exposure limits. For this purpose, countries such as Spain, Australia, the United Kingdom, Germany, Switzerland, United States of America, Sweden and France have established permissible exposure limits for some of these

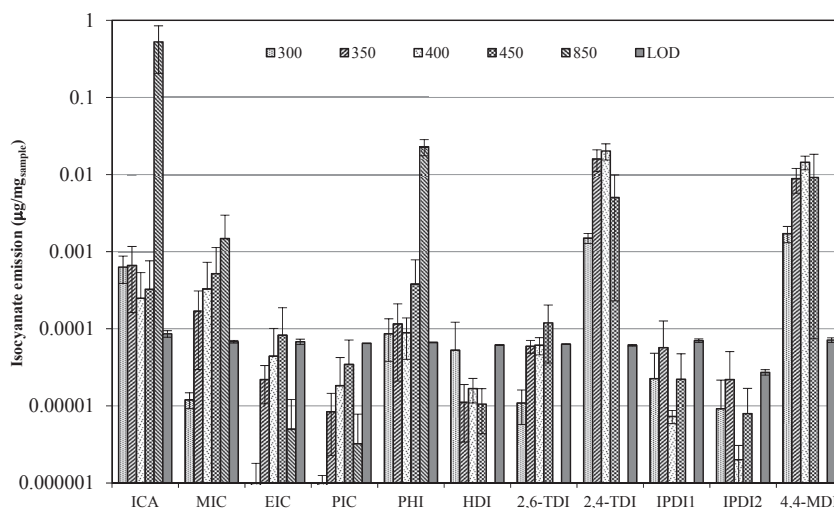


Fig. 3. Emissions of isocyanates from thermal degradation of VMF under inert atmosphere at different temperatures. The concentrations were calculated as average values of three different samples analysed for each temperature, standard deviations are also presented.

isocyanates, expressed as the mass of isocyanates per unit of air volume. The most common limits are based on an 8-h-time-weighted average (TWA) and a short-term exposure limit (15-minutes, STEL). The Spanish Government (INSHT, 2016) provides limit values of daily exposure (TWA) for some isocyanates which have been shown in Table S1, where the sum of the TLV-TWA values of all of them was 0.255 mg/m³.

In order to evaluate the possible exposure risk for workers in cement or incineration plants, the total isocyanate (volume-based) concentrations have been calculated for the different experiments performed and the results are shown in Table S6. These values represent the ratio between the total mg of isocyanates obtained and the total N₂ volume sampled, simulating the expected concentration of a punctual emission. From these results, it can be noted that all experiments except those carried out with VMF at 300 °C and 450 °C showed higher levels than the total exposure limit calculated (0.255 mg/m³). Both materials presented the highest levels at 850 °C reaching concentrations 47 and 24 times the exposure limit in FPUF and VMF, respectively. These values mean that workers of an FPUF or VMF pyrolysis system would be at risk of exposure and safety precautions would be necessary. However, the presence of oxygen in the incineration processes reduces the isocyanate emissions (Boutin et al., 2004), so an exposure risk lower than those shown in Table S6 should be expected, which is an important conclusion considering that the large amount of mattresses incinerated per year will increase progressively in future years due to more restrictive regulations for landfill waste.

3.4. Search for other isocyanates

The search of other isocyanates formed during the FPUF pyrolysis at three different temperatures (300, 400 and 850 °C) has been

achieved using QTOF-MS.

When DBA derivatives of isocyanates are ionised in the electrospray source, the most abundant ions are those obtained after a neutral loss of DBA. In this way, the scans in the QTOF-MS gave information about the most abundant ions obtained at different retention times. An example is showed in Fig. S5 for pyrolysis of FPUF at 300 °C. From some of the peaks, mass spectra were extracted and matching formulas were suggested, as shown in Table S7. With these ions detected, a bibliographic search was performed to know if they were observed previously and it was found that some of these compounds had been reported in other studies.

Tinnerberg et al. (1996) studied the emissions of isocyanates, aminoisocyanates and amines during the thermal decomposition of TDI-PUR employing two different derivatizing reagents, ethyl chloroformate (ET) for amines and DBA for isocyanates. They found that during the thermal degradation of TDI-PUR three isomers of toluene aminoisocyanates (TAI) were formed which are expected to produce ions with *m/z* values of 278 amu. Table 1 reports these three isomers. The elution order was: 2,6-TAI, 2,4-TAI and 4,2-TAI, with 2,6-TAI presenting the highest area followed by 4,2-TAI and 2,4-TAI. During air sampling, they employed only DBA as a reagent and the derivatization of amine groups was performed just before the LC-MS analysis monitoring ions at *m/z* = 350 amu, characteristic for TAI-ET-DBA. Additionally, Blomqvist et al. (2003) performed a series of small-scale combustions in a cone calorimeter (ISO 5660-1:1993), where generally well-ventilated combustion conditions are obtained. They studied the emissions for isocyanates, aminoisocyanates and amines from the combustion of 24 typically building materials being one of the flexible polyurethane foam. Three different toluene aminoisocyanates (TAI) isomers were found, 2,6-TAI, 2,4-TAI and 4,2-TAI. Isomer 2,6-TAI presented the

Table 1
Possible aminoisocyanates detected in pyrolysis samples of FPUF at 300, 400 and 850 °C.

<i>m/z</i>	Structure	Name	T (°C)
278		Toluene-2-amino-6-isocyanate	300, 400, 850
278		Toluene-2-amino-4-isocyanate	300, 400, 850
278		Toluene-4-amino-2-isocyanate	300, 400, 850
377		5-amino-N-(3-isocyanate-4-methylphenyl)pentanamide	300, 400, 850
426		1-aminomethyl-3-(4-(4'-isocyanobenzyl)phenyl)urea	300
453		1-butyl-3-(4-(4'-isocyanobenzyl)phenyl) urea	300, 400, 850

highest level in the exhaust gases, followed by 4,2-TAI and 2,4-TAI. Bearing these results in mind, it was assumed that the three peaks detected at $m/z = 278$ amu are the three isomers for the DBA-derivation of toluene aminoisocyanates (Fig. S5).

For the ions with $m/z = 377$, 426 and 453 amu, no references were found. Considering the molecular formulas suggested and the results obtained from HPLC-QQQ-MS showing a preference for TDI and MDI diisocyanates, molecular structures for these unknown degradation products were proposed. Table 1 shows the ions observed, the structures suggested, the name of these compounds and the experiments in which they had been detected.

To confirm the suggested structures, product ion scans were performed, for the respective precursor ions at four different collision energies (10, 30, 50 and 70 eV). Fig. S6A displays the product ion decomposition of precursor ions as $m/z = 278$ amu at 300 °C, where three peaks were detected at 3.6, 3.9 and 4.45 min.

The first eluting isomer which is tentatively assigned to 2,6-TAI considering the elution order of Tinnerberg et al. (1996) accounted for about 70% of the area, while the second and third isomers which were assigned to 2,4-TAI and 4,2-TAI accounted from 10% to 20%, respectively.

Assuming that the respective precursors are toluene aminoisocyanates, it was possible to suggest the main product ions that should be obtained. Extracting the mass spectra from these peaks indeed confirmed the postulated structures. Fig. S6B shows the product ion spectrum of the first eluting peak shown in Fig. S6A. All likely product ions of TAI-DBA were obtained. Similar spectra were obtained for the other two peaks.

With these results, it can be said that the ions with $m/z = 278$ amu are possibly the DBA derivatives of three toluene aminoisocyanate isomers (TAI).

Similar MS experiments were performed with product ions at $m/z = 377$, 426 and 453 amu. In all cases the suggested structures were confirmed based on the observed formed ions. The respective chromatograms from the product ion scans and mass spectra obtained can be found in Fig. S7–S9.

Almost all of the new aminoisocyanates were detected not only in samples exposed at 300 °C but also in these at 400 and 850 °C, except 1-aminomethyl-3-(4-(4'-isocyanobenzyl)phenyl)urea, which was obtained from the FPUF thermal degradation only at 300 °C. The general trend observed was a decrease of the aminoisocyanates levels with increasing pyrolysis temperature as a consequence of the fragmentation of larger isocyanates by thermal stress.

4. Conclusions

The measured emissions of various isocyanates from the pyrolysis of FPUF agreed with the kinetic model proposed previously. At lower temperatures, the long polyurethane chains broke and the respective diisocyanates were released. At temperatures of 850 °C, monoisocyanates and isocyanic acid were found in high levels as a consequence of the thermal cracking of diisocyanates released from the polymer chains.

Similar trends have been observed for the viscoelastic foam; however, VMF produced much fewer isocyanates than FPUF at the same degradation conditions due to a lower content of isocyanates in the raw material for producing this type of foam.

The total isocyanate concentrations obtained in almost all the experiments, except those with VMF 300 and 450 °C, presented levels higher than the total occupational exposure limit estimated as 0.255 mg/m³. Pyrolysis at 850 °C produced 11.95 and 6.13 mg/m³ in FPUF and VMF, respectively.

From the search of other potential isocyanates from the FPUF pyrolysis, we could confirm, based on daughter ion scans, the

presence of six additional aminoisocyanates already formed at 300 °C. All of them are aminoisocyanate derivatives TDI and MDI, which were the most dominant isocyanates species in these experiments performed at 300–450 °C.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.11.009>.

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Isocyanate emissions from pyrolysis of mattresses containing polyurethane foam

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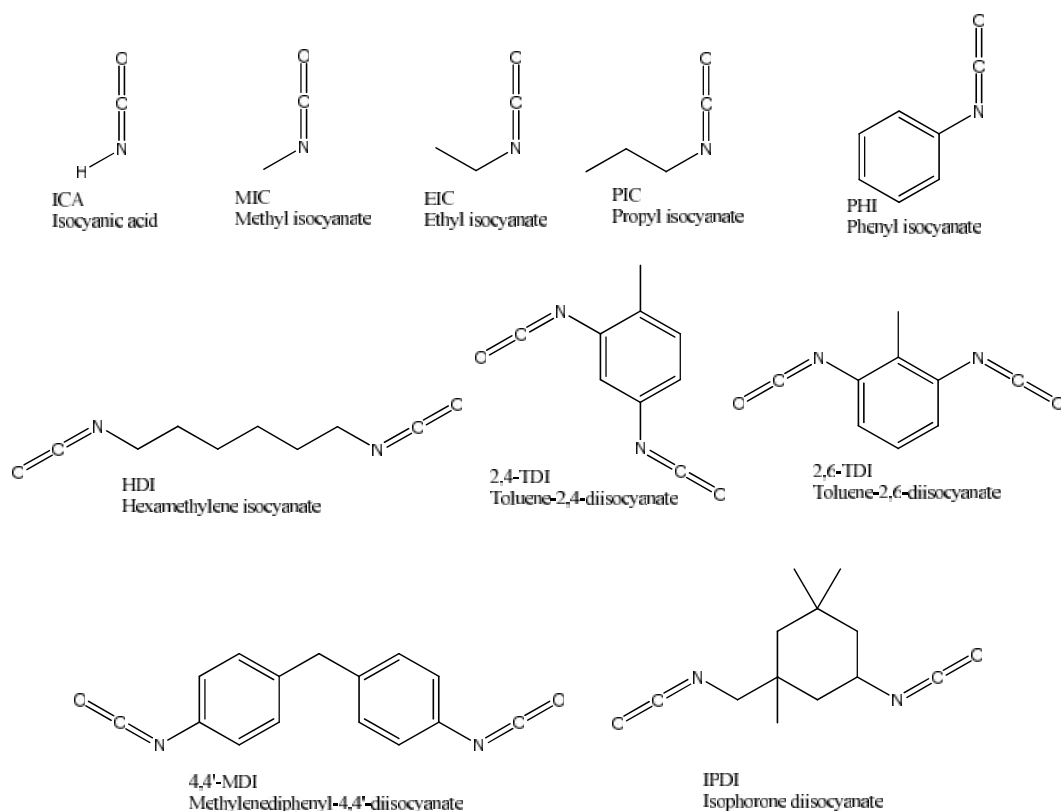


Figure S1. Important isocyanate structures, names and abbreviations used.

Table S1. Threshold Limit Value based on an eight-hours time-weighted average (TWA) proposed for some isocyanates. Occupational health legislation from Spain.

Isocyanate	TLV-TWA	
	ppm	mg/m ³
PHI	0.01	0.05
HDI	0.005	0.035
2,6-TDI	0.005	0.036
2,4-TDI	0.005	0.036
IPDI	0.005	0.046
4,4'-MDI	0.005	0.052
Total	0.035	0.255

Table S2. Elemental analysis and ash content of flexible and viscoelastic PUFs (dry basis).

Sample	N%	C%	H%	S%	Ash %	O% (by difference)
<i>FPUF</i>	5.95	57.79	7.36	0.00	5.47	23.43
<i>VPUF</i>	3.34	61.26	8.45	0.16	0.11	26.68

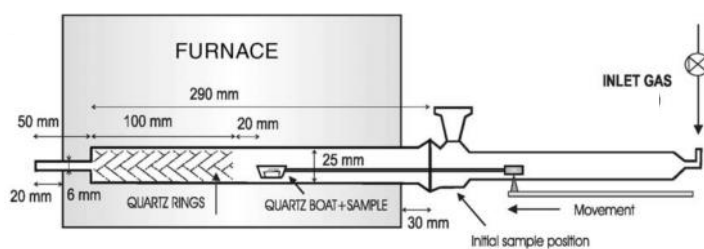


Figure S2. Scheme of the reactor inside the furnace.

Table S3. Concentration of isocyanate DBA derivatives (mg/mL) for seven calibration solutions and the correlation coefficient obtained for each compound.

	CALIBRATED CONCENTRATION (mg/mL)							Correlation Coefficient (R^2)
	L1	L2	L3	L4	L5	L6	L7	
<i>ICA-DBA</i>	0.001602	0.00587	0.0176	0.0646	0.194	0.711	3.91	0.989
<i>MIC-DBA</i>	0.001118	0.00410	0.0123	0.0451	0.135	0.496	2.73	0.998
<i>EIC-DBA</i>	0.000969	0.00355	0.0107	0.0391	0.117	0.430	2.36	0.994
<i>PIC-DBA</i>	0.000857	0.00314	0.00943	0.0346	0.104	0.380	2.09	0.998
<i>PHI-DBA</i>	0.000708	0.00260	0.00779	0.0285	0.0856	0.314	1.73	0.994
<i>HDI-DBA</i>	0.000857	0.00314	0.00943	0.0346	0.104	0.380	2.09	0.968
<i>2,6-TDI-DBA</i>	0.000820	0.00301	0.00902	0.0331	0.0992	0.364	2.00	0.970
<i>2,4-TDI-DBA</i>	0.000857	0.00314	0.00943	0.0346	0.104	0.380	2.09	0.970
<i>IPDI-DBA-1</i>	0.000745	0.00273	0.00820	0.0301	0.0902	0.331	1.82	0.961
<i>IPDI-DBA-2</i>	0.000298	0.00109	0.00328	0.0120	0.0361	0.132	0.727	0.960
<i>4,4-MDI-DBA</i>	0.000708	0.00260	0.00779	0.0285	0.0856	0.314	1.73	0.964

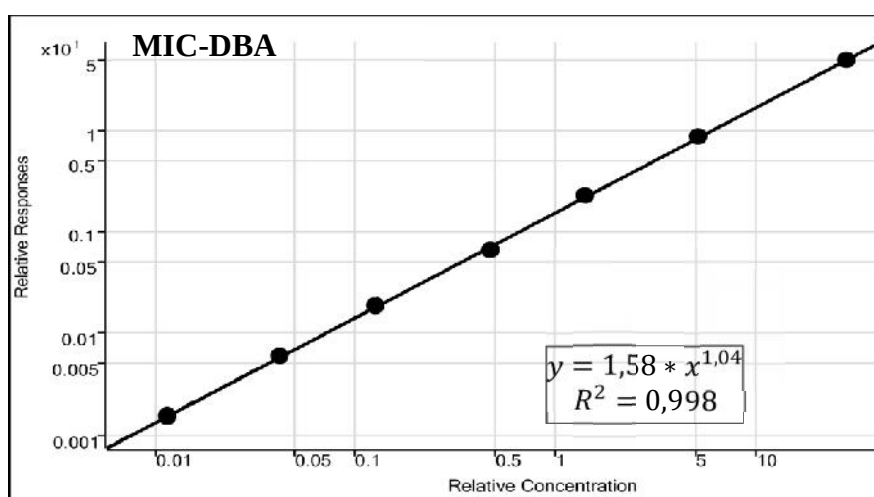


Figure S3. Calibration curve obtained for the DBA-derivative of methylisocyanate (MIC).

Table S4. Total isocyanate selected and NCO emissions at different temperatures from FPUF pyrolysis and relative contribution (%) of these selected isocyanates to the overall NCO sum.

		Run				
		300°C	350°C	400°C	450°C	850°C
Total Isocyanate emissions ($\mu\text{g}/\text{mg}_{\text{sample}}$)		0.127	0.167	0.191	0.170	1.068
Total NCO emissions ($\mu\text{gNCO}/\text{mg}_{\text{sample}}$)		0.081	0.096	0.110	0.100	1.032
% NCO	ICA	47	35	34	36	99
	MIC	2	3	1	1	1
	2,6-TDI	44	37	38	50	0
	2,4-TDI	7	19	24	11	0
	4,4-MDI	1	6	3	1	0

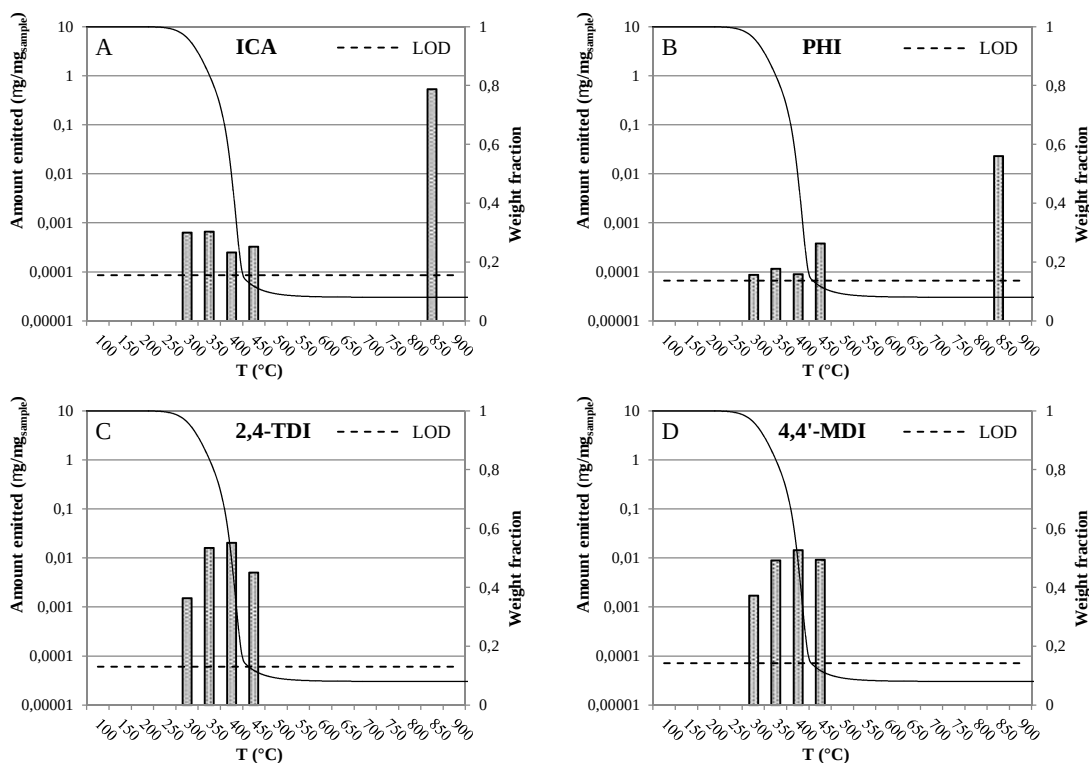


Figure S4. Comparison of weight loss curve (—) in the VMF pyrolysis process and the amount of ICA (A), PHI (B), 2,4-TDI (C) and 4,4'-MDI (D) obtained at each temperature (▒).

Table S5. Total isocyanate selected and NCO emissions at different temperatures from pyrolysis of VMF and contribution (%) of these selected isocyanates to the overall NCO sum.

		Run				
		300°C	350°C	400°C	450°C	850°C
Total Isocyanate emissions= $\frac{g}{mg_{sample}}$		0.004	0.026	0.035	0.016	0.551
Total NCO emissions= $\frac{g}{mg_{sample}}$		0.002	0.012	0.015	0.006	0.524
%NCO	ICA	31	6	2	5	98
	MIC	0	1	2	6	0
	2,6-TDI	0	0	0	1	0
	2,4-TDI	36	66	64	38	0
	4,4-MDI	29	26	32	48	0

Table S6. Total isocyanates concentration (volume-based) from FPUF and VMF pyrolysis experiments

T (°C)	300	350	400	450	850
Total isocyanate concentration (mg/m ³)					
FPUF	1.43	1.88	2.15	1.94	11.95
VPUF	0.05	0.29	0.40	0.18	6.13

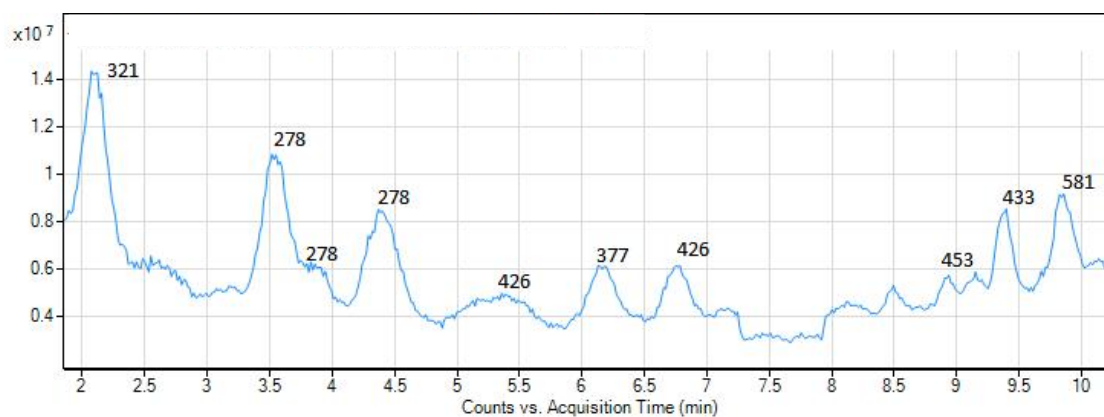


Figure S5. Chromatogram obtained in the single mass scan analysis in the QTOF-MS for the FPUF sample at 300 °C. Numbers indicate the main ions detected at each retention time.

Table S7. Suggested for characteristic ions obtained from mass scan analyses at the retention time indicated

m/z=[M-DBA] ⁺	Formula [M]	Ret. Time (min)	Score
278	C ₁₆ H ₂₇ N ₃ O	3.5, 3.8 and 4.4	98.62
377	C ₂₁ H ₃₇ N ₄ O ₂	6.2	99.7
426	C ₂₄ H ₃₅ N ₅ O ₂	6.7	99.96
453	C ₂₇ H ₄₁ N ₄ O ₂	9.2	99.8

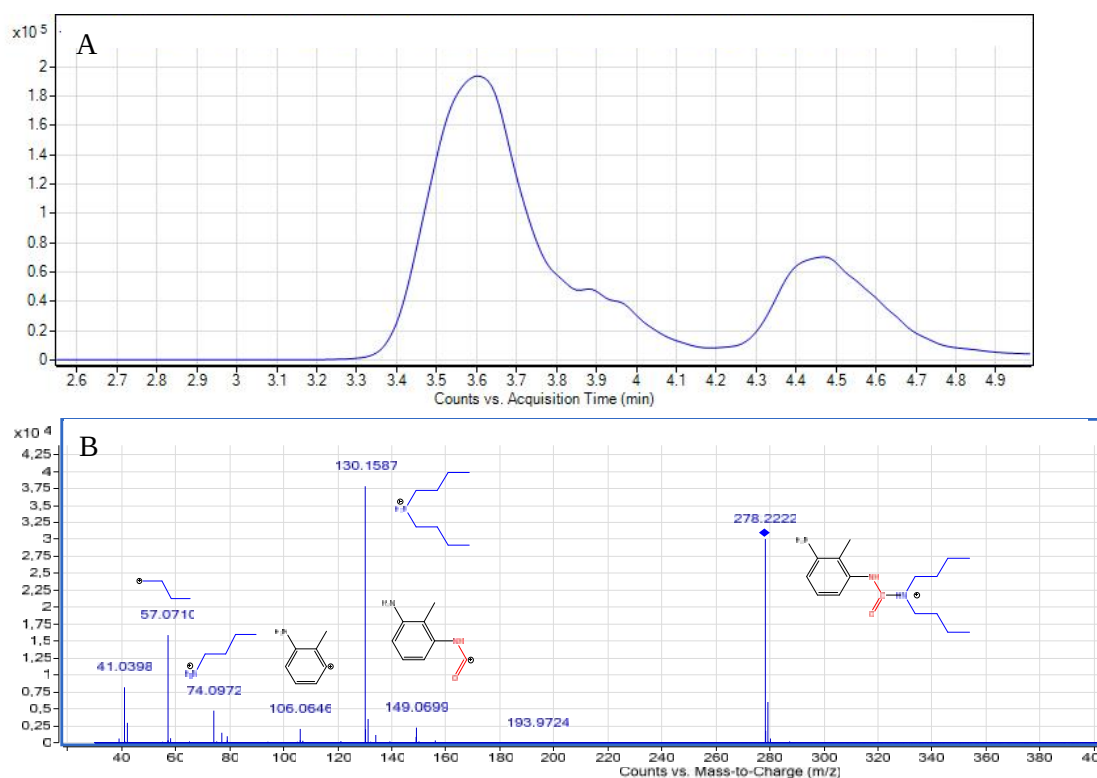


Figure S6. (A) Product ion scan chromatogram for the precursor ions at $m/z=278$ amu at 300 °C with a collision energy of 10 eV. (B) Product ion mass spectrum of the eluting peak at 3.6 min.

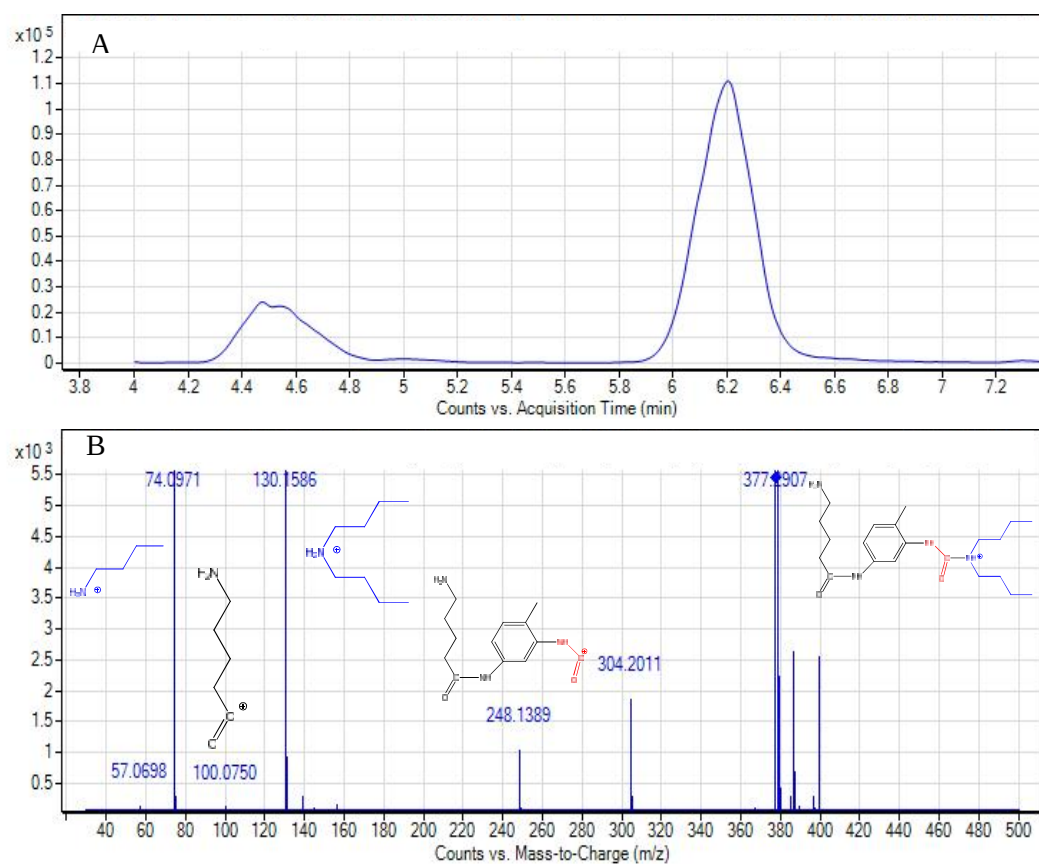


Figure S7. (A) Product ion scan chromatogram for the precursor ions at $m/z=377$ amu at 300 °C with a collision energy of 10 eV. (B) Product ion mass spectrum of the eluting peak at 6.2 min.

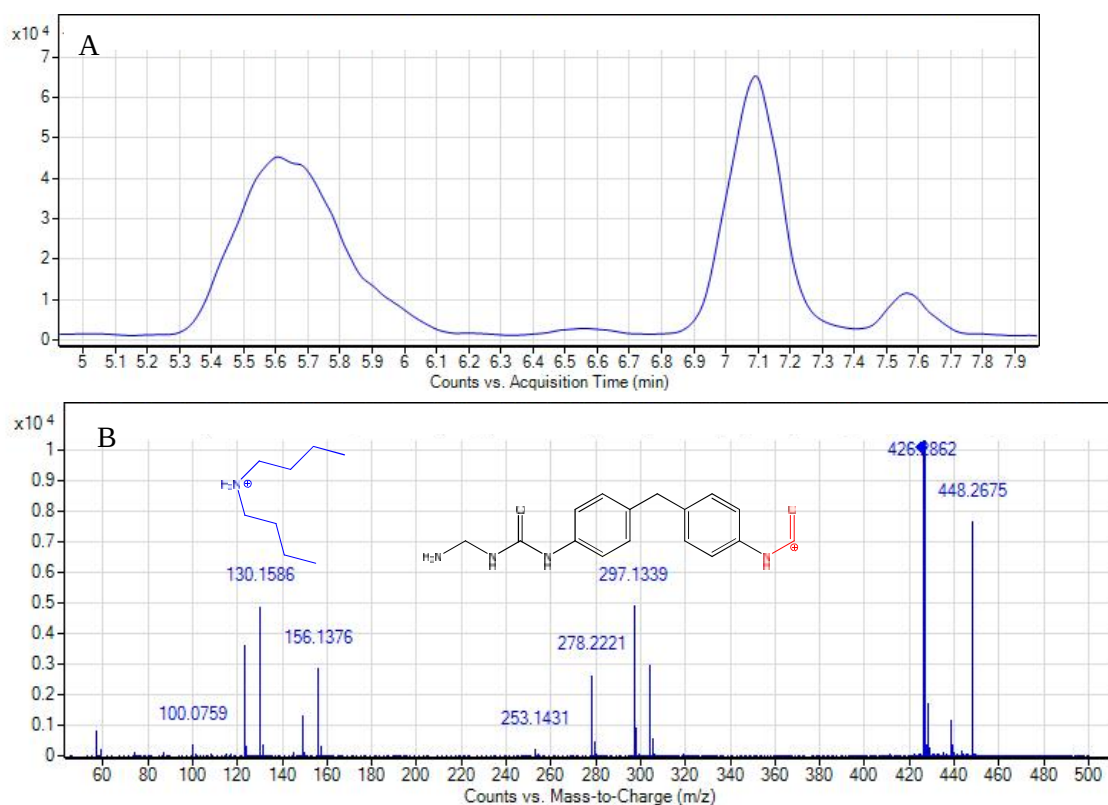


Figure S8. (A) Product ion scan chromatogram for the precursor ions at $m/z=426$ amu at 300 °C with a collision energy of 10 eV. (B) Product ion mass spectrum of the eluting peak at 6.7 min.

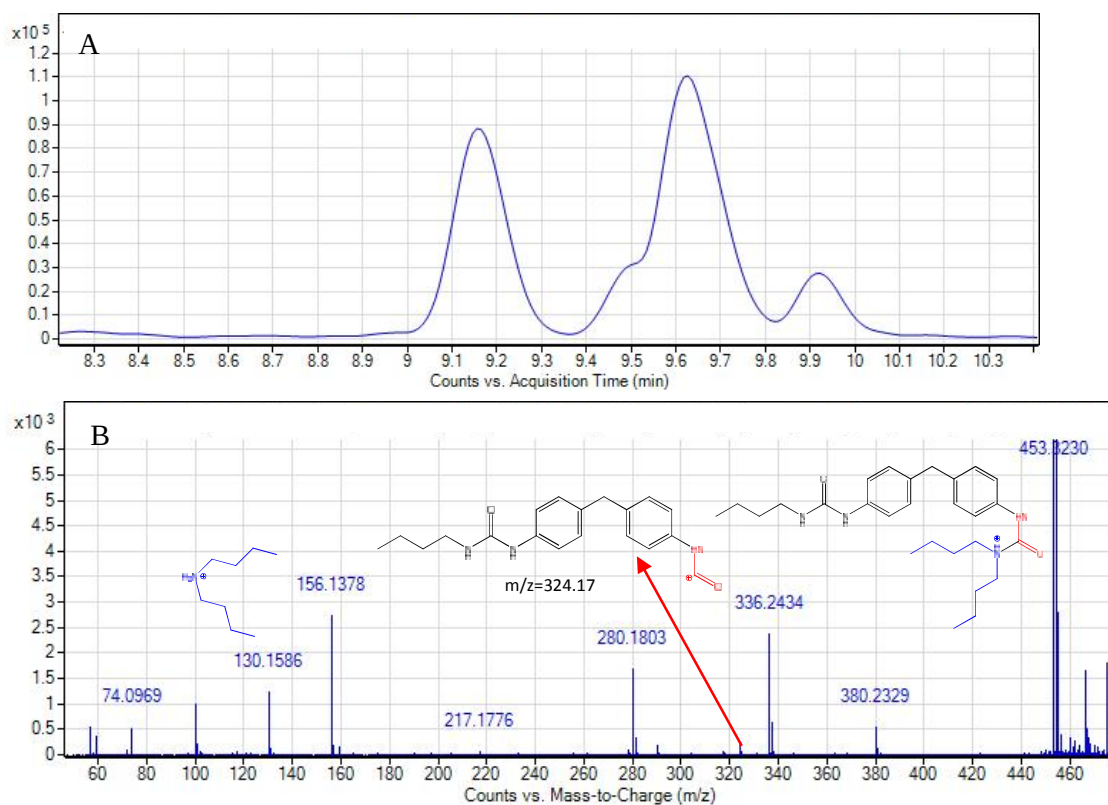


Figure S9. (A) Product ion scan chromatogram for the precursor ions at $m/z=453$ amu at 300 °C with a collision energy of 10 eV. (B) Product ion mass spectrum of the eluting peak at 9.2 min.