

Experimental analysis of waste polyurethane from household appliances and its utilization possibilities

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ABSTRACT

Polyurethane has a good insulation characteristic, and it is widely used as an insulation and lining material for refrigerators. Nevertheless, at the end of a product's lifetime, serious problems arise related to waste management. Recently, energy recovery has been marked as a promising solution, especially, waste-to-energy applications. To find an appropriate application for such waste, a thermal analysis was performed. An experimental analysis of polyurethane (PU) waste material was performed by the method of pyrolysis gas chromatography with mass spectrometric detection (Py-GC/MS) at various pyrolytic temperatures, namely, at 500, 600 and 700 °C. Waste polyurethane foam was conducted to investigations in the form of a bulk sample and sorted grain-size samples with a goal to detect the chemical composition of the pyrolysate. The investigation revealed various groups of organic compounds such as heterocyclic compounds of nitrogen and simple and polycyclic

aromatic hydrocarbons, while notable concentrations of compounds containing chlorine were detected as well. The experimental analysis found differences in the composition of amines and other compounds and in the dependence on grain size composition. Bulk samples produced the highest concentration of amines (> 40%) at a temperature of 500 °C. The sample homogenization led to a significant increase in amines production. Polyurethane waste of grain size from 0.125 to 0.25 mm contained approximately 80% amines. The pyrolysis of the bulk sample at 600 °C yielded only 24% nitrogen heterocyclic compounds, while from the sorted grain-size <0.045 mm and 0.045-0.063 mm, yields were increased to 47.4 and 45.7%, respectively.

KEYWORDS

Polyurethane waste, pyrolysis, waste-to-energy, pollutant emission, PAH

INTRODUCTION

Polyurethanes rank among the most important polymers in the plastics industry. They are the world's sixth most widely used polymers with an annual production of approximately 18 million tonnes (Fillers market forecast 2018). The presence of PU (polyurethane) foam in municipal waste is related to the end of product life, but it may also be derived as scrap from the manufacturing process which can account for approximately 10-15% of produced foam (Simón et al. 2018). Three types of polyurethane foam are distinguished: flexible, rigid and viscoelastic foam (Yang et al. 2014). These foams are typically either polyether or polyester based polyols, which are not considered to be biodegradable compounds (Velencoso et al. 2013). The most important commercial polyurethane products are either flexible or rigid foams, depending on their mechanical performance and cross-link densities (Król 2007). Rigid polyurethane foams (PURs) are widely used in building insulation, domestic appliances, the automotive industry and as an insulation and lining material for refrigerators and freezers. A single foam manufacturer may produce more than 150 different polyurethane foams, depending on the desired properties for the final product (Avcı and Özdemir 2017). A variety of possible applications, followed by continued demand growth, raised several issues related to disposal methods of the derived waste. As an example, a refrigerator mainly contains 10% polyurethane (Kang et al. 2016); therefore, in China alone, it is expected that approximately 93 200 tons of PU waste from refrigerators will be generated annually (Yang et al. 2012).

Currently, polyurethane waste is disposed of in three ways: landfilling, recycling and incineration. Landfilling, which is soon to be completely phased-out in the European Union, is an extremely undesirable disposal method (The Council of the European Union 1999). Not only because a valuable material is thrown away, but the physical and chemical properties of PU are strongly adverse for such practice. Polyurethane waste will hardly decompose in natural conditions, but even more, a low pile-up density followed up by the vast volume of such waste, makes this method completely unacceptable (Yang et al. 2012). Like other plastics, many PU products can be recycled in various ways to remove them from the waste stream and to recover the value inherent within the material. Polyurethane is recycled in the two primary ways: mechanical recycling, in which the material is reused in its polymer form, and chemical recycling that takes the material back to its various chemical constituents (Zia et al. 2007). If polymer waste cannot be recycled, energy recovery is preferred because of the great potential derived from its calorific value (Al-Salem et al. 2017). At the moment, the most prominent energy recovery method is waste-to-energy utilization. There are several advantages of this method, such as reduction of a waste volume, substitution of fossil fuels for power generation, destruction of hazardous compounds, etc. (Zia et al. 2007). It should be noted that chemical recovery methods such as glycolysis, hydrolysis or aminolysis are prospective since they can

convert waste materials to new, raw chemicals; nevertheless, an economically viable solution is still missing (Simón et al. 2018).

Due to the content of toxic flame-retardant chemicals in PU foams, there is pressure to limit their direct use without chemical treatment (Liang et al. 2012). Flame retardant chemicals historically added to PU belong to a class of chemicals considered persistent, bio-accumulative and toxic (PBT). Extremely harmful substances, primarily brominated flame retardants (BFRs) include hexabromocyclododecane (HBCD) and polybrominated diphenyl ethers (PBDEs). The results from construction and demolition waste revealed extremely high contents of HBCDs and PBDEs in polyurethane foam (Duan et al. 2016). Significant flame retardants used in the polyurethanes also include phosphorus compounds (Matuschek 1995). To find a suitable application of polyurethane waste, numerous experimental investigations have been performed. Occasionally, thermogravimetric analysis (TGA) coupled with some spectrometric technique is used, since with this way it is possible to determine a kinetic mechanism of thermal degradation and inspect the residue constitution (Rostek and Biernat 2013). A kinetics mechanism and residue constitution are essential for a co-firing process in existing power plants or incinerators since they significantly influence the fuel blends ratio and operational parameters of the combustion process (Mehmood et al. 2015).

The thermal stability and degradation mechanism of polyurethane have been studied extensively. The thermal degradation kinetics of polyurethane in different atmospheres was described by (Bilbao et al. 1996). It was shown that the degradation mechanism for PUF in a nitrogen atmosphere consists of two steps, while for the air atmosphere, only one step is noticed. Herrera et al. 2001 performed a thermal analysis (TA) coupled with mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) for N-containing polymers to determine the yield of toxic and harmful compounds. Particular focus was given to the yield of aliphatic N-containing compounds (isocyanate, amino, and cyano compound), azaarenes, amino-PAHs, cyano-PAHs, and nitro-PAHs since they are classified as harmful or hazardous. Wang et al. 2013 showed that the pyrolysis of polyurethane foams could be divided into two temperature ranges: one from room temperature to 400 °C and the other one above 400 °C, while decomposition is mainly concentrated between 200-400 °C. A similar decomposition mechanism was confirmed by other authors (Garrido and Font 2015) (Jomaa et al. 2015). The main problem of polyurethane pyrolysis is the high nitrogen content in RPUF (5-8%) (Guo et al. 2014). A high content of fuel nitrogen during the thermochemical process may lead to the formation of toxic and harmful compounds such as NO_x emissions, ammonia (NH₃), and hydrogen cyanide (HCN). To promote the formation of environmentally friendly nitrogen (N₂), metals and metallic compounds were used as a catalyst (Guo et al. 2016). It was shown that a catalyst could facilitate the formation of N₂, especially calcium oxide (CaO) and iron (Fe); nevertheless, their presence may strongly influence the formation of harmful HCN. Furthermore, the amount of gas generated during pyrolysis is temperature dependent and increases with the temperature increment. At 1000 °C, the highest gas yield was 55.3%. During the thermal decomposition of polyurethane, the addition of zeolite leads to the decomposition of ether and ester to monomers while diisocyanate units are converted to N-containing aromatic compounds (Bozi et al. 2013). From the point of view of the circulatory economy, pyrolysis liquids containing nitrogen heterocycles may be interesting. Nitrogen-containing compounds such as pyrrole, pyridine, indole and their derivatives from a pyrolysis liquid can be used to produce pharmaceuticals, dyes, perfumes, and other commercial products (Chen et al. 2016). Recently, the synthesis of polyurethane containing pyridine (PUPy) has been in focus, since the pyridine can improve thermal stability, especially at low temperatures (Chen et al. 2012). Moreover, pyridine shifted PU degradation to start and end at slightly higher temperatures.

The optimal setting of pyrolysis conditions and sample pretreatment allows the use of newly formed organic compounds from the liquid phase released during the thermal degradation of waste rigid polyurethane foam (WRPUF). The focus of experimental investigations has been to identify conditions (particle size, temperature) under which the maximum production of compounds can be achieved. Moreover, since the research aims to investigate if used WRPUF samples can be used for waste-to-energy applications, particular focus will be given to the formation of toxic and harmful compounds such as polycyclic aromatic hydrocarbons (PAHs), furans, dioxins and similar compounds. The novelty of this work is manifested in the fact that the detailed chemical constitution of polyurethane pyrolysis residue is presented. Since the previous work of other authors was more focused on the decomposition kinetics, such information is scarce. Moreover, the effect of the particle size on polyurethane decomposition is investigated. To the best of the authors' knowledge, the influence of the particle size on the polyurethane pyrolysis residue composition has not been previously reported.

MATERIALS AND METHODS

The sample of waste rigid polyurethane foam was obtained from the insulation of dismantled refrigerators, freezers, and cooling boxes. The mechanical properties of the sample were not studied extensively, but it is known that it was low-density and rigid in terms of stiffness since it was used as an insulation material. The polyurethane sample also contained waste fragments of polyethylene, rubber, and other polymers. The bulk sample of polyurethane was analysed including fragments of other wastes. A particle size analysis was carried out since the sample was expected to have a heterogeneous composition (laser particle sizer Malvern Instruments, Mastersizer 2000). The obtained sample was divided by the rotation splitter (PT100- Retsch) into two subsamples. These subsamples were pyrolyzed, and the results were evaluated using the t-test (Software Statgraphics Plus 5.0). The results showed that there was no significant difference between the investigated samples, and one of the subsamples was selected for further actions. The sample was then divided by screening into the 8 grain classes: < 0.045 mm, 0.045-0.063 mm, 0.063-0.125 mm, 0.125-0.25 mm, 0.25-0.5 mm, 0.5-1 mm, 1-2 mm, > 2 mm.

The organic compounds in the samples of polyurethane were analysed using the method of pyrolysis gas chromatography with mass spectrometric detection (Py-GC/MS). The samples (100 -200 µg) were inserted into a quartz tube sealed at both ends by quartz wool. The bulk sample has been analysed by analytical pyrolysis at temperatures of 500, 600, 700 °C, and two repeated measurements were always performed.

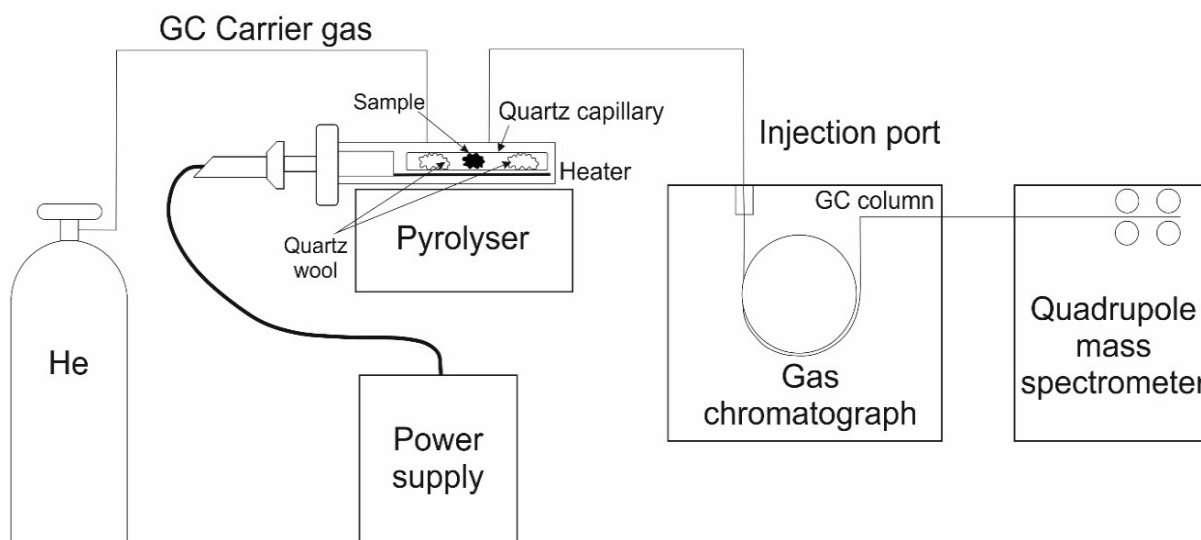


Figure 1- Scheme of the experimental setup

Each grain size from the classified polyurethane sample was analysed by analytical pyrolysis at the temperature of 600 °C. The temperature of 600 °C was selected based on the results obtained within the bulk sample analysis. The analytical pyrolysis conditions: time 10 s, and the temperature increase rate was 20 °C/ms. The interface between the pyrolytic unit and the gas chromatograph was heated to the temperature of 285 °C to prevent the condensation of pyrolytic products. The pyrolysate was then separated at the non-polar column HP 5 ms (60 m x 0.25 mm x 0.25 µm). The temperature programme for separation: 40 °C (retention time 2 min), 220 °C (retention time 10 min, temperature ramp 10 °C/min). From 220 °C the temperature increased at the rate of 33 °C/min up to 320 °C (retention time 5 min). The sample was injected automatically by the pyrolytic unit into the port of the chromatograph at the temperature of 290 °C in the split mode 1:100. The identification and quantification of the individual organic compounds were carried out by the comparison of their mass spectra with the library of mass spectra NIST 14 and measured standards. The identifications of chemical compounds are based on comparisons with standards, GC retention time, literature mass spectra, and the interpretation of mass spectrometric fragment patterns. The abundance of organic compounds varied between 0.01% and 3% of the total quantified peak area (TIC). The pyrolysis-GC/MS does not allow for a quantitative analysis due to the differences in response factors of the MS for different molecules and a residue of unknown quantity and quality. Therefore, the quantification was performed by a comparison of the GC peak area with that of the co-injected known standard (1,3,5-tri-tert-butylbenzene, Merck).

RESULTS AND DISCUSSIONS

The sample was obtained with the known ultimate and proximate analyses. The results (Table 1) were compared with previous investigations of polyurethane samples, and great correspondence was detected among different PU samples. Moreover, in Table 1, the ultimate and proximate analyses are provided for different waste materials that were examined for a waste-to-energy application in other research. As seen in Table 1, the main difference between the polyurethane samples and other forms of alternative fuel is in the content of nitrogen. The PU materials' share of nitrogen is approximately 6%, while that for the rest of the presented materials is approximately 1% or less. This is due to the fact that different amino-based catalysts are used to produce PU foams.

Table 1- Ultimate and proximate analyses of different polyurethane foams and alternative fuels

Type of investigated sample	Ultimate analysis [%]					Proximate analysis [%]		
	C	H	O	N	S	VOC	FC	Ash
WRPUF from a discarded refrigerator	62.69	6.32	24.01	6.37	0.63	83.2	10.6	6.2
WRPUF from the discarded refrigerators <i>(Guo et al. 2016)</i>	66.3	8.6	20.10	4.7		83.9	11.9	1.2
Flexible PU foam <i>(Garrido and Font 2015)</i>	57.79	7.36	23.43	5.95	0.01			
Rigid PU foam, building insulation <i>(Wang et al. 2014)</i>	61.89	6.24	20.10	6.14				
Paper sludge <i>(Yanfen and Ma 2010)</i>	23.99	5.21	25.01	0.14	0.40	48.74	6.01	45.25
Poplar wood <i>(Slopiecka et al. 2012)</i>	45.5	6.26	47.2	1.04		75.44	11.1	3.70
Tire rubber <i>(Tang et al. 2015)</i>	68.9	6.7	19.8	1.0	3.5	60.9	7.5	30.1
Mixed plastics (PE, PS, PP) <i>(Liu et al. 2018)</i>	82.92	12.64	2.28	0.58				
					Cl*			
Solid recovered fuel (SRF) <i>(Liu et al. 2017)</i>	41.15	3.41		1.58	0.324	48.04	10.54	35.19

A comparison with other potential alternative fuels was made since the observation in an electron scanning microscope (Figure 2), showed that the bulk sample contained, in addition to PU, extraneous material: plastics, rubber, titanium dioxide (TiO₂) particles and iron (Fe) particles. The increased levels of TiO₂ are related to its use in plastics. Titanium dioxide pigments in melt processable thermoplastics can affect UV and thermal stability, discolouration and the evolution of volatiles (Day 1990). The identified plastics and rubber material implies that the PU was probably extracted from the waste mixture.

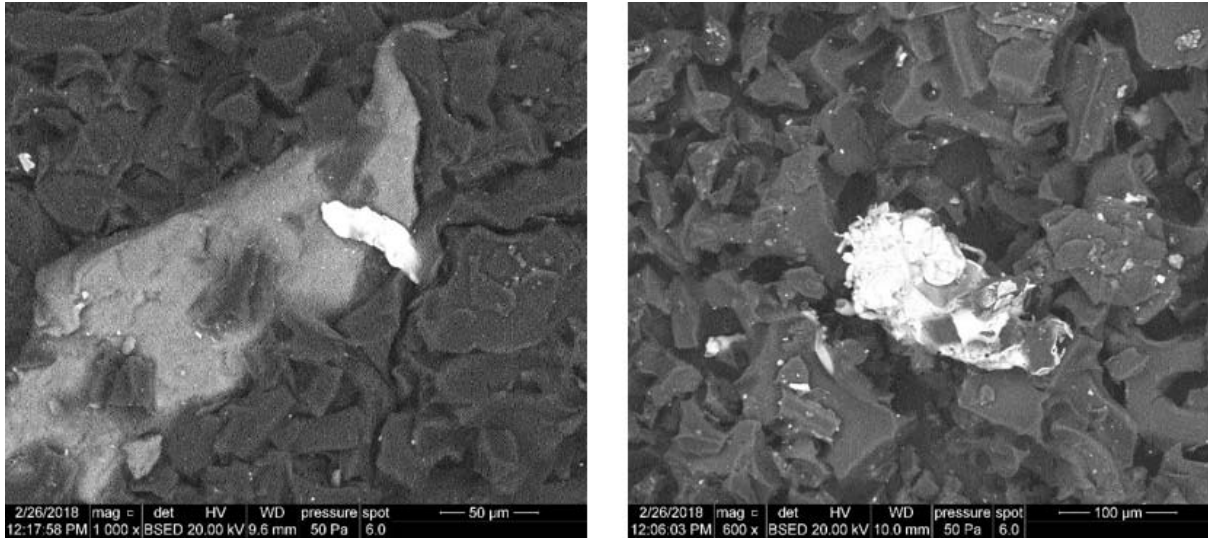


Figure 2- The nature of the waste PU (left), a particle of plastics covered by TiO₂ (right)

To determine the entire elementary constitution of the WRPUF, an X-ray fluorescence (XRF) spectroscopy was conducted. Before the investigation was carried out, the sample was divided by sieving through 2 mm mesh into 2-grain classes. Both grain classes obtained by sieving and the bulk sample were conducted to the XRF-spectroscopy, and the results are presented in Table 2. Various chemical elements were detected, even though most of them in traces with only Fe, titanium (Ti) and chlorine (Cl) of a significant yield. More important is to notice that mercury (Hg) was not detected at all, while lead (Pb) was present with no more than the average concentration in urban areas (Dimitrakakis et al. 2009). The absence of mercury in waste material, which is intended to be used for a waste-to-energy application, is of great interest since the mercury has been marked as one of the major pollutants from incineration processes (Rumayor et al. 2018) (Aljerf and Almasri 2018). Finally, a higher content of chlorine, especially for the grain class above 2 mm, should be monitored since it can cause damage to power plant equipment and promote the formation of toxic and hazardous compounds (Lu et al. 2018).

Table 2-An elementary constitution of waste rigid polyurethane foam

Sample	Fe (%)	Ti (%)	Cl (%)	Al	Si	P	S	K	Ca	Yield (%)		
Bulk	2.16	1.53	1.68	3023	3181	1902	388	1012	6222			
> 2 mm	1.67	1.95	1.85	3237	2960	2083	390	932	7285	22.4		
< 2 mm	2.29	1.42	0.95	2945	3253	1850	385	1050	5958	77.6		
Sample	Cr	Mn	Ni	Cu	Zn	As	Zr	Ag	Cd	Sn	Sb	Pb
	(mg/kg)											
Bulk	28.6	77	36	298	6492	2.4	17	46	3.2	18	26	154
> 2 mm	34.4	57	41	138	4202	3.4	10.2	46	3.2	28	29	175
< 2 mm	27.2	83	28	346	7212	2.1	19	47	3.1	15	25	148

Pyrolysis of a bulk sample at different temperatures

To obtain information on the sample's behaviour during pyrolysis, an analysis of the bulk sample was performed at temperatures of 500, 600 and 700 °C. By heating a sample of polyurethane at a given temperature, a pyrolysate containing organic compounds corresponding to the thermal degradation of the polyurethane was formed. In the pyrolysates,

18 groups of organic compounds were determined (Table 3). The dominant organic compounds for the bulk PU sample obtained at temperatures of 500, 600 and 700 °C form compounds containing nitrogen, compounds containing benzene, alkanates, carboxylic acids, alcohols, alkanes, cycloalkanes, and ethers. The presence of alcohols (especially polybasic – polyols), ethers, esters and isocyanate-containing compounds in pyrolysates represent the basic thermal degradation fragments of polyurethane.

Table 3- Organic compounds in pyrolysates from bulk samples at different pyrolytic temperatures

Compounds	500 °C		600 °C		700 °C	
	ng/mg	%	ng/mg	%	ng/mg	%
Compounds containing benzene + styrene	950.65	11.7	2290.73	26.5	302	7.0
Alkanes and cycloalkanes	416.71	5.1	620.59	7.2	212.11	4.9
Alkenes	172.51	2.1	155.38	1.8	107.63	2.5
Alkadienes	48.72	0.6	29.5	0.3	27.2	0.6
Aldehydes and ketones	7.77	0.1	5.57	0.1	3.94	0.1
Compounds containing nitrogen	3728.11	45.9	2154.89	24.9	1004.47	23.4
Nitriles	30.51	0.4	17.02	0.2	14.55	0.3
Compounds containing phenols	4.24	0.1	16.08	0.2	142.56	3.3
Heterocyclic acetals	77.68	1.0	71.11	0.8	37.31	0.9
Furans	57.91	0.7	38.13	0.4	36.27	0.8
Alcohols	729.11	9.0	1481.3	17.2	464.86	10.8
Oxiranes	37.42	0.5	67.58	0.8	17.76	0.4
Ethers	206.15	2.5	211.3	2.4	293.71	6.8
Acrylates	0.71	0.0	2.59	0.0	5.51	0.1
Carboxylic acids and anhydrides	462.7	5.7	307.21	3.6	398.09	9.3
Alkanates	816.03	10.1	805.57	9.3	424.26	9.9
PAHs and their derivatives	103.31	1.3	130.45	1.5	175.55	4.1
Phthalates, silane, phosphate flame retardants	177.8	2.2	146.89	1.7	231.42	5.4
Unknown organic matter	30.79	0.4	47.02	0.5	363.11	8.4
Sum of organics	8116.74		8637.05		4298.33	

The concentration of the compounds in the pyrolysates varies with the temperature. The chemical analysis by the Py-GC/MS method shows that the bulk sample contains, in addition to PU, rubber fragments and polymers based on plastics (acrylates, polyethylene). Rubber and plastics were identified based on the occurrence of plasticizers, such as phthalates (benzyl butyl phthalate, bis(2-ethylhexyl)phthalate, dibutyl phthalate), silane (triethylsilane, dimethylallyl(n-octyl)silane, octyl silane), acrylates (bis(2-ethylhexyl)acrylate), and styrene.

Significant organic compounds in the bulk sample include heterocyclic nitrogen compounds. In the pyrolysates from the bulk sample, 45 organic compounds containing heterocyclic

nitrogen were identified at different pyrolysis temperatures. Nitrogen heterocyclic compounds show the highest concentration at 500 °C when they represent up to 46% of the total composition of the pyrolysate. At temperatures of 600 °C and 700 °C, the pyrolysate contains 24-25% nitrogen heterocyclic compounds. At a temperature of 500 °C, the dominant compound found in the pyrolysate is aniline (primary aromatic amine) with the yield of 878 ng/mg. Anilines generation can be described in the reaction of NH₃, NH₂* and NH* with -OH from polyols (Xie et al. 2012). Aromatic primary amines, such as aniline, are thermally stable compounds. Although (Moldoveanu 2010) reports that aniline begins to decompose at a temperature above 700 °C to produce benzene, in the case of a PU sample, decomposition already occurred at a temperature of 500 °C to yield n,n-dimethylethylamine. The methylaniline at a concentration of 655 ng/mg was identified in the pyrolysate obtained at a temperature of 500 °C; at higher pyrolysis temperatures, it drops to a concentration of approximately 120 ng/mg. Both aniline and methylaniline are classified as toxic by inhalation, ingestion or skin adsorption, especially in these concentrations. However, a significant decrease in concentration at the higher temperatures shows that they can be easily handled with the temperature increment.

A decrease in concentration with increasing temperature is shown by alkenes, alkadienes, aldehydes and ketones, compounds containing nitrogen, nitriles, contaminants, alkanooates, and acetals. With increasing temperature, the concentration of compounds containing phenols, ethers, acrylates, PAHs and their derivatives, phthalates and the unknown organic matter is increasing. The same trend of increasing the concentration of PAHs with increasing temperature during the pyrolysis of plastics is also reported by Sharuddin et al. 2016. Monitoring the concentrations of PAHs, phthalates, furans, and compounds containing chlorine is of particular interest because of their toxic and hazardous nature (Lamichhane et al. 2017). Not only do they represent an environmental threat, but moreover, they can seriously damage power plant equipment since they can cause corrosion (Edo et al. 2018).

Table 4- Chemical compounds of high risk from the perspective of environmental and equipment impact

Chemical compound	500 °C		600 °C		700 °C	
	ng/mg	%	ng/mg	%	ng/mg	%
1,2- dichlorobenzene	12.5	0.5	2.47	0.1	55.59	9.0
1-chloro-4(chloromethyl) benzene	0.71	0.0	3.71	0.1	7.49	1.2
Toluene	218.9	8.9	1893.63	69.9	27.99	4.5
Butylated hydroxytoluene	19.77	0.8	56.91	2.1	30.75	5.0
Styrene	365.07	14.9	241.27	8.9	69.39	11.2
1,1-Dichloroethane	5.65	0.2	26.6	1.0	25.23	4.1
2-(2,2,2-trichlor-1-(2-furamido) ethoxy benzamide	44.99	1.8	44.54	1.6	6.31	1.0
2-chloro-n,n-dimethylethanamine	150.4	6.1	109	4.0	83.97	13.6
3-chloro-2-fluoro-n-(3-chloro-2-fluorobenzoyl-N-hexyl-benzamide	0.81	0.0	32.17	1.2	9.46	1.5
Aniline	878.42	35.8	39.84	1.5	18.14	2.9
m-methylaniline, n-methylaniline, o-methylaniline, p-methylaniline	654.58	26.7	121.32	4.5	115.26	18.7
2,5-dimethylfuran	57.2	2.3	35.96	1.3	31.93	5.2

2,3-diethyl oxirane	24.71	1.0	57.53	2.1	7.9	1.3
Bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate	5.25	0.2	15.6	0.6	9.07	1.5
3-chloro-1-propyl phosphate	1.09	0.0	5.96	0.2	9.46	1.5
1-chloro-2-propanol phosphate (3:1) (TCPP)	10.22	0.4	8.52	0.3	68.99	11.2
Bis(2-ethylhexyl) phthalate	4.24	0.2	15.26	0.6	41	6.6
Sum of harmful compounds	2454.44		2710.29		617.93	

The chemical compounds presented in the Table 4 are the ones identified with the highest yield among compounds classified as potentially hazardous or harmful (Garrido et al. 2016). As can be seen, the yield of these compounds is altering with temperature, and it is dependent on the chemical nature of the compound. Even though most of the presented compounds are not exceeding permissible concentrations, special concern should be given since some of them are of an extremely hazardous nature. Additionally, compounds containing chlorine are of special interest because of their corrosive activity, which may influence the equipment's performance (Liu et al. 2017). Compounds that are exceeding allowed concentrations and represent an immediate threat to human health are toluene, aniline, methylaniline and derivatives and 1-chloro-2-propanol phosphate (3:1), known as TCPP (Environment and Climate Change Canada 2016). Concentrations of these compounds are several times higher than the recommended values given by The National Institute for Occupational Safety and Health (NIOSH). Other compounds that are detected in allowed concentrations such as phthalates, furans, and oxiranes, should be monitored since most of them are marked as carcinogenic or potentially carcinogenic (Rathna et al. 2018).

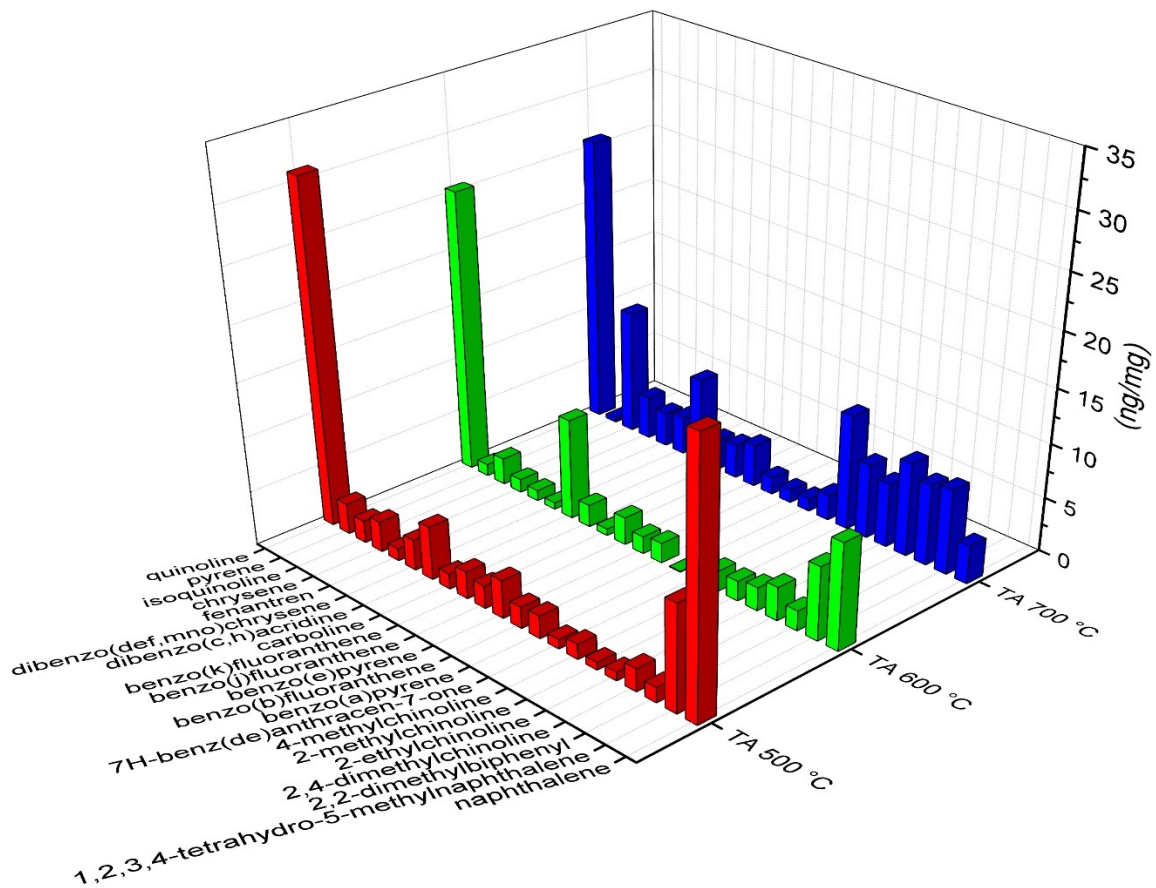


Figure 3- The relationship between PAHs concentration and pyrolysis temperature

Figure 3 presents the relationship between the yield of PAHs and pyrolysis temperature. It was already pointed out that the concentrations of PAHs are increasing with the temperature increment. The highest concentration of 175.55 ng/mg was detected at 700 °C, with quinoline and methylchinoline as the most abundant compounds with yields of 25.91 and 17.50 ng/mg, respectively. At the temperature of 500 °C, quinoline was again the most abundant compound with a yield of 33.12 ng/mg, while a notable yield of naphthalene is noticed as well, 24.71 ng/mg. Altogether, 21 PAHs are detected, with quinoline and naphthalene as the most prominent representatives for all examined temperatures. Simple PAHs such as naphthalene and quinoline are not exceeding the recommended exposure limit, but their concentrations are not negligible (Bodar et al. 2018). Complex PAHs such as benzo(a)pyrene, benzo(j)fluoranthene and similar are presented with significantly lower concentrations, up to 4 ng/mg, and their yield changes slightly with the temperature increment. Nevertheless, the number of detected PAHs and their overall concentrations demand a cautious approach because of their strong toxicity and carcinogenic nature (Kwon et al. 2015).

Effect of the particle size on the pyrolysate composition

The multiple nature of the particles in the sample can affect the yield of organic compounds in the pyrolysate. To achieve a greater homogeneity of the waste polyurethane batch, the sample was screened and divided into 8 grain-size classes. Samples of the sorted grain-size classes were pyrolyzed at 600 °C. It is known from the literature that both the maximum temperature and the heating rate increase with a decreasing particle size. With the falling biomass size, the amount of gas (up to 20%) increases during pyrolysis, while the solid and liquid yields decrease with the particle size. This dependence was determined for biomass in the range between 0.23 and 4 mm. Additionally, a higher proportion of the liquid than the solid

phase is formed for particles smaller than 0.14 mm (Huang et al. 2018). Additionally, for coal, Jayaraman et al. 2017 states that decreasing the coal particle size causes the burn-out time to be lowered and the burning rate to be increased. This is because smaller pulverized coal particles have a greater specific area than does larger ones and are propitious to the evolution and ignition of coal particles. Another aspect is that the increase in particle size may prolong the residence time of the volatile matter in a particle, which helps enhance the secondary reaction (thermal cracking) of tar in the particle, increasing the gas yield (Luo et al. 2010). Murillo et al. 2006, found no relation between the functional group composition of the pyrolytic oils and the process variables of heating rate, flow rate, particle size, and temperature. Information related to the influence of the particle size on the chemical composition of pyrolysate is not available.

The thermal decomposition of the sample from the individual grain-size classes provides different concentrations of organic compounds in the pyrolysate (Table 5). A comparison of the determined concentration of organic compounds in the samples from the individual grain-size classes (quantity balance) with the bulk sample shows a fair match, except for the compounds with heterocyclic nitrogen, for which the difference is up to 43%. The content of compounds with heterocyclic nitrogen is higher in the sorted samples.

The highest concentrations of compounds containing benzene, alkanes, cycloalkanes, alkenes, PAHs and their derivatives, and additives were found for pyrolysates prepared from particles >0.5 mm. The increased concentrations of these compounds are related to the higher content of plastics and rubber particles in the sample. The highest concentrations of alcohols, nitrogen heterocyclic compounds and carboxylic acids occur in grain-size classes <0.5 mm. The increased concentrations of these compounds (higher than the arithmetic mean value) are likely to be associated with the faster decomposition of smaller PU particles, which is indicated by a decrease in concentration with increasing particle size. The highest mass particle yield was found for the grain-size classes 0.063-0.125 and 0.125-0.25 mm, which is 47%. A high mass yield also affects the yield rate, which is up to 62% in nitrogen heterocyclic compounds for particles below 0.25 mm.

Table 5- Organic compounds in pyrolysates from different grain size classes at 600 °C

Grain size (mm)	Yield (wt.%)	Compounds containing benzene	Alkanes. cycloalkanes	Alkenes	Alkadienes	Alcohols	Aldehydes and ketones	Compounds containing phenols	Compound with heterocyclic nitrogen
<0.045	0.06	547.1	312.9	102.7	10.3	1872.8	4.8	24.9	3663.1
0.045-0.063	9.19	582.8	413.3	103.2	9.5	1674.9	4.3	13.2	3583.7
0.063-0.125	23.35	1088.7	415.8	130.4	10.2	1573.5	8.0	15.9	3691.9
0.125-0.25	23.66	1755.2	414.1	144.3	11.0	1568.5	9.0	17.1	3344.4
0.25-0.50	15.86	2035.4	414.4	155.7	15.1	1284.9	10.9	15.7	3474.8
0.5-1.0	15.83	2855.7	514.9	182.1	18.4	1067.9	14.8	14.9	2642.4
1.0-2.0	7.39	3868.3	550.4	196.1	28.8	1191.1	13.8	14.9	2329.5
>2	4.66	4148.7	614.0	205.0	32.0	1468.2	4.9	11.0	2070.6
Calculated from grain size		1977	450	152	15	1423	10	15	3223

Bulk sample		2347	621	175	21	1506	6	16	2154
Average		2110	456	152	17	1463	9	16	3100
Grain size (mm)	Yield (wt.%)	Carboxylic acids	Alkanoates, acetates and others	Oxiranes	PAHs and their derivatives	Additives (plasticizers, flame retardant)	Unknown organic matter	Sum of organic matter	
<0.045	0.06	188.5	702.5	2.8	68.2	210.5	11.3	7722.4	
0.045-0.063	9.19	310.8	811.7	3.9	88.0	212.7	29.7	7841.8	
0.063-0.125	23.35	288.5	879.8	5.0	98.0	284.1	65.5	8555.1	
0.125-0.25	23.66	310.6	821.8	7.8	94.6	276.5	62.7	8837.7	
0.25-0.50	15.86	277.6	722.4	5.5	76.3	388.5	56.9	8934.1	
0.5-1.0	15.83	210.7	804.3	3.1	89.1	421.2	71.3	8910.7	
1.0-2.0	7.39	210.8	844.2	1.3	108.2	586.2	81.6	10025.2	
>2	4.66	211.1	445.5	0.8	136.2	612.8	81.8	10042.6	
Calculated from grain size		272	800	62	94	352	63	8846	
Bulk sample		307	805	7	78	404	47	10677	
Average		251	754	4	95	374	58	8859	

The occurrence of plastics and rubber was confirmed by the presence of specific compounds derived from their thermal degradation only in the bulk sample and in the sorted particles above 2 mm. The main components of the thermal decomposition of rubber are compounds containing benzene, styrene, alkadienes (butadiene isomers), and alkenes (especially butene), which exhibit the highest pyrolysis concentrations in particles larger than 1 mm. PAHs (especially naphthalene, methyl naphthalene, benzothiazole) are also significant decomposition products of rubber. When pyrolyzing rubber, the pyrolysate contains plasticizers and flame retardants in the concentration of approximately 2-5%, and the nitrogen compounds form only 1-2%.

Only phthalates and flame retardants associated with the occurrence of plastic based polymers, including triethyl phosphate, HOSTAFLAM OP 820 and DEHP, have been identified in the grain-size classes of sorted samples (<2 mm). Only BHT antioxidant, α -methylstyrene and precursors of vulcanizing agents, such as piperidine and cyclohexylamine (cyclohexanamine) have been detected as the main degradation products of rubber.

Nitrogen heterocycles in pyrolysates

Compounds containing nitrogen are the dominant product of PU foam pyrolysis. The bulk sample produced the most significant amount of heterocyclic nitrogen compounds at 500 °C. With increasing pyrolysis temperatures, the concentrations of nitrogen heterocyclic compounds, including amines, are decreasing. In the sorted PU samples, the maximum content of nitrogen heterocyclic compounds was determined at 600 °C, with a concentration of 3223 ng/mg. For the bulk sample at 600 °C, the detected concentration of compounds containing nitrogen is 2155 ng/mg. The share of compounds containing heterocyclic nitrogen varies from 20 to 47% in the pyrolysates from the sorted polyurethane samples obtained at 600 °C. In the pyrolysates of the bulk sample of polyurethane obtained at pyrolysis temperatures of 500 to 700 °C, these compounds are formed in the range of 23 to 46%, and at a temperature of 600 °C, it is 25%. In the sorted polyurethane, the production of compounds containing heterocyclic nitrogen increases by approximately 1/3 at 600 °C.

In addition to the amines resulting from the thermal degradation of the PU, the pyrolysates contain amines that are released during the PU production to improve the reaction (catalysts). Detected compounds containing nitrogen are of low toxicity, and in general, their origin in the investigated sample can be presumed. Occasionally, amines are added during the production process in the form of a catalyst or to improve specific properties. Even though they do not represent a threat to human health due to low toxicity, their presence can significantly inhibit corrosive processes. A detailed review of detected compounds containing nitrogen from the bulk sample and grain-size classes is presented in Table 6. From the following, it is clear that the particle size can significantly influence the decomposition process in both terms, concentration, and the composition of pyrolysates. A results comparison between the bulk sample and grain-size classes reveal a significant disagreement in identified compounds. Grain-size classes produce more homogenous pyrolysates, which is especially visible from the yield of compounds containing nitrogen (Table 6).

Table 6- Nitrogen heterocycles in pyrolysates from individual grain-size classes at a temperature of 600 °C (ng/mg)

Comparison between the yield of compounds containing nitrogen and the compounds with hydroxyl groups

Detected organic compounds containing hydroxyl groups in the pyrolysate are alcohols (compounds containing one OH group) and phenols. Alcohols are released during the thermal degradation of polyurethane together with isocyanates (Im et al. 2008). The presence of easily hydrated alcohols causes the decomposition of polyurethane into primary amines and alkenes. Phenols are utilized in the production of phenol-terminated polyurethane or polyurea (urethane) with epoxy resins. Phenol-terminated polyurethane with epoxy resins forms a component of the analysed polyurethane waste. The pyrolysate contains organic compounds with a content of urea (1,1-dimethylethylurea). Phenol can be a component of additives, e.g., antioxidants as 2,6-di-tert.-butylphenol. Compounds containing phenols (2-(dimethylamino)phenol, 4,6-di(1,1-dimethylethyl)-2-methylphenol) are represented in all grain-size classes of the polyurethane sample in very low concentrations compared with alcohols and compounds containing heterocyclic nitrogen. The highest concentration of phenolic compounds (25 ng/mg) was found in the grain-size class of 0.045 mm (Table 7).

Table 7- Concentrations of alcohols, compounds containing phenols and compounds with heterocyclic nitrogen (ng/mg) in individual grain-size classes

Grain size (mm)	Yield (%)	Alcohols	Compounds containing phenols	Compound with heterocyclic nitrogen	Amine
< 0.045	0.06	1872.8	24.9	3663.1	2878.1
0.045-0.063	9.19	1674.9	13.2	3583.7	2976.2
0.063-0.125	23.35	1573.5	15.9	3691.9	3316.6
0.125-0.25	23.66	1568.5	17.1	3344.4	2816.1
0.25-0.50	15.86	1284.9	15.7	3474.8	3020.7
0.50-1.0	15.83	1067.9	14.9	2642.4	2225.2
1.0-2.0	7.39	1191.1	14.9	2329.5	1960.1
> 2.0	4.66	1468.2	11	2070.6	1734.8
Calculated		1423	15	3223	2775.0
Bulk sample		1503	16	2154	2324.2
Average		1463	16	3100	2615.9

Explanation: Red – max, blue – min.

Compounds with heterocyclic nitrogen have the highest concentration in the grain-size class <0.125 mm. Alcohols (1-dodecanol, 2-decanol, 2-ethyl-1-hexanol, n,n-diethylaminoethanol, tetracosanol and 1-(2-(2-methoxy-1-methylethoxy)-1-methylethoxy)-2-propanol) have the highest concentrations in the grain-size classes <0.25 mm. The highest concentration of amines is in the grain-size classes <0.045 to 0.5 mm in which the total yield of amines reaches up to 80%. Similar results were also obtained for the alcohols which reach a yield up to 85% for a particle of the size between 0.045 - 0.5 mm. The statistical linear relationship between alcohols and amines was confirmed by the critical value of the correlation coefficient at the significance level of 0.1. The particle grain-size substantially influences the intensity of the decomposition of PUR and the origin of primary compounds. The increased yield of amines was also confirmed by analyses performed for the individual grain-size classes in which the average value reaches 2775 ng/mg. Simultaneously, the bulk sample provides lower concentrations of 2324 ng/mg. The behaviour of compounds containing heterocyclic nitrogen, phenols and alcohols is also different at the various pyrolysis temperatures even in the bulk sample. The

concentrations of components with a content of heterocyclic nitrogen decrease with the increasing temperature while the concentrations of compounds containing phenol increase. Alcohols reach the maximum concentration at the temperature of 600 °C. The highest yield of compounds containing heterocyclic nitrogen in the bulk sample was obtained by the pyrolysis of polyurethane at the temperature of 500 °C.

CONCLUSION

By analysing rigid polyurethane waste (bulk sample), polyurethane has been found to contain admixtures of synthetic polymers based on plastics and rubber, inorganic TiO₂ compound and Fe/Fe-oxides. The highest proportion of plastics and rubber was found in coarse-grained classes (> 1 mm but mainly > 2 mm), which is related to the crushability and grindability of the waste material. In the sorted samples (<1 mm), there is a decrease in the number of compounds derived from the degradation of polymers, especially rubber.

In general, the dominant compounds in the pyrolysate are nitrogen compounds and polyurethane building blocks (alcohols, ethers, esters, urea). The pyrolysis of polyurethane in individual grain-size classes leads to an increased production of nitrogen-containing heterocyclic compounds, especially amines. Some of the identified amines are used as catalysts to produce the polyurethane. The highest yields of compounds containing nitrogen heterocycles (also amines) were identified in the grain-size class ranging from 0.063 to 0.125 mm.

At the same time, it has been confirmed that particle sorting contributes to an easier thermal degradation of polyurethane. A sorting sample of <2 mm assists in the cleavage of the polyurethane chain, which can be more easily pyrolyzed, resulting in the thermal degradation of the polyhydric polyols to less saturated ones and in the absence of ethers due to their decomposition.

Finally, the thermal degradation of the investigated PU foam showed that a significant amount of hazardous and harmful compounds may be formed during the decomposition process. Most of these compounds are detected in permissible concentrations, and as such should not represent a threat to the environment or human health. However, a relatively high share of chlorine in the elementary composition (>1%) followed by the significant yield of chlorine-containing compounds indicates that a cautious approach towards further utilization of such waste should be maintained. Furthermore, significant concentrations of PAHs and phthalates (flame retardants) detected in both the bulk sample and the grain-size classes indicates that the investigated sample should be further investigated prior to utilization in waste-to-energy applications. The direct utilization for waste-to-energy applications is not advised because of the chemical nature and degradation behaviour of the investigated sample. The chemical pretreatment or mixing with other waste materials is recommended to achieve safe and sustainable performance.

Blending waste polyurethane foam with some other non-polymer waste (paper, biomass, paper sludge or similar) could decrease the share of elementary chlorine and decrease the generation of PAHs or similar harmful compounds. In addition, the investigated PU sample could be pelletized to be used as refuse-derived fuel (RDF) and then examined with a scope to monitor changes in the decomposition kinetics and the yield of organic compounds. Pellets are highly dense and are produced with a very low content of moisture. Therefore, they are burned with a very high combustion efficiency. Moreover, emissions from the burning pellets are quite low in comparison with other combustion techniques, which enhances their sustainability. Nevertheless, further investigation should be performed to find an appropriate utilization of such fuel in waste-to-energy applications.

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Table 6- Nitrogen heterocycles in pyrolysates from individual grain-size classes at a temperature of 600 °C (ng/mg)

Nitrogen heterocycles	Bulk sample	Grain size							Avg.	S.D.	
		<0.045	0.045-0.063	0.063-0.125	0.125-0.25	0.25-0.50	0.5-1.0	1.0-2.0			>2.0
(ng/mg)											
	<i>(1,1'-biphenyl)-4-amine</i>	5.57									
	isopropylpent-4-enylamin	1.81	2.41	4.84	1.99	1.72	0.76	0.32	1.3	1.89	1.37
	2-chloro-n,n-dimethylathanamine	109.00	20.63	21.93	20.74	11.62	0.1	6.43	14.95	10.68	13.39
	n'-ethyl-n,n-dimethyl-1,2-ethanediamine	5.65	2.14	2.51	1.18	1.8	1.05	1.89	4.65	2.61	1.66
	n,n-dimethylbenzenemethanamine (BDMA)	155.06	56.18	65.59	91.27	62.65	75.61	1.36	70.26	78.42	62.67
	n,n-dimethylmethylamine	814.74	2624	2710	3026	2524	2756	2112	1686	1484	2365.25
	n-methyl-1-naphthalenamine	6.59									
	n-methylcyclohexanamine	47.63	52.7	62.78	79.95	73.83	53.38	31	94.47	61.38	63.69
	n,n-dimethylcyclohexanamine= n,n-dimethylcyclohexylamin	97.74	56.61	49.37	47.28	98.87	59.32	41.67	58.22	63.24	59.32
	5,6,7,8-tetrahydro-1-naphthalenamine	9.05									
	n-(2-dimethylamino)ethyl-n,n'-trimethyl-1,2-ethanediamine	5.23	0.8	1.54	1.9	2.5	9.35	0.65	2.92	4.89	3.07
Amine	triethylamine (3,3-diethylpiperidine-2,4-dione)	30.90	3.11	0.4	0.43	0.44	5.75	1.05	1.8	1.71	1.84
	n,n,n',n'-tetramethyl-1,3-propanediamine		1.74	1.47	2.25	2.28	0.86	1.05	0.73	4.24	1.83
	n,n'-(1-methyl-1,2-ethanediylden)bis(2-methylbenzenamine)	10.59									
	n,n,n',n'-tetramethyl-1,2-ethanediamine		6.15	6.49	5.01	1.4	20.51	0.99	4.22	0.24	5.63
	n,n,n',n'-tetramethyl-1',6-hexanediamine		0.87	0.53	0.69	0.66	2.83	0.99	0.59	0.98	1.02
	n-ethylmorpholine (DABCO NEM)		2.32	1.94	2.51	0.59	2.4	1.11	0.97	0.65	1.56
	<i>aniline</i>	39.84	42.4	37.8	30.5	32.4	28.7	24.2	22.3	16.7	29.38
	<i>m-methylaniline</i>	36.50									
	<i>n-methylaniline</i>	12.36									
	<i>o-methylaniline</i>	62.00									
<i>p-methylaniline</i>	10.52										
	n,n,n',n'-tetramethyl-1,6-hexanediamine										
	3,3-diethylpiperidine-2,4-dione		3.04	2.81	0.78	1.62	2.4	0.89	0.52	1.71	1.72
	Sum	1453.32	2878.01	2967.2	3316.66	2816.03	3020.73	2225.2	1960.16	1734.79	2614.85
Amide	1H-indole-6-carboxamide	15.52									
	3-chloro-2-fluoro-n-(3-chloro-2-fluorobenzoyl)-N-hexylbenzamide	32.17									
	3-chloro-2-fluoro-n-(3-methylbutyl)benzamide	1.09									
	compounds containing benzamide	2.05									
	compounds containing carboxamide	35.88									
	hexadecyl formamide	1.06									
	2-(2,2,2-trichlor-1-(2-furamido)ethoxy)benzamide	44.54									
	n,n'-dimethylloxamide	116.30	186.3	152.4	104.7	87.6	64.6	52.8	49.6	47.4	42.20
	n,n-dimethylethanthioamide	15.52									
	n,n-dimethylpropanamide	15.26									
	4-ethyl-n-butyl-n-hept-2-yl-benzamide	2.85									
	Sum	282.24									
Pyridin	2,4-dimethylpyridine	1.24									
	2-methyl-5-(1-methylethenyl)pyridine	111.24	184	126	108	92	101	106	102	86	113.13
	2-methylpyridine	4.52									
	3-methylpyridine	1.28									
	3-(1H-pyrazolyl-4-yl)pyridine	7.39									
	3,4-dimethylpyridine	2.59									
	Sum	128.26	184.00	126.00	108.00	92.00	101.00	106.00	102.00	86.00	113.13
Indol	1,2,3,4,7-pentamethylindole	5.69									
	1,2,3,4-tetrahydro-6-methylpyrido(4,3-b)indole	1.52									
	1,2,3,7-tetramethylindole	3.76									
	pentamethylindole	49.49									
	Sum	60.46									
Urea	<i>(1,1-dimethylethyl)urea</i>	15.47	1.09	0.74	0.78	1.62	1.52	1.12	1.1	0.73	1.09
Imidazole	1-(4-methylphenyl)-1H-imidazole	22.52									
Piperazine	2,6-dimethylpiperazine	68.05	75.5	65.35	55.01	52.57	44.21	31.05	25.04	23.18	46.49
Triazin	compounds containing benzotriazine	0.79									
Pyrazin	2-methyl-6-(1-propenyl)pyrazine	10.58									
Benzonitril	2-methylbenzonitrile	4.50									
	4-methylbenzonitrile	6.23									
Phenols	2-(dimethylamino)phenol		1.67	2.61	5.01	5.81	4.55	0	3.41	1.87	
Quinazoline	2-methylquinazoline	102.47	154.2	146	198.7	202.6	141.71	120.22	89.6	92.5	143.19
Total		2155	3663.1	3583.69	3691.85	3344.42	3474.77	2642.39	2329.5	2070.6	3074.07
	Unknown origin		Pyrolysis products					Pigments			
	Catalyst		Precursors for the synthesis of organic compounds					Building blocks			

AVG - average, S.D. - standard deviation