Fast pyrolysis of polyurethanes and polyisocyanurate with and without flame retardant: Compounds of interest for chemical recycling

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1. ABSTRACT

To date, the recycling of polyurethane (PU) and polyisocyanurate (PIR) waste still poses a significant problem. Within this contribution, the thermal degradation of high-resilient ether PU, semirigid PU, rigid PU, and (PIR) with and without TCPP flame retardant was studied at different temperatures to identify and quantify the main products. For this, a tandem micropyrolyzer coupled to GC × GC with FID and ToF-MS detectors was used, and the yield volatiles, light gases, and residue was quantified. The volatile pyrolysis vapours obtained from pyrolyzing high-resilient ether PU and semirigid PU at 600 °C were very similar, and the main products obtained were ethylene and propylene (combined yield of ~13 wt%), ~16 wt% of various oxygenates, and 4-6 wt% organic nitrogen compounds. The oxygenates included mostly poly-ether type compounds with varying molecular weight, and these are attributed to the decomposition of the polyol chains forming the soft segments of the polymer. The main semi-volatile nitrogen compound was 4,4'-methylenedianiline, attributed to the decomposition of the hard segments in the PU structure synthesized from MDI. The pyrolysis vapours from rigid PU contained several ether-type compounds and high yields of heteroatom-free monoaromatics—in particular styrene.

The PIRs were more difficult to decompose and volatilize than the PUs, resulting in ~20 wt% higher residue yields. The charring propensity was even higher in the absence of a flame retardant in the formulation. Pyrolysis of TCPP-containing PIR produced Cl-containing pyrolysis vapours such as allyl chlorides. While the yield of H_2O was comparable for the different PUs and PIR, pyrolysis of PIR produced higher yields of CO_2 and less CO compared to the different PUs. The use of catalysts can help to convert PU waste pyrolysis vapours more efficiently to desirable chemicals.

2. INTRODUCTION

Polyurethanes (PUs) are widely used in industrials applications and daily life due to their versatility, cost benefits, and durability. Their applications include furniture, bedding, carpets, automotive seating, molded polyurethane foam, insulation in building and automotive, electronic components and other commercial goods [1]. In addition, polyurethanes are used as adhesives with different solvents such as ketones.

PUs are co-polymers comprising hard segments from the use of *p,p*-methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) in their formulation and soft segments such as polyester or polyether polyols. Polyether-based polyurethanes are preeminent in the industry, accounting for ~90% [1]. The ratio of polyol to diisocyanate is 2:1 to form polyurethane [2], and the -OH groups of the polyol react with the -NCO groups of isocyanate forming urethane (=carbamate) linkages. By adding water, two water molecules react with the NCO of isocyanate, thereby forming urea and CO_2 acting as a blowing gas needed to create polyurethane foams. For most applications, using water alone would not result in satisfactory product quality or durability, and therefore additional organic blowing agents are used [3].

The molecular weight, functionality, and molecular structure of the polyol chains are important parameters in the formulation. Thus, foams with a wide range of densities can be produced that can be flexible, semi-flexible or rigid in structure [4]. Compared to flexible foams, rigid foams have a higher degree of branching or cross-linking, which gives rigid PUs an increased chain stiffness, interchain attraction, and crystallinity [1]. This is achieved by using lower MW polyols with a higher functionality and hydroxyl number for the production of the latter [1]. Flexible PU foams have a nearly complete open-cell structure with bulk densities as low as 20 kg/m^3, while rigid PUs have a mostly closed cell structure with higher bulk densities, typically ~35 kg/m^3 [5]. Commercial PU formulations often also include catalysts, chain extenders, flame retardants, pigments, cross-linkers, fillers, blowing agents, stabilizers, lubricants, and surfactants which are either useful during the synthesis of the PU and/or which enhance specific properties in the cured PU [1].

Polyether polyols are synthesized by polyaddition of propylene oxide (PO) and/or ethylene oxide (EO) to a polyfunctional low MW initiator molecule (polyalcohol or polyamine), for example glycerol.

On the other hand, rigid polyurethane foams (PUR) are produced using methylene diphenyl diisocyanate (MDI) and an (aromatic) polyester polyol instead of using an ether polyol. This creates a highly cross-linked thermoset plastic of low density and low thermal conductivity, used as a high-performance material for insulating materials in the construction sector.

As a further development of PUR, the variant polyisocyanurate (PIR) displays excellent thermal insulation properties. Compared to PUR, for PIR production, an excess of the MDI component is used, which results in a different chemical structure with an increased level of linkages, creating a very rigid and highly stable material. Chemical reactions occurring in the manufacturing of PIR foam are the reaction of isocyanate with alcohol (gel reaction), the reaction of isocyanate with water, releasing CO_2 that contributes to the expansion of the foam, and the trimerization of isocyanate [6]. The reactions are catalysed with tertiary amines, carboxylates and/or tin organic compounds. PIR's most notable differentiating factor is its higher resistance to flame and smoke compared to PUR products.

Out of the ~3 Mt/year PU consumption in Europe in 2020, ~36% were as flexible foams, ~32% as rigid foam, and ~32% as reaction injection molding and elastomers [5]. Owing to their advantageous properties, including lightweight, high thermal insulation, good strength, resistance, and rigidity, PUs are used in many everyday applications and industrial uses [5,7]. However, they are difficult to recycle, and the continuous growth of PU demand results in an enormous waste accumulation [5,7,8]. To date, only ~30% is recycled, ~40% is recovered through energy recovery processes, and the remainder, unfortunately, is landfilled [4]. PUs are non-biodegradable and enter the municipal solid waste stream in the form of discarded products from consumers and industry such as upholstered furniture, mattresses and automobile parts [3]. Recycling approaches for PU wastes include mechanical, chemical, and thermo-chemical degradation approaches [8]. In mechanical/physical recycling, the particle size of the PU waste is reduced, and the resulting powder is used as a filler for new PU compounds. The chemical route tries to break down the PU backbone to recover raw materials that can be re-processed into new PUs of similar nature [4]. Chemical recycling approaches include glycolysis, hydrolysis, aminolysis, and biodegradation processes [4]. The thermo-chemical route attempts to convert the PU waste to valuable monomers (pyrolysis) or syngas (gasification) [8]. Notable concentrations of chlorine compounds were reported in the pyrolysis of PU waste from household appliances at 500-700 °C [9], originating from Cl-containing flame retardants such as tris(2-chloropropyl) phosphate (TCPP) [10]. To make rigid urethane foams more resistant to burning, special flame-retardant additives based on phosphorous, sulfur, nitrogen, and halogens are added to the foam components by simple mechanical mixing. Alternatively, if phosphorous and/or chlorine-containing polyols are used, they can chemically bound in the polymer chain due to their functional hydroxyl group [1].The research objective of the present work was to study the thermochemical conversion of industrially relevant PUs and PIRs via pyrolysis to identify and quantify potentially valuable products for chemical recycling. Like energy recovery via combustion, pyrolysis reduces the volume of the PU waste, thereby avoiding landfilling. However, compared to combustion, a pyrolysis approach would allow collecting high-valuable chemicals released as volatiles. Considering that there exists limited research in this field reporting quantitative product yields from the pyrolysis of commercially relevant samples, an essential objective of the present work was to close this gap; in particular, concerning semi-volatile organic products for which sometimes only very low yields <5 wt% [9,11] or often only qualitative data was reported [12–17].

In addition to different commercial PU samples (flexible foam, semirigid and rigid), the pyrolysis of PIR was studied to determine if a fast pyrolysis approach could recover valuable products from mixed PU/PIR waste that waste handling facilities will encounter in the decades to come. Finally, pyrolysis of a TCPP-free PIR formulation was studied to assess if the absence of flame retardant in PIR would increase the recovery of valuable chemicals. The present work also lays the basis for future work to develop catalysts that positively affect the recovery of valuable chemicals from PU and PIR waste by thermochemical conversion.

3. EXPERIMENTAL

3.1 Feedstock

Commercial flexible PU foams, i.e. semirigid, and ether PU samples, were provided from the company Recticel (Belgium), and a commercial rigid PU foam was provided from the company Unilin (Belgium). The high resilient (HR) ether polyol was produced using polyalcohol glycerol and EO/PO to obtain a MW around 6000 g/mol and a hydroxyl value of 28 mg KOH/g sample. The final functionality (number of OH groups per polyol molecule) was around 2.2. In addition, a polyoxyethylene triol obtained by ethoxylation of glycerine with a MW of 1600 g/mol was used in the formulation. The rigid polyurethane foam was produced using methylene diphenyl diisocyanate (MDI) and an aromatic polyester polyol instead of ether polyol. This created a highly cross-linked thermoset plastic of low density and low thermal conductivity.

Unilin produced non-commercial PIR samples of high industrial relevance according to the formulation given in **Table 1**, similar to available literature [6]. The used polyol was Stepanpol PS2352, which is an aromatic polyester polyol. Note that all compounds that have a hydroxyl value will react with the MDI isocyanate. As a silicone surfactant and foam stabilization product, Tegostab B 8462 (Evonik) was used. As a trimerization catalyst, Kosmos 75 was chosen, which consists of potassium octoate dissolved in polyglycol. As amine co-catalyst, the tertiary amine pentamethyldiethylenetriamine (PMDETA) was used. While in earlier literature, chlorofluorocarbons such as $CFCl_3$ were used as blowing agents besides water [18], the Montreal Protocol restricted chlorinated blowing agents in the 1990s to reduce their impact on the ozone layer. Nowadays, pentanes have mostly replaced the environmentally harmful chlorofluorocarbons [8,19]. For the production of PIR in the present work, iso-pentane was used as a blowing agent.

As a widely used flame retardant, tris (1-chloro-2-propyl) phosphate (TCPP) was added [20]. The industry is aware that TCPP will need replacement in the medium term; however, in polyurethane insulations installed to date and in the polyurethane insulations to be recycled in the coming decades, TCPP will be found [10]. In addition to the flame retardant-obtaining formulation, a TCPP-free PIR was synthesized under otherwise same conditions.

Table 1. PIR Formulation with TCPP flame retardant

	OH number	pphp*
Polyol (Stepanpol PS2352)	240	100
Water	6233	0.5
Silicone surfactant (Tegostab B 8462)	42	2
Flame retardant (TCPP)	0	15
Trimerisation catalyst (Kosmos 75)	420	5.5
Amine co-catalyst pentamethyldiethylenetriamine (PMDETA)	0	0.2
Iso-pentane (blowing agent)	0	17
Low functional MDI		200

*weight parts per 100 weight parts of the polyol (Stepanpol PS2352)

All samples were ground to obtain particles <500 µm for the pyrolysis tests to facilitate thermal degradation [9].

3.2 Feedstock characterization

The fraction of volatiles, fixed carbon, and the content of inorganics (=ash) in the different PU samples was determined by thermogravimetric analysis using a Netsch STA 449F3 instrument following the procedure described by Johnston [21]. 10 mg of sample was loaded in an alumina crucible, and the temperature was first ramped to 105 °C at 10 °C/min in a nitrogen atmosphere (100 ml/min) and held at that temperature for 40 min in order to determine any moisture content. For the analysis of volatiles, the temperature was ramped under the same flow conditions in N_2 from 105 to 900 °C at 10 °C/min, and the temperature was held at 900 °C for 20 min. Finally, nitrogen was replaced by air, and the temperature was held at 900 °C for 30 min, to determine the fixed carbon content. The remaining mass after the combustion of fixed carbon was considered ash.

3.3 Analysis of pyrolysis products

The pyrolysis tests were performed using a tandem micro-pyrolyzer (RX-3050 TR, Frontier Lab., Japan) coupled to two-dimensional gas chromatography (GC) and a separate GC dedicated to analysing light gases, H_2O and light oxygenates. The unit has been described in detail in earlier work [22–24]. The first reactor was used for pyrolysis at different temperatures between 300 and 800 °C. The second reactor contained an empty quartz tube and was operated at 350 °C which was considered a high enough temperature to avoid the condensation and deposition of tars and/or high molecular weight compounds on the reactor walls. At the same time, 350 °C of this transfer section was considered low enough to avoid secondary thermal decomposition during the short additional residence time (<0.1 s). The column flow was controlled to 2.1 mL/min, and a split-flow of 105 mL/min was used as the carrier gas in the micropyrolyzer, resulting in a short vapour residence time [25]. The interface between the micropyrolyzer and the GC inlet was maintained at 350 °C, and the GC inlet was maintained at 300 °C. The gases and volatile components from the reactor were trapped inside the GC × GC oven by a cryo-trap (MJT-1035E) cooled with liquid nitrogen. The cryo-trap was held for 14 min and then switched off. During that time, the GC oven was held at -40 °C by cryogenic cooling. As soon as the cryo-trap was switched off, the column temperature instantly increased to the oven temperature, and trapped vapours were released according to their boiling points. The oven program consisted of 14 min hold at -40 °C, followed by heating at 3 °C/min to 320 °C and holding the final temperature for 5 min. Downstream the cryo-trap, the product vapours were split into two streams. The first allows for the simultaneous analysis of permanent gases and water in a customized multicolumn GC (Trace 1300). The second stream is send to a GC × GC (TRACE Ultra, Thermo Scientific, Belgium). For the product separation by GC × GC, a two stage cryogenic modulator (liquid CO_2) was positioned between the first and second dimension column and the modulation time was set to 5 s. The 1st dimension column was a non-polar RTX-1 PONA (50 m, ID = 0.25 mm) and the 2nd dimension column was a polar BPX-5 column (2 m, ID = 0.15 mm). Tests with time-of-flight mass spectrometer (ToF/MS) and FID detectors were run separately for the identification and quantification of the products. The ToF/MS was a BenchTOF-Select™ (Markes, United Kingdom) and the spectra obtained in a scanning range of m/z = 20–600 at 70 eV were compared with the NIST library database (MS search 2.2). The FID data was processed using GC Image software.

The sample amount for the fast pyrolysis tests was ~300 μg and loaded with a high precision balance (±1 μg) into a deactivated stainless steel sample cup (Eco-cup SF). For FID tests, fluoranthene (Sigma Aldrich, purity >99%) was added as an internal standard. Since the loading of ~10 μg pure fluoranthene would result in a peak saturating the FID detector, a solid mixture comprising a low surface area α-Al_2O_3 and fluoranthene at a weight ratio of 30:1 was prepared. This reduced the uncertainty inherent in weighing an extremely small amount of internal standard.

In addition, certain runs were also performed using iso-butane as internal standard, which was dosed using a six-port sample loop with known volume, pressure, and temperature of the sample loop, thereby improving the accuracy of the internal standard quantification. The yield of all other compounds was calculated using the effective carbon number method [26]. In addition, aniline calibration was performed by preparing a solution of aniline in acetone and injecting different volumes directly into the pyrolyzer operated at 200 °C. A dedicated multicolumn GC (Thermo Scientific Trace 1310) equipped with thermal conductivity (TCD) and pulsed discharge (PDD) detectors were used for the analysis of light gases (H_2, CO, CO_2, CH_4), H_2O, and small oxygenates. Calibration was performed by feeding different certified gas mixtures via the six-port sample loop to the micro-pyrolysis reactor.

Due to the small weight of char remaining after pyrolysis, the balance precision became more relevant. In order to determine the char yield after pyrolysis tests more accurately, higher sample loadings of ~600 µg were pyrolyzed at different temperatures without detailed analysis of the volatiles. Once the pyrolysis reactor had cooled down to <100 °C, the sample cups were carefully retrieved and weighed together with the remaining char/residue. The higher sample loadings significantly improved the accuracy and repeatability of the char determination.

The volatiles from pyrolysis of semirigid PU and high-resilient ether PU were almost identical, and the precise determination of the gas and char yields were limited to high-resilient ether PU, rigid PU, and PIR samples.

4. RESULTS

4.1 Properties of PU and PIR

Table 2 summarizes the elemental composition of the different PU and PIR samples studied in the present work, and their elemental composition lies well within the range reported by other research groups reported for different polyurethane waste: 2–6 wt% N, 58–66 wt% C, 6–9 wt% H, and the difference being made up of primarily oxygen but also other elements contained in flame retardants such as Cl, P, Br [11,13,27–33]. Amongst the different materials, the PIR materials with and without TCPP showed the highest N content (~7 wt%), while the different PUs had a N content of ~4 wt%. Chlorine was not detected by the elemental analysis method; as such, the indicated oxygen content as determined by difference will be lower for the TCPP-containing PIR compared to what is indicated in Table 2.

Table 2. Elemental composition of PU and PIR samples

	N wt%	**C wt%**	**H wt%**	**Other elements wt% (by difference)**
Ether PU	4.4	65.5	8.6	21.5
semirigid PU	4.3	64.7	8.8	22.2

Rigid PU	3.9	63.4	7.5	25.2
PIR (with TCPP)	6.8	66.0	5.6	21.6
TCPP-free PIR	7.5	68.1	5.3	19.1

Thermogravimetric analysis revealed that for temperatures >400 °C, a higher char residue remained for PIR compared to the different PUs when heated in an inert atmosphere (Figure 1). At 900 °C, 26 wt% of the initial mass remained for PIR while only 8-12 wt% remained for the different PUs (Table 3), even though the initial weight loss occurred at a lower temperature of ~210 °C for the PIR than the PUs (~280 °C). Among the different PUs, rigid PU showed the highest fixed carbon content, which may be attributed to a higher aromatics content due to the presence of an aromatic polyester polyol in its formulation. The higher resilience towards thermal deconstruction and decreased volatility of the PIR sample can be explained by its different chemical structure (higher degree of linkages) and higher density. PIR contains isocyanurate rings from the trimerization of isocyanates [20] with higher thermal stability compared to urethane groups [34] and therefore requires higher temperatures to degrade these stabilized structures. From an application point of view, high char formation tendency is desirable since it limits the amount of volatile fuel produced by the burning polymer and it provides an insulating layer at the surface of the burning polymer that reduces heat and mass transmission into the material [20]. Phosphorous compounds from the flame retardant, Si in the silicone surfactant and K present as potassium octoate in the KOSMOS® 75 catalyst were either volatile enough to be released under inert atmosphere, or they were released during the combustion together with the fixed carbon since there was no appreciable mass of inorganics/ash remaining at the end of the TGA program (see Figure 1).

The different PU/PIR samples primarily comprised volatiles and fixed carbon, with negligible moisture content (<0.5% for PUs and ~1% for PIR). For polyurethane waste, 8-12 wt% of fixed carbon and low ash residue was also reported by other researchers [27,30,32], albeit one study [33] found a fairly high ash content of 5.5 wt% in mattresses made from flexible polyurethane. For all samples there was a continued weight loss even when holding the temperature constant at 900 °C under N_2 atmosphere, indicating a continued but very slow thermal decomposition of the char. A continued and slow weight loss between ~500 and 950 °C was also reported by Yao et al. when heating PUR waste in inert atmosphere [15].

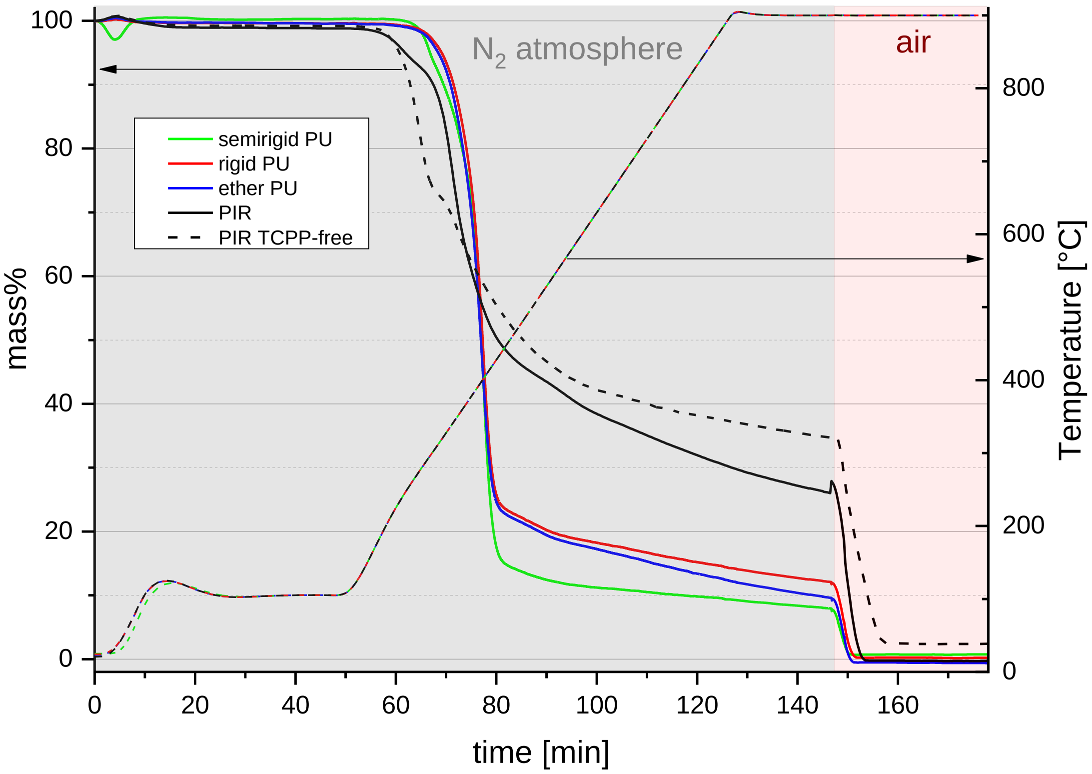

Figure 1. Proximate analysis by thermogravimetric analysis of different PU and PIR samples.

Table 3. Content of volatiles and fixed carbon as determined by thermogravimetric analysis

	Semi-rigid PU	ether PU	rigid PU	PIR	PIR (TCPP-free)[a]
Volatiles (wt%)	92	90	88	74	65
Fixed carbon (wt%)	8	10	12	26	33

[a] difference to 100% are ~1% moisture and 1% ash

4.2 Product yields from fast pyrolysis

Figure 2a shows the yield of char/residue determined in 100 °C steps for pyrolysis temperatures ranging from 300 to 800 °C. In line with the TGA observations, rigid PU and ether PU are much more prone to volatilization compared to PIR since the PU char yield was already very low (<5%) at a pyrolysis temperature of 500 °C (Figure 2a). Despite the differences in heating rate between TGA (0.167 °C/s) and the micropyrolyzer (~100-250 °C/s [35]), the different trends between the PUs in terms of reactivity and fixed carbon content agree well. The residue at relevant pyrolysis temperatures (400-800 °C) was lower using the micropyrolyzer compared to the TGA. The slower heating using the TGA likely allowed for poly/oligomerization reactions of the molten/softened polymer and thus promoted char formation, e.g. via the condensation of aromatic rings to PAHs. The high heating rate during fast pyrolysis using the micropyrolyzer, on the other hand, promoted devolatilization and limited the extent of secondary reactions. This is in line with observations for thermochemical conversion of lignocellulosic feedstocks [36–40] and implies that there is an effect of particle size since both the maximum temperature and the heating rate increase with decreasing particle size [9].

Considering the combined yield of gas and water shown in Figure 2b, there was a moderate increase when increasing the pyrolysis temperature from 400 to 600 °C, but a much more severe cracking to lighter gases (predominantly H_2, CH_4, CO) occurred when conducting the pyrolysis at 800 °C. This is attributed to the decomposition of methylene bridges, cracking of pendant methyl-groups, and H_2 release via further condensation of aromatic rings in the PAH residue/char. Rigid PU was most prone to volatilization with higher yields of light gases compared to high-resilient ether PU and PIR (Figure 2b). Besides H_2O, the identified and quantified light gases included CO_2, C_2H_4, C_2H_6, H_2, CH_4, CO, NH_3, HCN, MeOH, acetaldehyde, and acetonitrile (Table S1). PUR was the most prone to decarbonylation (=release of CO), followed by ether PU and PIR. Pyrolysis of PIRs, on the other hand, produced 3-6 times more CO_2 than ether PU and PUR. For ether PU and PUR, the yield of NH_3 decreased with increasing pyrolysis temperature, an observation in line with the results by Font et al. [11]. Appreciable amounts of HCN were only observed from PIR at temperatures >700 °C. Some MeOH and acetaldehyde were detected among light oxygenates, albeit without a consistent trend between the different samples and pyrolysis temperatures. Grittner et al. [18] reported water yields of ~4 wt% for a polyether PU based on MDI and poly(ethylene oxide)-poly(propylene glycol) at fast pyrolysis temperatures of 700 and 800 °C. This agrees well with the H_2O yields observed in the present work.

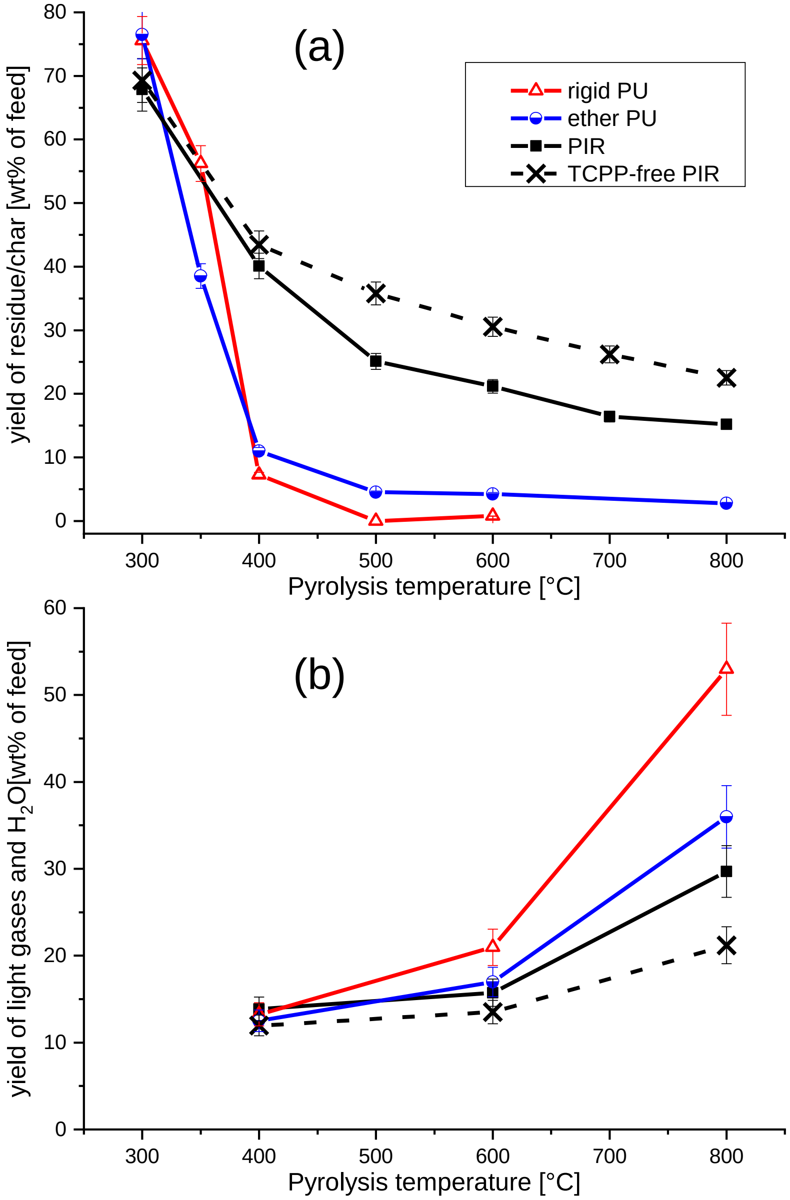

Figure 2. (a) Char yield as a function of pyrolysis temperature for different PUs and PIR. b) Combined yield of light gases and H_2O as a function of pyrolysis temperature. Yields of individual compounds are listed in Table S1.

The two-dimensional gas chromatograms obtained from pyrolyzing high resilient ether PU (Figure S2) and semirigid PU (Figure 3) at 600 °C show a multitude of different oxygen functionalities; most notably, oxygen is bound as ether, ester, ketone, or aldehyde, and also some primary alcohols were detected. Ether-type compounds such as ethoxy-ethene likely stem from the cracking/breakdown of polyether polyols representing the soft segments in the PU structure [41]. Nishiyama et al. [12] reported that the soft segments require higher pyrolysis temperatures for their decomposition, while the diphenylmethane containing hard segments are the first to decompose [20]. Yao et al. [15] observed that for pyrolysis/combustion of PUR, the rupture of the C–N bond of the urethane bond could result in 2-ethoxyethanol, and compounds similar to 2-(2-ethoxyethoxy)-ethanol were also observed in our work. The polyalcohols used for the production of the flexible foams were synthesized by polyaddition of propylene oxide (PO) and/or ethylene oxide (EO) to glycerol, thereby forming a polyfunctional initiator molecule with a low MW in the range of 500–6000 g/mol [42,43]. The polyether and polyether alcohols observed with MW of ~150 to 300 g/mol (RT~60 to 110 min) may thus be attributed to cracking the straight polyalcohols from the glycerol segment. Since the fragmentation patterns of the polyether alcohols with a different number of repeating units were very similar, future studies may need to use lower ionization voltage to enable more accurate identification of the parent m/z by mass spectrometry.

The existence of different ethylene oxide (also called oxirane) structures, most notably EO with ~4 wt% yield at 600 °C, ~2 wt% methyl-oxirane (=PO), tetramethyl-oxirane, and (1-methylethoxy)methyl-oxirane could be related to the use of PO and EO in the production of the polyalcohols. Tetramethyl-oxirane, EO, and PO, or there decomposition products ethanal and propanal were also observed by others during the pyrolysis of PUs with polyether polyols in their formulation [17,41,44,45], particularly in the 400-600 °C range [41] while they were not detected at higher pyrolysis temperatures (850 °C) anymore, indicating their thermal decomposition [45]. Our results are in line with observations by Nishiyama et al. [12] as their results showed that the soft segments decompose sufficiently at a fast pyrolysis temperature of 450 °C. Besides low MW cracking products such as CH_4, ethylene, and propylene, also formaldehyde and dimethylamine were detected in the present work. The latter may be a product of the thermal decomposition of dimethylethanolamine and triethylene diamine, which was used as catalysts to produce the flexible PU foams. Formaldehyde is a known thermal decomposition product from oxymethylene dialkyl ethers and has also reported by others when pyrolyzing flexible polyurethane foam [45].

The isocyanate compound 4-ethylphenyl isocyanate at a yield of ~0.6 wt% could be a product from C-C bond scission of unreacted MDI, or, more likely, from the dissociation of urethane linkages to isocyanate and alcohol [12,46–48], in agreement with the presence of several polyether alcohols. Linear polyether compounds without terminal -OH group may result from dehydration of polyether alcohols. Phenyl isocyanate compounds were also reported by others from thermal decomposition of a PU elastomer [12,49] and rigid PU foams [50], and in both studies MDI was used in the foam preparation.

Notably, for pyrolysis of ether PU and semirigid PU, 4,4’-diaminodiphenylmethane at RT ~105 min was observed in high concentration. Note that also the tailing peaks towards the end of the chromatogram are related to the diaminodiphenylmethane structures (MDA). This was recently addressed by attempting in-situ derivatization of the highly reactive PU pyrolysis products such as amines and isocyanates with the objective to prevent their polymerization in the GC column [51]. 4,4’-diaminodiphenylmethane was also observed by others as the main nitrogen-containing tar compound for pyrolysis of polyurethane foam [12,30,51], and higher temperatures promote the formation of the amine end. Even when heated at a much slower ramp of 10 °C/min using a TGA, 4,4’-diaminodiphenylmethane was reported among the main evolving products during PU degradation [12,52]. It is noteworthy that some works suggest MDI as the primary product from PU pyrolysis [53], and in the presence of water MDI may then hydrolyse to yield MDA and CO_2 [54]. Despite the short vapour residence time and dilution of the pyrolysis vapours in the helium carrier stream, these seemed to have been the case in the work. The combined yield of the different diaminodiphenylmethane structures amounted to 3.8 wt% for ether PU and 1.8 wt% for semirigid PU. The most likely pathway would be the decomposition of the urethane bond to an amine end, carbon dioxide, and olefin via a six-membered ring transition state [1,12]. While the exact formulation of the PUs cannot be disclosed due to proprietary reasons, the presence of the diaminodiphenylmethane compounds is a strong indication that MDI was used in the formulation to synthesize the urethane groups. 4,4’-diaminodiphenylmethane is a valuable product since it may be used as an aromatic amine extender [42] to produce new PUs, or it can be reconverted into isocyanate and thereby used for the production of new PU in a circular approach [8,51].

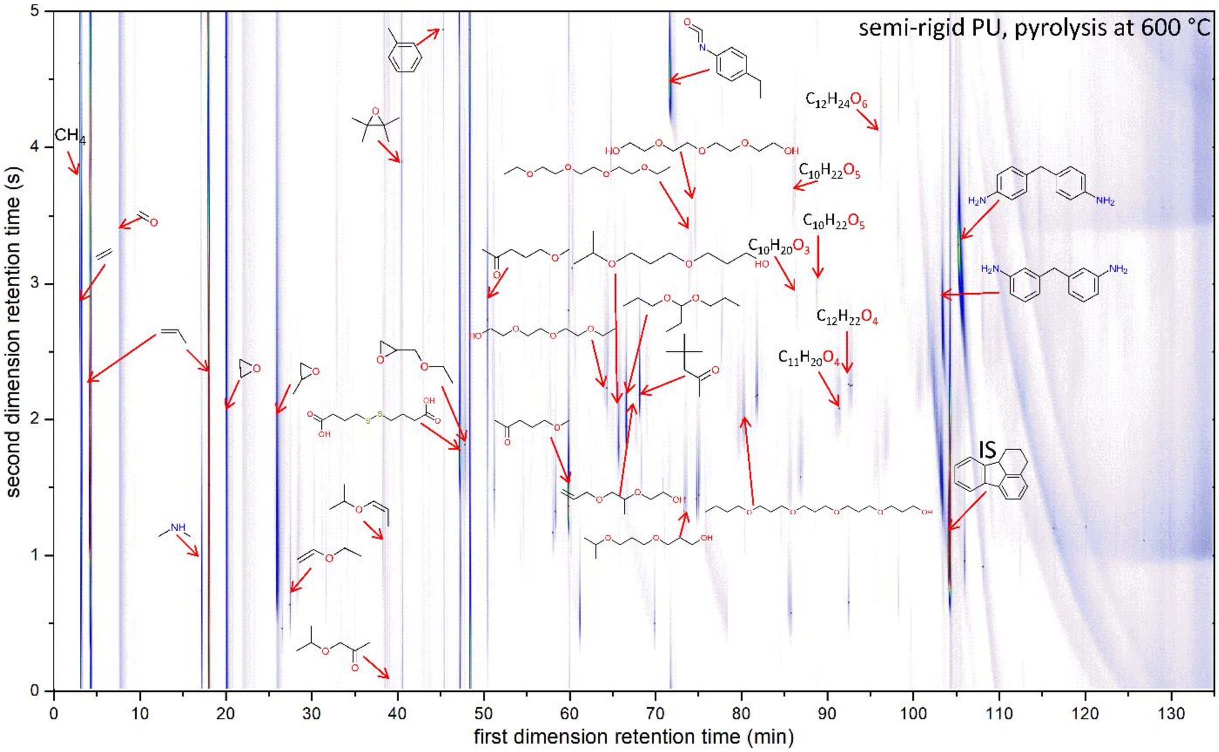

Figure 3. GC×GC-FID analysis of volatiles from fast pyrolysis of semirigid PU at 600 °C. The internal standard (IS) fluoranthene is not a product of PU pyrolysis.

The main pyrolysis vapour compounds detected from pyrolyzing rigid PU at 600 °C are shown in Figure 4. Since rigid PU was produced with an aromatic polyester polyol, the rigid foam had different pyrolysis products than the semirigid and flexible foam produced with a polyether polyol (vide supra). This can explain why the pyrolysis of rigid PU showed a much higher content of monoaromatic compounds, particularly styrene, with a yield of 11 wt%. Styrene as a pyrolysis product from waste rigid polyurethane foam was also observed by others[9] .

In the present work, rigid PU polyethylene oxide derived compounds in varying chain lengths were observed. In addition, different types of monoaromatic nitriles were observed for both PUR and PIR pyrolysis, and reports of elevated concentrations of nitriles such as benzonitrile in the pyrolysis vapour slate of waste polyurethane can be found in the literature [11,18,30,33,45,50,55].

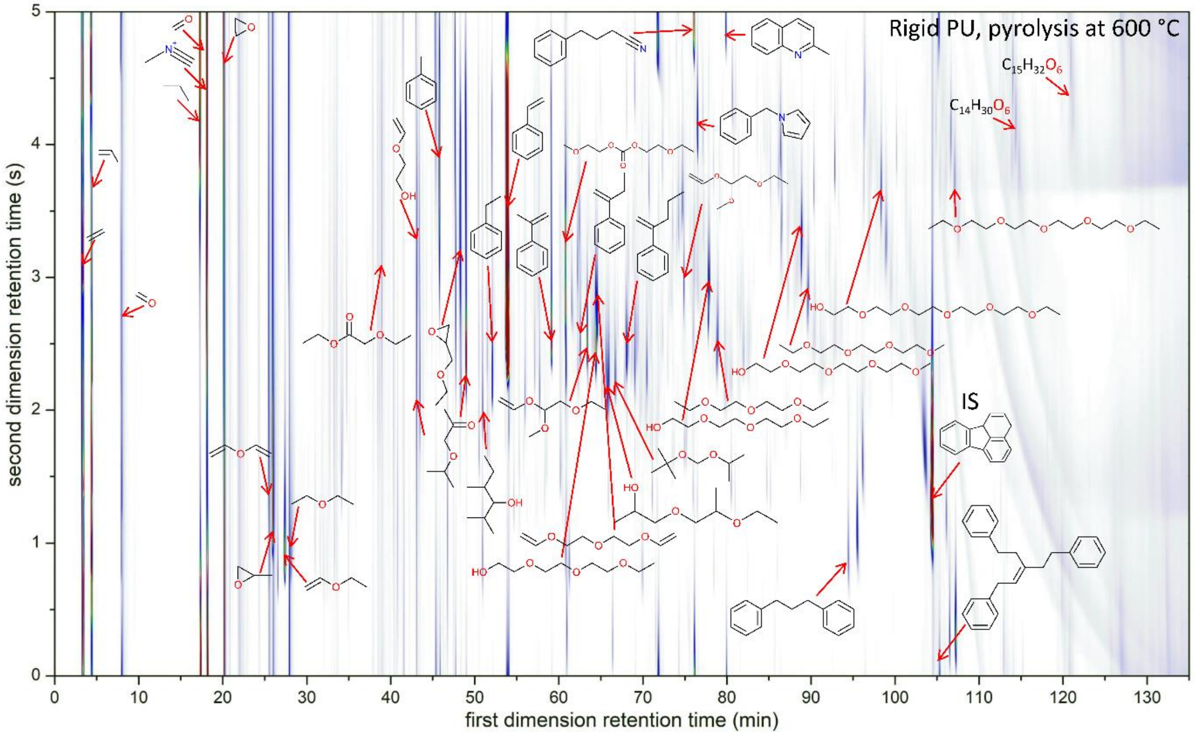

Figure 4. GC×GC-FID analysis of volatiles from fast pyrolysis of rigid PU at 600 °C. Fluoranthene at RT = 103 min was used as internal standard (IS) and is not a product from PU pyrolysis.

PIR thermal decomposition.

At low pyrolysis temperatures of 400 °C, TCPP was observed as a product from pyrolysis of the flame retardant-containing PIR formulation (Figure 5). As expected, by excluding the TCPP in the PIR formulation, the pyrolysis products did not contain any Cl-containing compounds (see Fig S1). The absence of the flame retardant, however, did not have a significant effect on the decomposition mechanism, considering that similar products were observed (see Figure S1).

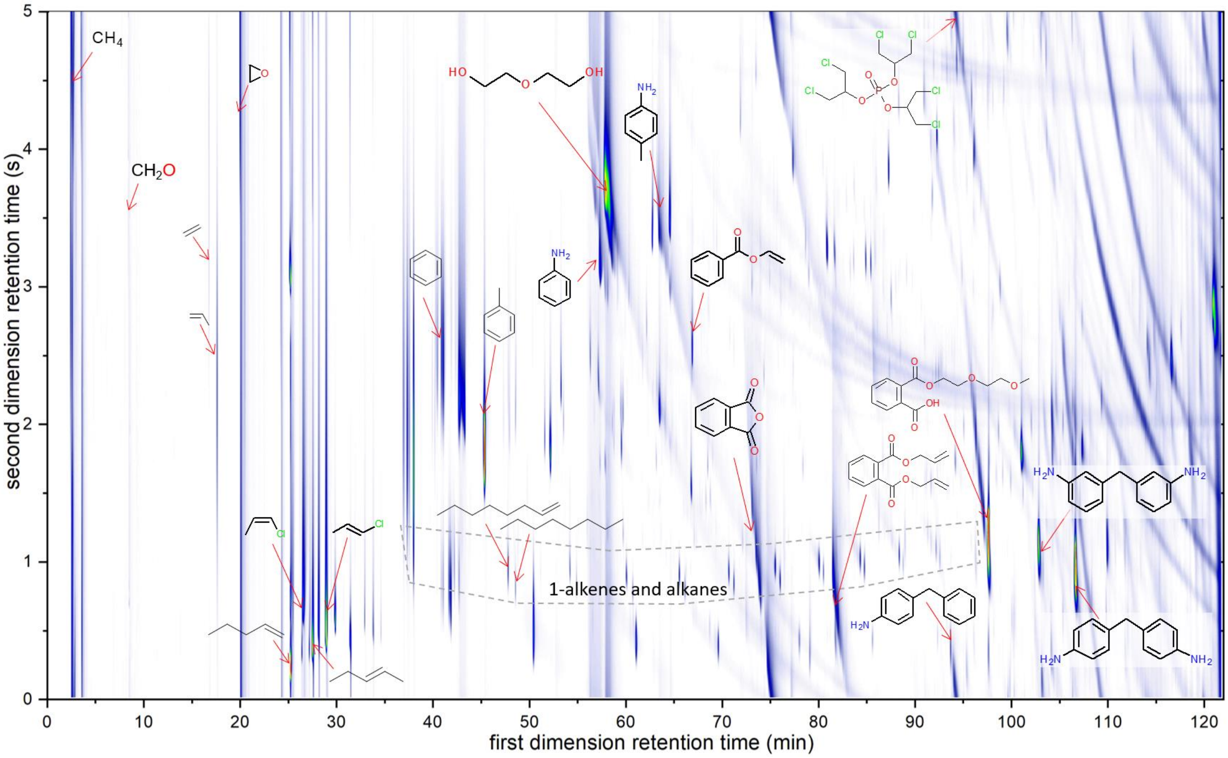

Figure 5. GC × GC-FID analysis of volatiles from fast pyrolysis of TCPP-containing PIR at 400 °C.

Pyrolyzing TCPP-containing PIR at a higher temperature such as 700 °C produces a range of other products such as HCN, higher yields of heteroatom-free aromatics, benzene-nitriles, isocyanato-benzenes, and several phenyl-substituted 1H-isoindole-1,3(2H)-dione structures (Figure 6). Possible pathways that could explain the formation of this phenyl-substituted 1H-isoindole-1,3 (2H)-dione structures are discussed in the Supporting Information (Figure S3 and S4).

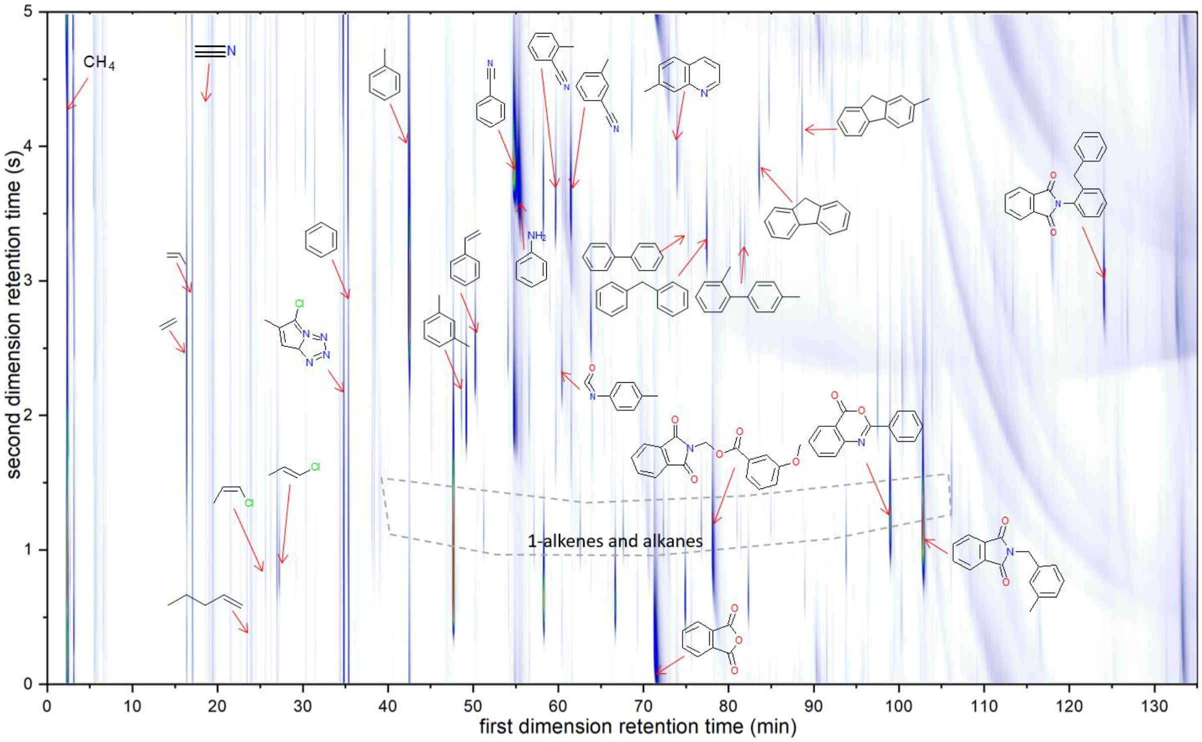

Figure 6. GC × GC-FID analysis of volatiles from fast pyrolysis of TCPP-containing PIR at 700 °C.

Effect of temperature on yields of volatiles from PIR and TCPP-free PIR

The yields of the major volatile products observed from TCPP-free PIR as a function of pyrolysis temperature are summarized in **Figure 7**. Increased cracking to light gases such as CH_4, light olefins, and CO was observed at pyrolysis temperatures of 600 °C and higher. There was a continued increase in the yield of hetero-atom free aromatics with temperature, but even at 800°C, the recovery of benzene and toluene was relatively low with ~0.7 wt% (**Figure 7**a). A steeper increase in Di+ polyaromatic hydrocarbons (PAHs) was observed at temperatures >700 °C, and this observation is in line with reports by Garrido et al. [45] who observed PAHs amongst the most abundant products at 850 °C at yields of 0.7 wt% when using flexible polyurethane foam as the feedstock. Considering the high concentration of monoaromatics compared to PAH, it seems likely that the PAHs are a result of the monoaromatics condensing and growing together to from heavier PAHs. The likelihood of this increases with increased residence time.Maximum yields of aniline and methyl-aniline of ~1 wt% were recovered at a pyrolysis temperature of ~500 °C, and their yields decreased at higher temperatures, in agreement with observations by Stančin et al. [9]. Interestingly, these researchers found that the yields of aniline increased with decreasing particle size, and as such, there may be further potential to increase the recovery of aniline at an optimized particle size and pyrolysis temperature. Aniline and formaldehyde are the reactants for producing the diisocyanate MDI used in many PU formulations [42,43]. Therefore, the isolation and purification of aniline could be a route to chemically recycle a portion of PIR waste via pyrolysis and produce new PU/PIR materials. The recovery of benzyl-nitrile compounds reaches appreciable yields from 500 °C and higher (**Figure 7**b). Similarly, an increase in the yield of benzonitrile from 0.25 to 0.85 wt% was observed by Garrido et al. [45] at a pyrolysis temperature of 550 and 850 °C, respectively, when pyrolyzing flexible polyurethane foam. From pyrolysis temperatures of 700 °C and higher, benzene, 1-isocyanato-4-methyl- was observed in the present work. High prevalence of simpler phenyl-and tolyl-isocyanates at high pyrolysis temperature of 800 -850 °C was also observed by other researchers for fast pyrolysis of rigid PU foams and elastomers [12,33,45,49,50]. This could be due to the breakdown of diisocyanates and radical reaction between phenyl radicals and isocyanates groups at high temperatures. Isocyanates are strong skin and respiratory irritants and the European Commission considers TDI as a possible carcinogen to humans. Hence, regulations for permissible exposure limits exist. On the other hand, capturing 1-isocyanato-4-methyl- and adding another isocyanato group to it would allow to produce the monomer TDI, which could be used to produce new PU. We note that the ~1 wt% yield quantified in our work for the benzene, 1-isocyanato-4-methyl- compound is considerably higher than 0.023 wt% of phenyl isocyanate emission at reported by Garrido et al. [33] in a dedicated study measuring the isocyanate emissions from pyrolysis of mattresses containing flexible and viscoelastic PU foam. This is likely due to the different chemical structure and higher nitrogen content of PIRs compared to PUs. In addition, the residence time of the pyrolysis vapours in the heated zone was reported to 7 s in Garrido et al.'s work [33], while the residence time in our work was considerably shorter (<0.1 s).

Amongst larger phenyl-containing nitrogen compounds, 4,4'-diaminodiphenylmethane was recovered with the highest yield of close to 4 wt% at a pyrolysis temperature of 500 °C (**Figure 7**c). This compound is also observed for pyrolysis of PUs [12,30,51] and is a valuable product to recover since it is the main precursor yielding MDI after treatment with phosgene, thus facilitating the production of new PU in a circular approach [8,51]. In addition, 4,4'-diaminodiphenylmethane may be used as an aromatic amine extender [42] in the production of new PUs.

Regarding oxygenates (Figure 7d), subjecting the material to a low pyrolysis temperature of 300 °C allowed to recover high yields of diethylene glycol (2.1 wt%) and benzoic acid derivate (6.1%). Diethylene glycol is not observed at temperatures above 400 °C anymore, while the yield of 2-((2-(2-Methoxyethoxy)ethoxy)carbonyl)benzoic acid more gradually decreased and was only completely cracked at temperatures >600 °C. In the temperature range of 400-700 °C, small amounts of ~0.1 wt% vinyl benzoate and 1,2-Benzenedicarboxylic acid are observed as likely decomposition products. This qualitatively agrees with reports in literature that oxygenates with ester linkages were observed from pyrolysis of polyurethanes at 600 °C, but these were missing at higher temperatures [53], indicating their thermal decomposition.

Part of the weight loss observed in the TGA at temperatures <400 °C is associated with the release of oxygen-containing compounds (diethylene glycol and benzoic acid derivate), CO_2, H_2O, diaminodiphenylmethanes, and TCPP. The pyrolysis of TCPP-containing PIR showed similar products and trends with temperature (not shown). However, the TCPP-containing PIR produced Cl-containing pyrolysis products in addition to the products observed from pyrolyzing the TCPP-free material. At a low pyrolysis temperature of 400 °C, TCPP was recovered in high yields of ~3 wt% since it is not chemically bound in the structure. However, at higher temperatures, the TCPP yields rapidly declined, likely primarily reacting to a stable char product in the melted phase and decomposition, as there was an increasing trend for allyl chlorides (**Figure 7**). The yield of allyl-chlorides peaked at ~600 °C, and their decline at higher temperatures most likely resulted in increased yields of HCl, which was not analysed in the present work. HCl would be a corrosion concern for larger-scale continuous thermochemical recycling plants [56], and replacing TCPP with a Cl-free flame retardant could limit this issue. It is interesting to note that for pyrolysis of TCPP-containing PU using Py-GC-MS, other researchers [9,50] observed TCPP at pyrolysis temperatures of 700-800 °C, while in our work TCPP was practically absent at temperatures of 700 °C and higher.

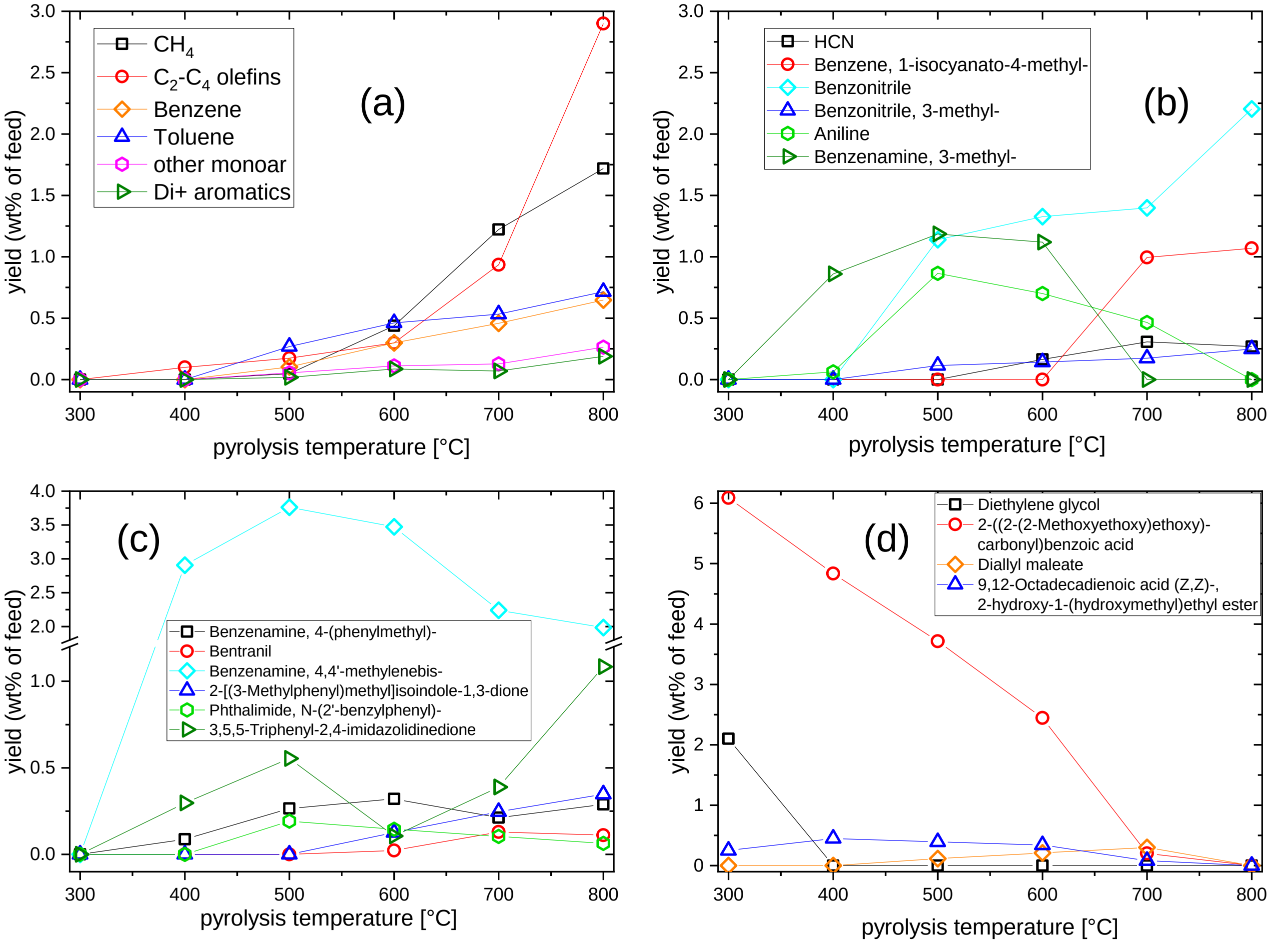

Figure 7. Product yields of (a) oxygen-free hydrocarbons, (b) HCN and N-containing monoaromatics, (c) N-containing di-phenyl structures, and (d) oxygenates as function of temperature for pyrolysis of TCPP-free PIR.

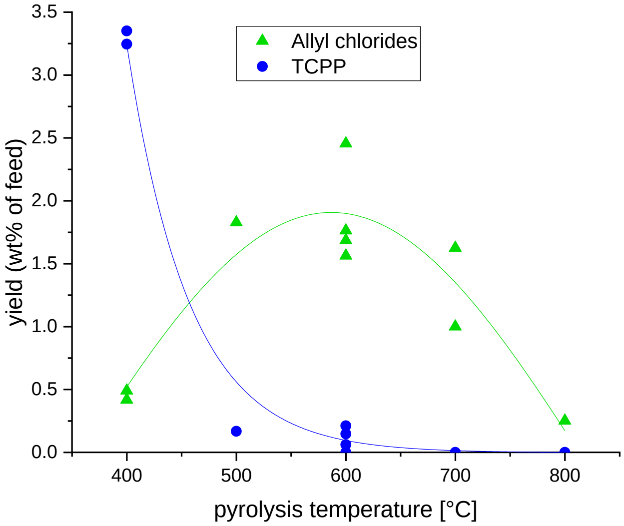

Figure 8. Yield of main Cl-containing compounds observed in pyrolysis of TCPP-containing PIR. Lines are fits to guide the eye.

Table 4 summarizes the yields of the main products from the different PUs and PIRs for a pyrolysis temperature of 600 °C. Amongst the pyrolysis vapours, the main product group were oxygenates for the different PUs and PIR. However, no cyclic ketones were observed. C_5 and C_6 cyclic ketones were reported by others [13,49] for polyester-polyurethanes and attributed to the degradation of the polyester. This indicates that no polyester polyol was used in the formulation of the samples subjected to pyrolysis in the present work.

N-containing heteroatoms were found in appreciable yields, with the highest yield found in PIR pyrolysis vapours. The yield of monoaromatics was particularly high for pyrolysis of rigid PU. In addition, the pyrolysis of the different PUs yielded 12-14 wt% ethylene and propylene, which could either go into the production of different plastics such as PE/PP or be incorporated into new PUs by producing EO and/or PO, which is then used for the production of polyols (via epoxidation of glycerol) as a key component in the formulation of PUs. From PIR, the yields of C_2-C_3 olefins were much lower compared to what was obtained from pyrolysis of PUs; however, pyrolysis of PIR produced more C_5+ aliphatics as pairs of n-alkanes and alpha-olefins, which could indicate that a small amount of polyethylene was produced during the synthesis.

At a pyrolysis temperature of 600 °C, a mass balance of 96 wt% was obtained for rigid PU while for ether PU and PIR, the mass closure was less than 60 wt%. This is in line with the observations from TGA that rigid PU was most prone to volatilization. The undetected mass likely comprises higher MW fragments with higher boiling points, and either deposited inside the reactor-transfer section (350 °C), the GC inlet (300 °C), or inside the columns since the maximum oven temperature used in the present work was 320 °C.

Considering the list of chemicals used for PIR production (see **Table 1**), PIR contains several other heteroatoms besides oxygen and nitrogen, which the FID did not detect. Further inorganics that likely remained in the char may include Si from the silicone surfactant (2 pphp) and K contained in the form of potassium octoate in the KOSMOS® 75 catalyst (5.5 pphp). Any volatile Si compounds could not unambiguously be attributed to the PU-derived pyrolysis vapours due to the bleeding of Si compounds from the stationary column phase, which was not quantified in present work but is sometimes erroneously attributed to PU pyrolysis products [50].

The elemental composition of the PIR derived vapours quantified by FID contained ~3 wt% N, 71 wt% C, 8 wt% H, 6 wt% Cl, and 12 wt% O. A comparison with the elemental composition of the solid sample (Table 2) suggests that a higher proportion of oxygen and nitrogen was removed as light gases compared to the vapour phase compounds. This agrees with a high yield of CO_2 (~11 wt%) for pyrolysis of PIR at 600 °C. While no appreciable amounts of HCN, NH_3, or C_2H_3N were detected at 600 °C from PIR pyrolysis, the release of nitrogen as N_2 or NO (which were not analysed for), and the presence of N in the char residue or high MW tar deposits cannot be excluded. Comparing the elemental composition of the volatile pyrolyzates (including light gases) at pyrolysis temperatures of 400 and 700 °C for TCPP-containing PIR reveals concentrations of around 47% C wt% (for both 400 and 700 °C), 1.4 and 7.0 wt% N, 10 and 9 wt% H, 37 and 34 wt% O, and 5 and 2 wt% Cl at 400 and 700 °C, respectively. The lower concentration of C and higher concentration of H and O compared to the feedstock suggests an enrichment of carbon in char, and it is well known that pyrolysis char from plastic waste and biomass often is highly carbonaceous. Noteworthy deviations to the feedstock elemental composition include the lower N content (1.4 vs 6.8 wt%) and high Cl concentration (5 wt%) of the pyrolyzate obtained at a pyrolysis temperature of 400 °C. This can be explained by the selective desorption of TCPP at this low pyrolysis temperature, while on the other hand little of the nitrogen contained in the thermally stable isocyanurate groups decomposed. At a higher pyrolysis temperature of 700 °C, the N concentration in the pyrolyzate matches the feedstock N content of ~7 wt%.

Table 4. Yields (in wt% of feed) for the main products observed at a pyrolysis temperature of 600 °C.

	ether PU and semirigid PU	rigid PU	PIR	TCPP-free PIR
CO	2.4	2.1	0.5	0.2
CO_2	3.3	3.0	10.7	9.7
H_2O	3.8	4.6	4.0	2.6
H_2	0.1	0.1	0.1	0.1
C_1-C_3 alkanes	1.6	1.2	0.2	0.4
C_2-C_3 olefins	12.6	14.4	1.0	0.5
C_5+ aliphatics	0.2	0.1	1.5	1.0
HC aromatics	0.1	13.8	1.0	1.0
O-containing	16.3	36.2	5.3	3.2
N-containing	7.6	5.4	6.6	7.6
Cl-containing	0.0	0.0	3.2	0.0
char/residue	4.2	0.8	21.2	30.5
mass closure (%)	56	96	55	56

A slight increase in mass closure by 4–8 %-points could be obtained when pyrolyzing ether PU and PIR at an increased pyrolysis temperature of 800 °C. This was mainly due to the increase in light gases, while the yield of vapours identified by GC × GC (excl. C_2-) decreased from 31 to 20 wt% for ether PU and from 18 to 11 wt% for PIR.

When comparing the 2D GC chromatograms obtained from pyrolyzing ether PU at 800 °C and 600 °C (Figure S2), a higher concentration of low MW compounds such as allyl ethyl ether derived from the soft segments was observed for 800 °C. The terminal unsaturation is a strong indication that this is a secondary product resulting from the dehydration of an initially formed alcohol. In addition, at 800 °C, there was an increased yield of heteroatom-free monoaromatics and phenyl-amines and nitriles, likely resulting from the thermal decomposition of the di-phenyl amines observed at high concentration at the lower pyrolysis temperature at RT ~103 min and 106 min (Figure S2). For ether PU, the extent of dehydration and the yield of C_2-C_3 olefins did not further increase when raising the pyrolysis temperature from 600 to 800 °C, indicating the dehydration of fragmented alcohols from the polyol had already reached its maximum rate at 600 °C. Gaboriaud and Vantelonand [41] reported that for the thermal degradation of PU based on MDI and trimethylolpropane propoxylate at a heating rate of 20 °C/min, the main mechanism up to 400 °C was the fracture of the polyurethane molecule into a primary amine, carbon dioxide, and propenyl ether, the last leading to propene. For temperatures above 400 °C, a depolymerization process followed by the radical breakdown of the polyol chain and rearrangement of simple radicals may become more dominant [41]. Nishiyama et al. [12] also observed more low molecular weight compounds at an increased pyrolysis temperature of 850 °C.

5. DISCUSSION & OUTLOOK

While the present work suggests that valuable O and N-containing chemicals can be recovered via thermochemical conversion of PU and PIR waste, for the valorisation routes, the product separation needs to be studied in more detail in order to recover the desired chemicals, e.g., using a staged condensation or selective extraction from the liquid product.

Catalytic upgrading of PU/PIR pyrolysis vapours could be another approach to boost the recovery of heteroatom-free monoaromatics such as benzene, toluene, ethyl-benzene, and styrene, as these base chemicals could be used to produce aniline and MDI, this way increasing the recycling rates. Considering the high concentration of nitrogen and oxygen-containing vapour compounds present in the fast pyrolysis vapours of commercial PUR and PIR samples, upgrading the vapours over a solid acid cracking catalyst may not be ideal as this will likely lead to rapid catalyst deactivation by coking. Instead, a catalytic vapour upgrading under hydrogen atmosphere could significantly reduce the loss of carbon in the feedstock towards coke on the heterogeneous catalyst that will eventually be lost to CO_2 during catalyst regeneration. In addition, this approach may increase the recovery of alcohol functionalities by in-situ hydrogenation of esters, aldehydes, and ketones.

Preliminary results from our group indicate that using a MoO_3-promoted HZSM-5/γ-Al_2O_3 catalyst active in hydro-deoxygenation [57,58] under hydrogen atmosphere (p_{H2} ~ 1.3 bar) can boost the yield of heteroatom-free aromatics from 1% in the thermal pyrolysis of PIR at 500 °C to ~15%, with 4.4 wt% benzene and 4.8 wt% toluene recovered. When operating the pyrolysis at 700 °C and the catalyst at 500 °C, the recovery of benzene and toluene from PIR increased to 6.6 and 7.5 wt% (total yield of aromatics = 19%), from ~0.5 and 0.8 wt%, under thermal conditions. From the recovered benzene, aniline can be produced as an important building block in MDI production. From toluene, TDI can be produced. The recovered MDI and TDI could then be used to produce new rigid polyurethane foams with increased recycled content.

Instead of using a catalyst, the secondary vapour-phase thermal decomposition of tars and/or high molecular weight compounds at moderate temperatures is another approach that may allow increasing the yields of desirable compounds. This approach will require optimization of the reactor temperatures of the primary and secondary reactor. Particularly for the ether and semirigid PU, and the PIRs for which the incomplete mass balance (
Table 4) suggests the presence of volatile high molecular weight compounds, this approach deserves future attention. Likewise, testing the effect of vapour residence time as a means to affect bi-molecular secondary reactions and studying different reaction atmospheres such as steam, H_2, and recycled product gas is of interest. Lastly, it is worth considering the processing of PIR waste in a single reactor but in two thermal stages. Firstly, subjecting the waste to low-temperature pyrolysis at ~300-400 °C could recover DEG and benzoic acid derivates at high yields while removing TCPP, and since only a few compounds volatilize at low temperature, their isolation would be straightforward. In a second stage, the remaining residue (~70% of initial mass) could then be subjected to either thermal pyrolysis at ~500 °C for the recovery of aromatic-amine functionalities or catalytic fast pyrolysis (e.g. thermal pyrolysis at 700 °C followed by vapour upgrading at 500 °C). Due to PIR's high charring propensity, the combustion of the char residue is expected to provide sufficient process heat, but further investigations in this regard are required.

For economic considerations, a multitude of factors needs to be taken into account in addition to the value of certain valuable chemicals than can be produced from PU/PIR waste. For once, pyrolysis itself can be an attractive technology for reducing the volume of the waste, similar to combustion. On the other hand, pyrolysis requires heat to be supplied to the reactor, and there is an interplay between the desired pyrolysis temperature and the energy available by combusting product gas and solid residue. In addition to the operating costs associated with the pyrolysis reactor, there are cost associated with product separation and purification. Introducing a catalyst for vapour-phase upgrading may improve the selectivity to desired compounds and facilitate the product separation, but it also constitutes an extra cost. As such, if cheaper approaches such as "moderate (steam) cracking" would have a similar effect than using a catalyst, this would be economically preferred. Lastly, emissions of harmful pollutants such PAHs and isocyanates can be of concern, requiring efficient vapour condensation systems and product gas treatment, hence further contributing to the overall plant operational cost.

6. CONCLUSIONS

The thermochemical degradation of different PUs (high-resilient ether PU, semirigid PU, and rigid PU) and polyisocyanurate (PIR), with and without TCPP flame retardant, was investigated using a TGA and a fast pyrolysis unit coupled to two-dimensional gas chromatography. The main volatile products obtained from pyrolyzing ether PU and semirigid PU were light olefins, various oxygenates derived from the polyether polyols, and methylenedianiline compounds, next to CO, CO_2, H_2O, and light nitrogenous gases such as NH_3 and dimethylamine. While the light gases obtained from rigid PU were in a similar range compared to ether PU and semirigid PU, the pyrolysis vapours from rigid PU not only contained products from the conversion of polyether polyols, but also high yields of styrene and other heteroatom-free monoaromatics. Pyrolysis temperatures above 600 °C caused excessive gas formation.

PIR was more difficult to thermally decompose and volatilize compared to the different PUs and also produced more CO_2 and less CO compared to the different PUs. Pyrolysis of PIR at a low temperature of 300 °C allowed to recover diethylene glycol (2 wt%) and benzoic acid derivate (6%), and the yield of these rapidly decreased with increasing temperature.

Maximum recovery of aromatic compounds with amine functionality such as aniline, methyl-aniline, and diaminodiphenylmethanes was obtained at a pyrolysis temperature of 500 °C with yields of ~1 wt%, ~1 wt%, and ~4 wt% from PIR. The isolation and purification of these amines could be a route to chemically recycle a portion of PIR waste via pyrolysis and produce new PU/PIR materials. Towards higher pyrolysis temperatures, the yield of aromatic amines declined, whereas more aromatic nitriles and isocyanates were formed. In addition, the yield of heteroatom-free monoaromatics increased with temperature, reaching ~0.7 wt% at 800 °C.

Since the multitude of pyrolysis products with different heteroatoms and functionalities make purification difficult, an alternative strategy could be to favour the production of benzene and toluene, which are used in the production of MDI and TDI, thereby limiting the fraction of fossil-derived chemicals used in the production of new PU/PIR. Preliminary results using a MoO_3-promoted HZSM-5/γ-Al_2O_3 catalyst under hydrogen atmosphere suggests that benzene and toluene yields can be increased from <1 wt% under thermal conditions to ~7 wt% with direct catalytic vapour upgrading. This was the first attempt of direct catalytic upgrading of PIR pyrolysis vapors via a shape-selective (hydro)deoxygenation catalyst for the production of valuable base chemicals.

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ABBREVIATIONS

EO, ethylene oxide; TGA, thermogravimetric analysis, GC, gas chromatography; MDI; methylene bisphenyl diisocyanate; TDI, toluene diisocyanate; MS, mass spectrometry; FID, flame ionization detection; TCD, thermal conductivity detector; PO, propylene oxide; pphp, part per hundred parts polyol by weight; PIR, polyisocyanurate; PU, polyurethane;

SUPPORTING INFORMATION

Yield of light gas components and H_2O; chromatogram from pyrolysis of TCPP-free PIR at 400 °C; chromatogram from pyrolysis of ether PU at 600 °C and 800 °C; possible formation pathways for 1H-isoindole-1,3(2H)-dione structures;

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