

Isocyanate emissions from pyrolysis of mattresses containing polyurethane foam

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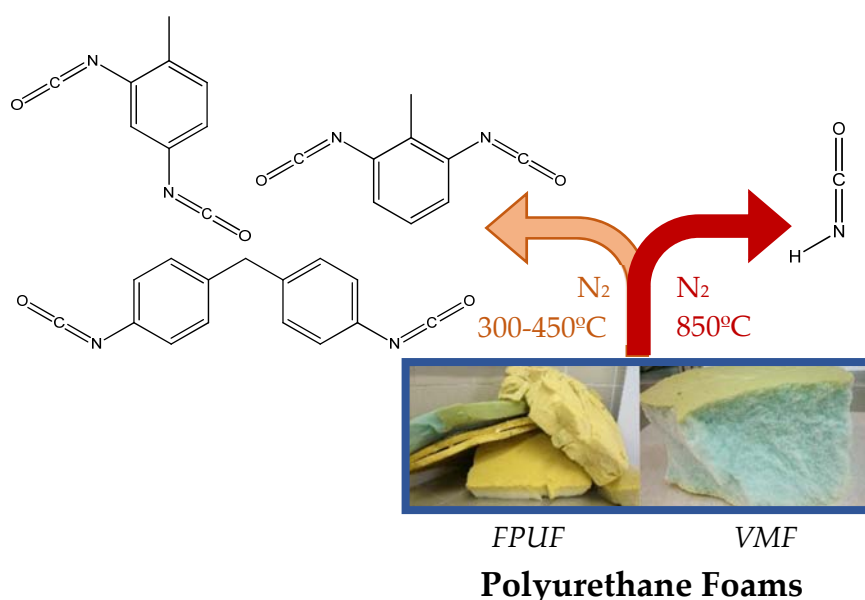
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Graphical abstract



Polyurethane Foams

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18 **Abstract**

19 This study examined the emissions of powerful asthmatic agents called isocyanates from
20 small-scale pyrolysis experiments of two common foams employed in mattress
21 production such as flexible polyurethane foam (FPUF) and viscoelastic memory foam
22 (VMF). A nitrogen atmosphere and five different temperatures, 300, 350, 400, 450 and
23 850°C, were selected to carry out the experiments in order to evaluate the worst possible
24 conditions for thermal degradation.

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

29 The total yields of isocyanates were in the range of 1.43-11.95 mg/m³ for FPUF at 300-
30 850°C and 0.05-6.13 mg/m³ for VMF, 300-850°C. This difference could be a consequence
31 of the lower amount of isocyanates employed in the VMF production which was
32 confirmed by the nitrogen content of the foams, 5.95% FPUF vs. 3.34% in VMF.

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

38

39 **Keyword:** flexible polyurethane foam, viscoelastic memory foam, pyrolysis,
40 isocyanates, aminoisocyanates

41

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

44 **1. Introduction**

45 Organic isocyanates are reactive compounds which contain one or more isocyanate
46 functional groups (R-N=C=O) joined to aliphatic or aromatic residues (R). The most
47 common isocyanates, their names and abbreviations used herein are shown in **Figure S1**,
48 Supporting Information.

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

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

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

62 The relationship between work exposure and health problems has triggered studies on the
63 emissions of these compounds during synthesis of polyurethane products and during
64 thermal or mechanical treatment of the final products, analysing the airborne isocyanates
65 at different workplace atmospheres. In this way, Rosenberg (1984) analysed the
66 workplace environment during the production of polyurethane-coated wire employing
67 two different polyurethane varnishes and a horizontal and a vertical coating machine.

68 Karlsson et al. (2000) studied airborne isocyanates emitted during grinding, cutting and
69 welding operations in a car repair shop. An extensive study by Karlsson et al. (2001) also
70 included aminoisocyanates and amines alongside isocyanates from the thermal
71 degradation of polyurethane during welding in district heating pipes and PUR-coated
72 metal sheets. The highest concentrations were obtained in the welding operation and
73 isocyanates were the most abundant in both processes.

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

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

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

92 In Europe, 30 million mattresses reach their end of life annually (Turner, 2014). About
93 60% are dumped in landfill sites; the remaining 40% are incinerated. In order to decrease
94 the amount of waste sent to landfills, the European Commission modified Directive
95 1999/31/EC on the landfill of waste in 2014. After January 1st 2015, only 25% of the total
96 amount of municipal waste generated in the previous year was to be accepted in landfills;
97 whereas, from January 1st 2030, this rate will be finally reduced by up to 5%. This new
98 legislation requires a substantial reduction of mattresses sent to landfill sites and a
99 respective increase of mattresses being incinerated.

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

109 **2. Experimental**

110 **2.1. Materials**

111 Flexible polyurethane foam (FPUF) and viscoelastic memory foam (VMF) were used as
112 they are the most frequently used materials for mattress production. These foams were
113 collected from a landfill in Alicante (Spain) as waste material and their composition was
114 unknown. For the characterization, elemental analyses were performed with a Flash EA
115 1112 Elemental Analyzer. The respective results are given in **Table S2** together with the
116 ash contents obtained by calcination of the samples in a muffle furnace at 950°C for 8

117 hours.

118 **2.2. Thermal degradation of polyurethane foams.**

119 A tubular quartz reactor located inside a horizontal laboratory furnace (**Figure S2**)
120 described previously (Aracil et al., 2005) was employed to study the evolution of
121 isocyanates from the pyrolysis of FPUF and VMF at 300, 350, 400, 450 and 850°C. About
122 50 mg of the sample were placed in the quartz boat and 150 ml/min of N₂ was fed parallel
123 to the sample. The residence times of the gas along the reactor zone at nominal
124 temperatures were calculated obtaining 17 s at 300°C, 15.5 s at 350°C, 14 s at 400°C, 12.7
125 s at 450°C and 7.1 s at 850°C.

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

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

133 **2.3. Exhaust analysis**

134 **2.3.1. Sampling procedure**

135 Isocyanates are highly electrophilic reacting with nucleophiles such as amines, alcohols
136 and even water. To prevent uncontrolled reactions with nucleophiles during sampling and
137 work-up, isocyanate groups are derivatized. In addition, the derivatisation can also
138 improve the sensitivity and selectivity of the analytical method (Streicher et al., 2000).
139 Primary and secondary amines such as 9-(N-methylaminomethyl) anthracene (MAMA)
140 (Karlsson et al., 1998), 1-(2-methoxyphenyl) piperazine (MOPIP) (Henriks-Eckerman et

141 al., 2000; Boutin et al., 2004) or di-n-butylamine (DBA) (Spanne et al., 1996; Blomqvist
142 et al., 2003; Blomqvist et al., 2014) are often used. In this study, DBA was used according
143 to the ISO norm 17734-1:2013 (ISO 17734-1, 2013) which describes sampling and
144 analysis of airborne isocyanates in workplace air. Therein, gas and particle phases were
145 collected by impinger flasks containing DBA solutions and DBA-coated glass fibre filters
146 in series. However, bearing in mind the low amounts of isocyanates collected in the
147 particle fraction, as shown in previous studies (Blomqvist et al., 2003; Dahlin et al., 2008),
148 only 100 mL impinger flasks were employed in this study containing 50 mL of
149 0.01 mol/L DBA in toluene. Before collecting the exhaust gases, the sampling solutions
150 were spiked with 1 mL of a solution containing 100 µg of 4,4'-methylenediphenyl
151 diisocyanate derivatized with di-n-ethylamine (DEA) (4-4'-MDI-DEA) and 100 µg of
152 2,4-toluene diisocyanate derivatized with di-n-ethylamine (2-4-TDI-DEA) which were
153 employed to calculate losses during the experimental procedure.

154 **2.3.2. Work-up procedure.**

155 Impinger flask samples were diluted with toluene up to a final volume of 100 mL and 10
156 mL of these solutions were concentrated in a rotary evaporator to about 1 mL and finally
157 concentrated to dryness with a moderate stream of nitrogen. The residues were solved in
158 1 mL acetonitrile (ACN).

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

162 **2.3.3. HPLC-QQQ-MS analysis**

163 *Calibration*

164 A commercial mix of isocyanate concentrated DBA derivatives (Supelco, USA) was

165 employed to prepare seven solutions covering a specific concentration range for different
166 isocyanate DBA derivatives (see **Table S3**, Supporting Information). These standard
167 solutions were also spiked with the same amount of D18-DBA isocyanates (Supelco,
168 USA).

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

171 *Analysis conditions*

172 Samples were analysed with an Agilent 6460 Triple Quadrupole (QQQ) LC/MS system
173 (San Jose, CA, USA). For analysis, 2 μ L of the samples were injected and passed through
174 a reversed phase column Zorbax Bonus-RP, 2.1 x 150 mm, 5 μ m, at a flow rate of 0.25
175 mL/min at 40°C. Mobile phases were A: buffer solution of 5 mM ammonium acetate
176 (pH=6) and B: acetonitrile with a gradient: 0-8 min from 50% to 95% B; 1 min 95% B; 2
177 min from 95% to 50% B; 1 min 50% B. Electrospray ionization was performed
178 monitoring positive ions using N₂ as nebulizing gas at 45 psi with a flow rate of 8 L/min
179 at 325°C. The temperature in the ion source was 325°C, the desolvation temperature
180 340°C.

181 Ions were monitored in the multiple-reaction monitoring (MRM) mode with individually
182 optimized collision energies, ranging from 8 to 45 V. Monoisocyanates (ICA-DBA, MIC-
183 DBA, EIC-DBA, PIC-DBA, PHI-DBA) were monitored as $m/z=130$ amu [DBA+H] and
184 $m/z=57$ amu [C₄H₉]⁺, which are both typical fragment ions of isocyanate-DBA
185 derivatives (Karlsson et al., 2000) together with the protonated molecular ions [DBA-
186 M+H]. Diisocyanate derivatives (HDI-DBA, 2,6-TDI-DBA, 2,4-TDI-DBA, IPDI-1-
187 DBA, IPDI-2-DBA, 4,4'-MDI-DBA) were in addition to the previous ions, also studied
188 as respective fragment ions [M+H-129] in order to increase the selectivity. These ions are

189 fragments for the corresponding diisocyanates (Karlsson et al., 2005).

190 **2.3.4. HPLC-QTOF-MS**

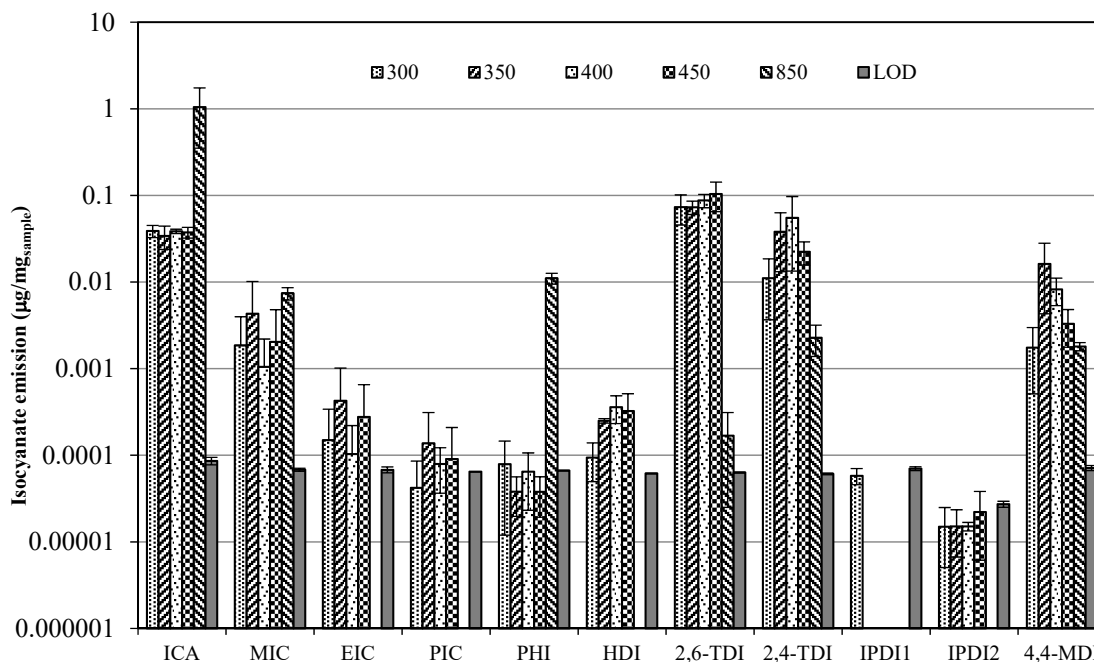
191 A search for other isocyanates present in the pyrolysis samples of FPUF (300, 400, 850°C)
192 was performed with an Agilent 6530 Accurate-Mass Q-TOF LC/MS system (San Jose,
193 CA, USA). The mass spectrometer was operated in the positive electrospray mode. The
194 nebuliser flow gas was set to 10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

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

199 **3. Results and Discussion**

200 **3.1. Isocyanate emissions from FPUF**

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



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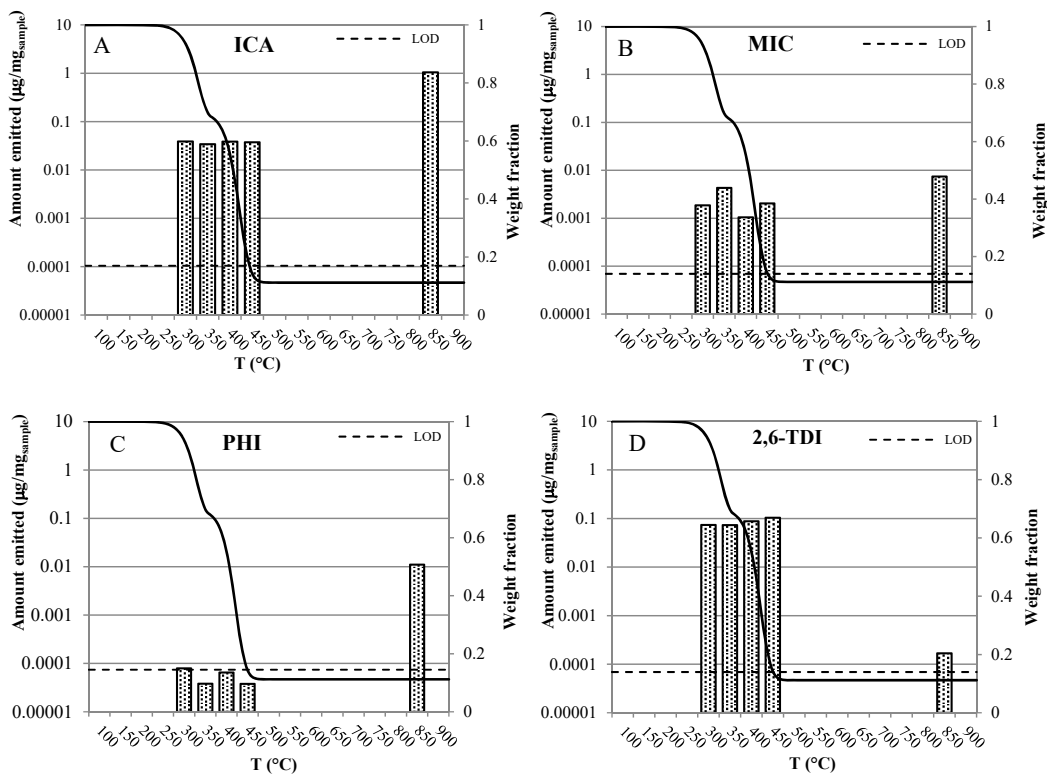
Figure 1

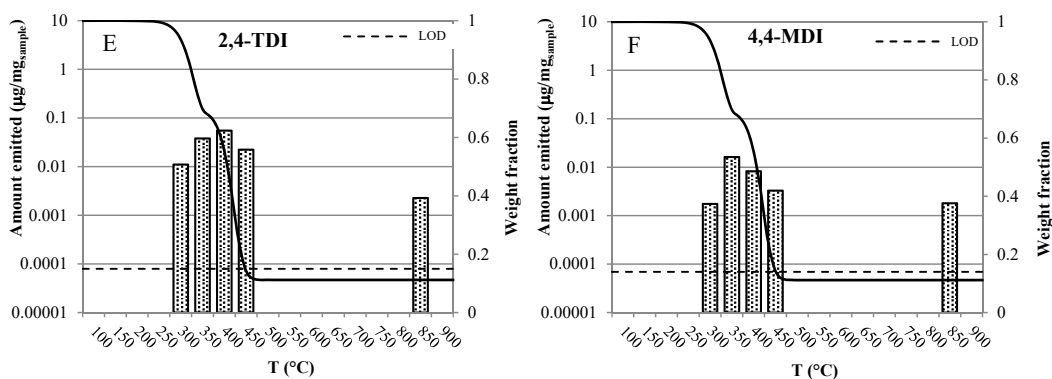
206 ICA, MIC, 2,6-TDI, 2,4-TDI and 4,4'-MDI were the most abundant isocyanates obtained
 207 at all temperatures. In addition, PHI emissions exhibited 100 times higher levels at 850°C
 208 than those found at lower temperatures.

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

213 **Figure 2A-Figure 2F** (note the logarithm scale) display the observed temperature
 214 profiles together with the weight loss curve calculated with the kinetic model of Garrido
 215 et al. (2015) for the thermal degradation of FPUF under an inert atmosphere. They
 216 postulated that the pyrolysis of FPUF occurs in two consecutive reactions, the first at
 217 about 280°C and the second at 370°C. The kinetic model was based on TGA
 218 measurements with accurate temperature measure, whereas the horizontal furnace

219 employed in this study exhibits a parabolic temperature distribution with the highest
 220 values in the middle of the furnace and the lowest at the edge (Aracil et al., 2005). Thus,
 221 when moving the sample inside the furnace, it is on average exposed at lower than
 222 nominal temperatures. Experiments at the lowest selected temperature (300°C) are
 223 expected to induce the first degradation step when the urethane bonds are broken resulting
 224 in the emission of isocyanate monomers, such as 2,6 and 2,4-TDI and 4,4'-MDI. The
 225 formation of longer chains of polyol segments are expected in the second step (Garrido
 226 and Font, 2015). In the second step, not only the chains of polyols but also the released
 227 isocyanate monomers decomposed to more simple products such as ICA, MIC and PHI,
 228 resulting in increased emissions at 850°C.





229

230

Figure 2

231 Variations of isocyanate concentration with the temperature have been reported
 232 previously. Rosenberg (1984) analysed the amount of TDI obtained from the combustion
 233 of polyurethane varnishes in a laboratory oven at 220 and 370°C observing that the TDI
 234 concentration decreased when the combustion temperature was raised. Karlsson et al.
 235 (2000) undertook an intensive study of isocyanates released (from MIC to IPDI) from
 236 polyurethane coatings heated from 100 to 500°C in a tube furnace employing an
 237 impinger-filter system with DBA as the derivatization agent. In spite of employing air as
 238 the carrier gas, they observed a similar isocyanate profile as obtained in this study. At
 239 temperatures lower than 350°C, diisocyanate monomers such as TDI dominated, whereas
 240 at higher temperatures than 350°C monoisocyanates exhibited the highest concentrations
 241 in the exhaust gas.

242 The most simple isocyanate, isocyanic acid (ICA), showed increased emissions at 850°C
 243 (**Figure 2A**). This behaviour can be explained by the conclusion of Blomqvist et al.
 244 (2003) in their study of isocyanates, aminoisocyanates and amines from combustion of
 245 buildings materials including FPUF. They observed that ICA was the main product from
 246 the degradation of FPUF and postulated that ICA is the “final” breakdown product of the
 247 polyurethane structure. Karlsson et al. (2001) analysed ICA and MIC emissions from the

248 combustion of polyurethane lacquers from car metal sheets in a tube furnace at
249 temperatures between 100 and 700°C. Thereby, they observed the largest emissions at
250 600°C and a decrease at temperatures higher than 600°C. The presence of oxygen might
251 explain the difference in the results of our study. These hypotheses agree with the results
252 obtained by Blomqvist et al. (2014) in their study of the effects of the combustion
253 atmosphere on isocyanate emissions from polyvinyl chloride carpet and wood board
254 employing the ISO/TS 19700 steady-state tube furnace. They showed that tests performed
255 under well-ventilated conditions exhibited a more efficient degradation than the oxidative
256 pyrolysis and under-ventilated conditions. In other words, these tests produced more
257 degradation products compared with tests under well-ventilated conditions. They
258 postulated that the reason for this difference must be a lack of oxygen to achieve complete
259 oxidation of the material.

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

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

267 At 850°C, monoisocyanates such as ICA, MIC and PHI exhibited a higher concentration
268 than diisocyanates. As has been said, ICA and MIC are the final breakdown products
269 from the thermal cracking of larger compounds, which explains their increase with
270 temperature. The increased PHI emissions (**Figure 2C**) could be the consequence of two
271 different processes. Firstly, it is known that PHI is an intermediate product from the

272 thermal breakdown of technical MDI (Blomqvist et al., 2003). But observing the low
273 decreased in the MDI concentration, this cannot be single reason for the increased PHI
274 emissions at 850°C. Secondly, the high amount of naphthalene obtained by Garrido et
275 al.(2016b) from the pyrolysis of FPUF at 850°C, performed in the same horizontal
276 laboratory reactor, could be responsible for the PHI formation at this temperature. This
277 fact can be explained by the hypothesis of Parker et al. (2012) who suggested that the
278 formation of naphthalene is via a reaction between phenyl radical and vinylacetylene.
279 This means that with an increase of temperature, naphthalene could break down to
280 produce the phenyl radical which will react with isocyanate groups present in the urethane
281 structure to produce PHI.

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

288 Considering a nitrogen content of 5.95% in FPUF (**Table S2**), the recovery of the initial
289 N as NCO was 0.1% for experiments performed at 300, 350, 400 and 450°C, whereas at
290 850°C this value increased up to 0.6% due to the highest ICA emissions.

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

296 here at 850°C, which is the expected result bearing in mind that in flexible polyurethane
297 mattress fires temperatures are around 600-800°C (Commision, 2006).

298 Other nitrogen compounds were detected by Garrido et al. (2016b) from the pyrolysis of
299 FPUF at 550 and 850°C. In addition to ammonia, 22 volatile nitrogen containing
300 compounds were detected. Hydrogen cyanide, acetonitrile and acrylonitrile were the most
301 abundant of them. The N recovery for ammonia was 34% and 20% at 550°C and 850°C,
302 respectively, whereas for the other 22 compounds N recoveries were: 4% at 550°C and
303 70% at 850°C. Also, more than 75 different nitrogen containing semivolatile products
304 were detected in the pyrolysis runs. The most important were: benzonitrile, aniline,
305 indole, isoquinoline, indene, 4-methyl-benzonitrile and quinolone. The N recovery for
306 these semivolatile compounds were 0.8 and 3.9% at 550°C and 850°C, respectively. In
307 conclusion, the release of nitrogen containing compounds reported by Garrido et
308 al.(2016b) agrees with the results presented in this study. With increasing temperatures,
309 the thermal cracking resulted in an increased emission of ICA (the simplest isocyanate)
310 and nitrogen-containing aromatic compounds. A similar product distribution was
311 obtained by Marks and Metcalfe. (1996) in a pyrolysis study of *para*-toluene isocyanate.

312 **3.2. Isocyanate emissions from VMF**

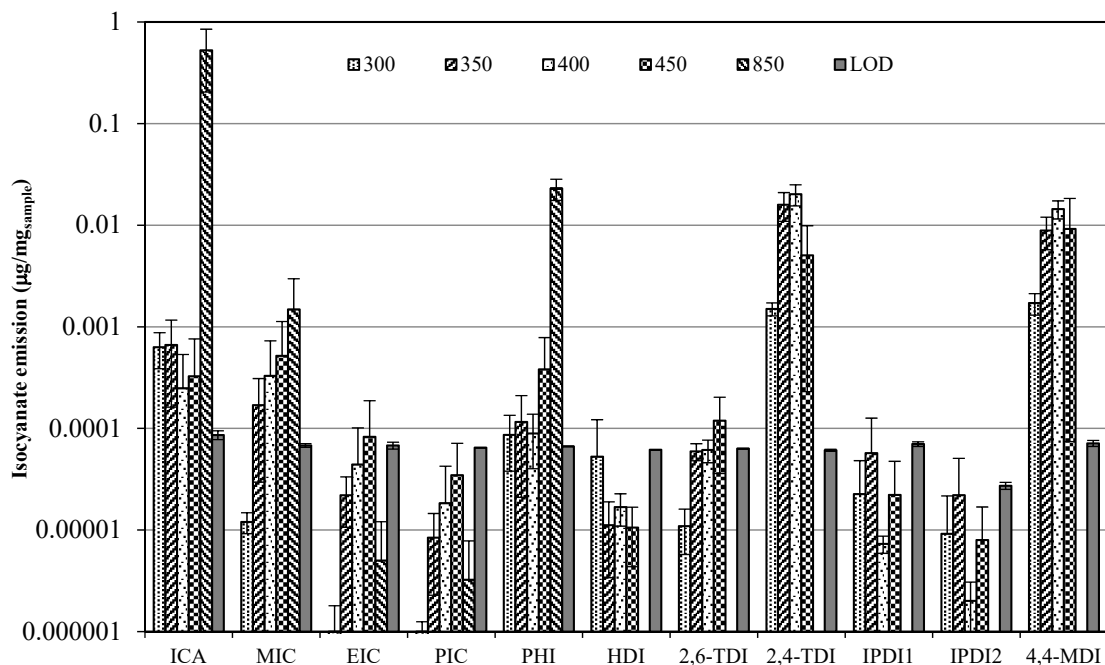
313 **Figure 3** (logarithm scale) displays the results from the thermal degradation of
314 viscoelastic memory foam (VMF) under an inert atmosphere at 300, 350, 400, 450 and
315 850°C.

316 Viscoelastic memory foams are produced with the addition of MDI, to obtain the elastic
317 properties. The isocyanate profiles obtained are similar to those of FPUF pyrolysis. The
318 experiments performed between 300°C and 450°C presented the same isocyanate profiles
319 with TDI and MDI monomers dominating, in this case, 2,4-TDI and 4,4'-MDI. The

320 recoveries obtained in the VMF sample were in the range 71-80%.

321 The clear differences between 2,4- and 2,6-TDI isomers, agrees with the commercial
322 blend used to produce more flexible polyurethane foams. Typically, an 80/20% 2,4- and
323 2,6-TDI mixture is used (Chanda and Roy, 2008). The MDI emission at lower
324 temperatures also confirms the use of this isocyanate in the respective foam formulation
325 in order to achieve the desired mechanical properties.

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



332

333

Figure 3

334 **Figure S4A-Figure S4D** show the calculated curve with the kinetic model proposed by

335 Garrido et al.(2016a) for the pyrolysis of VMF. This also consists of two consecutive
336 reactions; the first located around 372°C and the second at 412°C where the most
337 important weight loss was obtained. 2,4-TDI and 4,4'-MDI (**Figure S4C and Figure**
338 **S4D**) levels at 400°C were higher than those at the other temperatures and coincided with
339 the highest weight loss. Thus, in the experiments performed between 300°C to 450°C,
340 only the break of urethane chains occurred whereas at 850°C the monomers released were
341 terminally degraded to monoisocyanates (**Figure S4A and Figure S4B**), mainly ICA.

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

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

354 The N recoveries achieved in the VMF samples were of the same order of magnitude as
355 those obtained from the FPUF pyrolysis, 0.002% at 300°C, 0.01% at 350 and 450°C,
356 0.02% at 400°C and 0.52% at 850°C. These values suggested that in the same way as
357 FPUF, it is expected that the main nitrogen-containing compounds will be detected in
358 volatile and semivolatile compounds.

3.3. Estimation of potential health hazard

359 It is known that isocyanates are strong skin and respiratory irritants which are able to
360 induce isocyanate asthma. Furthermore, the European Commission (EC) considers
361 monomer toluene diisocyanate (TDI) as a possible carcinogen to humans (Roberge et al.,
362 2013). In order to prevent harmful health effects and these diseases, it is important to
363 evaluate the exposure of workers employing occupational exposure limits. For this
364 purpose, countries such as Spain, Australia, the United Kingdom, Germany, Switzerland,
365 United States of America, Sweden and France have established permissible exposure
366 limits for some of these isocyanates, expressed as the mass of isocyanates per unit of air
367 volume. The most common limits are based on an eight-hour-time-weighted average
368 (TWA) and a short-term exposure limit (15-minutes, STEL). The Spanish Government
369 (INSHT, 2016) provides limit values of daily exposure (TWA) for some isocyanates
370 which have been shown in **Table S1**, where the sum of the TLV-TWA values of all of
371 them was 0.255 mg/m³.

373 In order to evaluate the possible exposure risk for workers in cement or incineration
374 plants, the total isocyanate (volume-based) concentrations have been calculated for the
375 different experiments performed and the results are shown in **Table S6**. These values
376 represent the ratio between the total mg of isocyanates obtained and the total N₂ volume
377 sampled, simulating the expected concentration of a punctual emission. From these
378 results, it can be noted that all experiments except those carried out with VMF at 300°C
379 and 450°C showed higher levels than the total exposure limit calculated (0.255 mg/m³).
380 Both materials presented the highest levels at 850°C reaching concentrations 47 and 24
381 times the exposure limit in FPUF and VMF, respectively. These values mean that workers
382 of an FPUF or VMF pyrolysis system would be at risk of exposure and safety precautions
383 would be necessary. However, the presence of oxygen in the incineration processes

384 reduces the isocyanate emissions (Boutin et al., 2004), so an exposure risk lower than
385 those shown in **Table S6** should be expected, which is an important conclusion
386 considering that the large amount of mattresses incinerated per year will increase
387 progressively in future years due to more restrictive regulations for landfill waste.

388 **3.4. Search for other isocyanates**

389 The search of other isocyanates formed during the FPUF pyrolysis at three different
390 temperatures (300, 400 and 850°C) has been achieved using QTOF-MS.

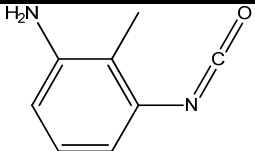
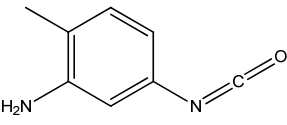
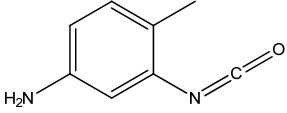
391 When DBA derivatives of isocyanates are ionised in the electrospray source, the most
392 abundant ions are those obtained after a neutral loss of DBA. In this way, the scans in the
393 QTOF-MS gave information about the most abundant ions obtained at different retention
394 times. An example is showed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

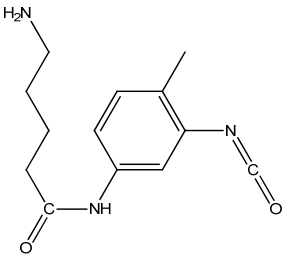
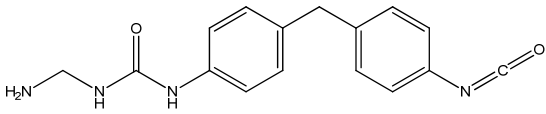
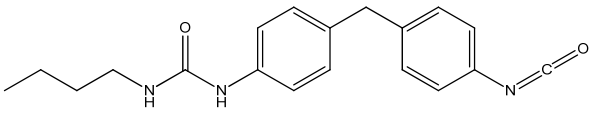
399 Tinnerberg et al. (1996) studied the emissions of isocyanates, aminoisocyanates and
400 amines during the thermal decomposition of TDI-PUR employing two different
401 derivatizing reagents, ethyl chloroformate (ET) for amines and DBA for isocyanates.
402 They found that during the thermal degradation of TDI-PUR three isomers of toluene
403 aminoisocyanates (TAI) were formed which are expected to produce ions with m/z values
404 of 278 amu. **Table 1** reports these three isomers. The elution order was: 2,6-TAI, 2,4-TAI
405 and 4,2-TAI, with 2,6-TAI presenting the highest area followed by 4,2-TAI and 2,4-TAI.
406 During air sampling, they employed only DBA as a reagent and the derivatization of
407 amine groups was performed just before the LC-MS analysis monitoring ions at $m/z=350$

408 amu, characteristic for TAI-ET-DBA. Additionally, Blomqvist et al. (2003) performed a
 409 series of small-scale combustions in a cone calorimeter (ISO 5660-1:1993), where
 410 generally well-ventilated combustion conditions are obtained. They studied the emissions
 411 for isocyanates, aminoisocyanates and amines from the combustion of 24 typically
 412 building materials being one of the flexible polyurethane foam. Three different toluene
 413 aminoisocyanates (TAI) isomers were found, 2,6-TAI, 2,4-TAI and 4,2-TAI. Isomer 2,6-
 414 TAI presented the highest level in the exhaust gases, followed by 4,2-TAI and 2,4-TAI.
 415 Bearing these results in mind, it was assumed that the three peaks detected at $m/z=278$
 416 amu are the three isomers for the DBA-derivation of toluene aminoisocyanates (**Figure**
 417 **S5**).

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

424 **Table 1**

m/z	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

425

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

430 The first eluting isomer which is tentatively assigned to 2,6-TAI considering the elution
 431 order of Tinnerberg et al. (1996) accounted for about 70% of the area, while the second
 432 and third isomers which were assigned to 2,4-TAI and 4,2-TAI accounted from 10% and
 433 20%, respectively.

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

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

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

445 Almost all of the new aminoisocyanates were detected not only in samples exposed at
446 300°C but also in these at 400 and 850°C, except 1-aminomethyl-3-(4-(4'-
447 isocyanobenzyl)phenyl)urea, which was obtained from the FPUF thermal degradation
448 only at 300°C. The general trend observed was a decrease of the aminoisocyanates levels
449 with increasing pyrolysis temperature as a consequence of the fragmentation of larger
450 isocyanates by thermal stress.

451 **4. Conclusions**

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

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

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

464 From the search of other potential isocyanates from the FPUF pyrolysis, we could

465 confirm, based on daughter ion scans, the presence of six additional aminoisocyanates
466 already formed at 300°C. All of them are aminoisocyanate derivatives TDI and MDI,
467 which were the most dominant isocyanates species in these experiments performed at
468 300-450°C.

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569 **Figures**

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

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

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

579 **Tables**

580 Table 1. Possible aminoisocyanates detected in pyrolysis samples of FPUF at 300, 400 and 850
581 °C

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