

Polycyclic Aromatic Hydrocarbons Formed During the Pyrolysis Process of Plastics – Characterization, Quantification and Risk Assessment

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ABSTRACT

Occurrence, distribution, and toxicity assessment of 16 Polycyclic Aromatic Hydrocarbons (PAHs) prioritized by the US Environmental Protection Agency in pyrolysis products – pyrolysis oil and pyrolysis wax – of different plastics are characterized. PP, HDPE, LDPE, PVC, PS (respectively, polypropylene, high- and low-density polyethylene, polyvinylchloride and polystyrene) and their mixture named 5P are chosen as a feed material for pyrolysis. Pyrolysis process is carried out in a custom-built laboratory batch reactor with the pyrolysis temperature of 450 °C for PP, PVC, PS and 500 °C for HDPE and LDPE. 5P mixture is pyrolyzed at 500 and 700 °C. PAHs quantification is used to determine the toxicity equivalency quantity TEQ (BaP) for each pyrolysis product and to establish the degree of toxicity. The highest total concentration of 16 PAHs in pyrolysis oil is found to decrease in the order of PVC > PP > PS > LDPE > HDPE. According to TEQ (BaP), the toxicity of the most toxic pyrolysis oils correlates with the aforementioned order of the total concentration, i.e., being lowest for HDPE and highest for PVC. For pyrolysis wax, the highest total concentration of 16 PAHs is for PVC > PS > LDPE > PP > HDPE, while TEQ (BaP) value decreases as PVC > LDPE > PP > PS > HDPE. The PAHs concentration and TEQ (BaP) values of 5P mixture show similar trends in both products (oil, wax), i.e., they both increase with increasing pyrolysis temperature.

Keywords: pyrolysis of plastics, polycyclic aromatic hydrocarbons (PAHs), pyrolysis oil, pyrolysis wax, risk assessment.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) belong to a class of organic compounds containing two or more aromatic rings. PAHs are primarily generated during incomplete combustion (in an oxygen atmosphere) of organic materials such as coal, petrol, oil or wood. Some PAHs in the environment originate from natural sources such as open burning, natural loss or seepage of petroleum or coal deposits and volcanic activity. Nevertheless, emissions from anthropogenic activities

predominate the PAHs origin in the environment. The major anthropogenic sources of PAHs include residential heating, coal gasification, coal tar pitch and asphalt production, coke and aluminum production, motor vehicle exhaust etc. (Abdel-Shafy and Mansour, 2016). Referring to several scientific studies, the International Agency for Research on Cancer (IARC), and the Working Group on the Evaluation of Carcinogenic Risks to Humans, numerous PAHs have been classified into carcinogenic groups (Skupinska et al., 2004). According to the evaluation of the IARC (IARC, 2010),

15 PAHs are classified as carcinogenic, these are: Group 1 – carcinogenic to humans (benzo[a]pyrene), Group 2A – probably carcinogenic to humans (cyclopenta[cd]pyrene, dibenz[a,h]anthracene and dibenzo[a,l]pyren); and Group 2B – possible human carcinogens (benz[j]aceanthrylene, benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[c]phenanthrene, chrysene, dibenzo[a,h]pyrene, dibenzo[a,i]pyrene, indeno[1,2,3-cd]pyrene and 5-methylchrysene). The US Environmental Protection Agency (EPA) selected 16 priority PAHs as pollutants for regular environmental monitoring. Those are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene and dibenz[a,h]anthracene. These 16 PAHs are of high environmental concern because of their potential toxicity in humans and other organisms, their prevalence and persistence in the environment. The transformation of plastic waste into useful industrial input chemicals represents an essential approach in modern applied research. Understanding the mechanism(s) of chemical transformations is important for advancing the concept of circular economy and is crucial for environmental topics.

Pyrolysis, mostly an oxygen-free thermal decomposition process of materials, is one of the attractive technologies in how different types of waste materials (industrial and municipal plastics, hospital waste, biomass, plastics from e-waste etc.) can be utilized. The condition of pyrolysis and technological unit set-up affect the distribution of products into three main groups, which are gas, liquid (pyrolysis oil and pyrolysis wax) and solid (pyrolysis char) (Chen et al., 2015). Pyrolysis can convert waste into various products, which are considered alternative resources in the petroleum and chemical industries. In the case of pyrolysis of plastics, the most promising direction considered is the petrochemical use of the liquid product through its co-processing on a steam cracker and the production of virgin polymers (Kusenberget al., 2022). The pyrolysis process of plastics (polymers) is known to produce PAHs which can form a significant fraction of pyrolysis oil (Koo et al. 1991; Zhou et al., 2015; Kaminsky et al., 1980). PAHs yield mostly increases with higher pyrolysis temperature (Conesa et al., 2009; Williams et al., 1999; Williams and Williams, 1999; Zhou et al., 2016).

The significant routes of PAHs associated occupational exposure is through inhalation (briefing of air containing) and dermal contact. Two-to four-ring PAHs volatilize sufficiently and it makes them more readily available for inhalation intake in industrial processes involving the pyrolysis (Atkinson and Arey, 1994; Srogi, 2007). Therefore, detailed knowledge and understanding of the PAHs formation during pyrolysis and their content in pyrolysis products is essential to minimize the negative impact on human health and to control, prevent, or reduce the risk of environmental contamination. From the industrial point of view, the presence of PAHs in a steam cracker can also lead to processing complications caused by coke deposition and resulting blockages in the system (Towfighi et al., 2002).

In this article, we focus on the analysis of the concentration distribution of PAHs in pyrolysis products (wax and oil) formed during pyrolysis of different plastics such as PP, HDPE, LDPE, PVC, PS and their mixtures. The pyrolysis of plastics is done in a laboratory batch reactor in nitrogen atmosphere. The PAHs in the pyrolysis oil and wax are detected by GC-MS. PAHs quantification is used to determine the toxicity equivalency quantity TEQ(BaP) for each product. The risk assessment is assigned by using toxic equivalence factors TEF(BaP) (Nisbet, 1992). TEF(BaP) assessment allows the toxicity of a mixture of PAHs to be expressed as a single number representing the equivalent concentration of the most toxic or carcinogenic compounds. For the TEF(BaP), the benzo[a]pyrene is considered to be the most carcinogenic and toxic one and is classified with factor 1. Factor 0 is applied to all non-carcinogenic PAHs (Nisbet, 1992).

MATERIALS AND METHODS

Raw and reference materials

Raw polymers were obtained from Dow Europe GmbH (LDPE), ORLEN Unipetrol RPA s.r.o. (HDPE, PP), Synthos Kralupy a.s. (PS) and Spolana s.r.o (PVC), Czech Republic. LDPE, HDPE and PP were in the form of pellets. PVC and PS were in the form of fine powder and flakes. Polymers were studied separately and in a mixture (named 5P in this paper) of 35 wt.% LDPE, 20 wt.% HDPE, 25 wt.% PP, 10 wt.% PS, and 10 wt.% PVC. The mixture composition

corresponds approximately to the major components of municipal plastic waste in the EU (Vilanova and Eder, 2014). PET was not included in this study as well-established recycling technologies already exist (Achilias and Karayannidis, 2004). All pyrolysis products were stored in glass containers in a fridge at 5 °C.

Certified reference materials: Standard PAH mixture (Mix 1, EPA 610) was purchased from VWR international s.r.o, Czech Republic; internal standard anthracene d-10 from Sigma Aldrich s.r.o, Czech Republic. Anhydrous magnesium sulphate p.a., sodium chloride p.a. and sodium sulphate p.a. were obtained from Verkon s.r.o., Czech Republic and ethylacetate of HPLC grade from Chromservis s.r.o., Czech Republic.

Pyrolysis procedure

Pyrolysis was carried out in a laboratory-scale unit schematically shown in Fig. 1. A 2-l volume pyrolysis reactor is made from stainless steel cylinder (a length of 38 cm; and an inner dimension of 8 cm) placed in a lined resistively-heated furnace. Pyrolysis products leaving the reactor passed through a heated path into a 1st condenser, which served to separate the heaviest (wax) fraction at 200–300 °C. The next heated path directed to a 2nd condenser, where light liquid products were collected (oil). Non-condensed gases passed through three scrubbers containing 1 M NaOH solution for HCl removal, and continued to a Horiba Gas analyzer VA-5000 where CH₄, CO₂,

and CO were detected. The following settings and parameters were used for each pyrolysis experiment: batch weight of 300 g; temperature of 450 °C for PP, PVC, PS; 500 °C for HDPE, LDPE, 5P mixture; 700 °C 5P mixture; a heating rate of 10 °C min⁻¹; N₂ flow of 10 l hod⁻¹; and a pyrolysis time of 4 h. After the placement of polymers or the mixture into the reactor, a pressure test was done, and the entire system was purged with N₂ at a flow rate of 60 l hod⁻¹ for 1 hour before initiating the pyrolysis. Pyrolysis products were subsequently collected from the different parts of the pyrolysis unit, i.e., char from part A, wax from the condenser B, liquid from the condenser C, and the outlet gas from part D in Figure 1.

Sample preparation and PAHs analysis

Sample pretreatment and preparation – pyrolysis oil

Liquid-liquid extraction was used to neutralize the acidity of the samples. Extraction was applied mostly to samples that originated from PVC as hydrochloric acid is formed during pyrolysis. A 1 ml of pyrolysis oil with 10 µl IS anthracene d-10 (200 mg·l⁻¹) was mixed with 1 ml of deionized water (3 ml of H₂O was used for PVC). The mixture was shaken well and centrifuged. The organic top phase was transferred to a vial and a drying agent anhydrous sodium sulphate was used to remove the remaining water. For GC-MS analysis, the organic phase was diluted with ethylacetate.

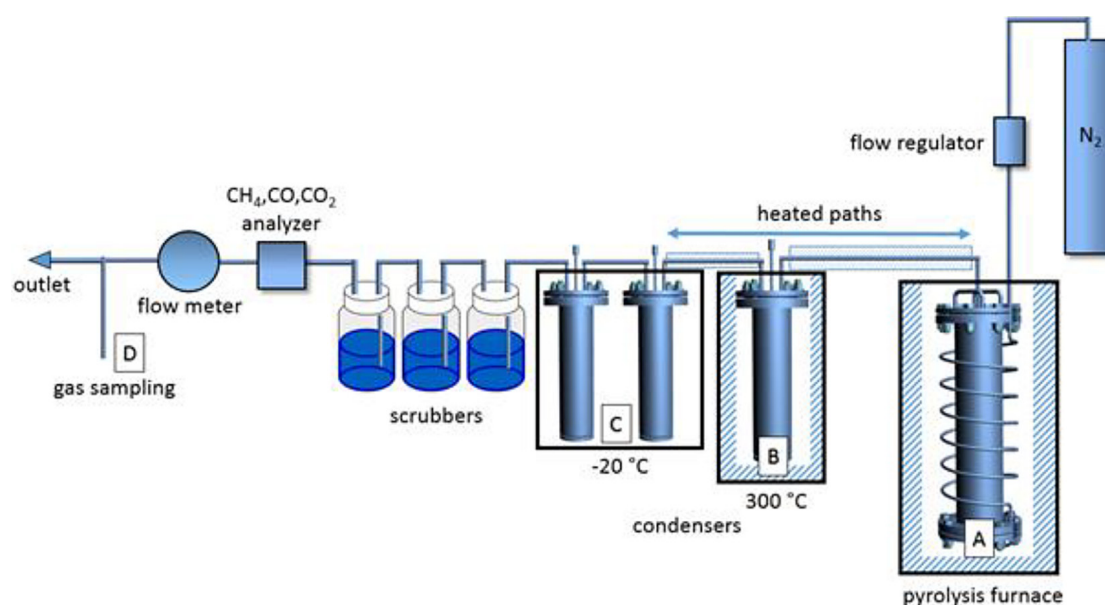


Figure 1. Schematic showing different parts of the laboratory-scale pyrolysis setup used in the experiments

Sample pretreatment and preparation – pyrolysis wax

Dispersive solid phase extraction was done for the quantitation of PAHs. A sample (wax) mass of 1 g with 50 µl IS anthracene d-10 (200 mg·l⁻¹) was weighted into a PP centrifuge tube with 10 ml of ethylacetate and 10 ml of deionized water. The mixture was vortexed. Then 4 g of magnesium sulphate and 1 g of sodium chloride were added and shaken in a vortex mixer. To enhance solvent extraction and for a better disruption, a MiniGTM 1600 SPEX®SamplePrep was used (two ceramic grinding cylinders were added to the sample mixture before MiniG application). Afterwards, the sample was centrifuged and 1.5 ml of the supernatant was transferred to the extraction and clean-up QuEChERS tubes. An aliquot of the supernatant was transferred to a vial for GC-MS analysis. The blank preparation followed the same steps except for the sample (wax) addition.

GC-MS setup

The GC-MS analyses were done on a system consisting of a gas chromatograph Bruker 456-GC, an ion source Apollo II with atmospheric pressure chemical ionization and a mass spectrometer Bruker Compact Q-TOF. GC configuration was the following: An autosampler Combi PAL, split/splitless injector heated to 300 °C set to split 1:50. Column ZB-5 HT (5% phenyl, 95% dimethylpolysiloxane) 30 m long with inner diameter of 0.25 mm and film thickness of 0.25 µm was held at 35 °C for 5 min followed by ramping at 3 °C min⁻¹ up to 300 °C, where it was held for 30 minutes. A sample volume of 1 µl was injected followed by washes with multiple polar/nonpolar solvents to avoid crosscontamination. Helium was used as the carrier gas with a constant flow of 1.4 ml min⁻¹. The temperature of the ion source and transferline was 250 °C and 300 °C, respectively.

Quantitative analysis of PAHs in pyrolysis oil

PAH calibration standards (MIX 1, EPA 610, VWR s.r.o.) were prepared by diluting PAHs in ethylacetate. Anthracene d-10 was chosen as internal standard. The peak area was calculated from the extracted ion chromatogram. Qualitative analysis was done by comparing retention times of chromatographic peaks of PAHs standards with those in the sample under identical

conditions of analysis and on the molecular ion for each compound (cation radical or protonated molecule). Quantification was achieved by using a linear calibration plot with isotopically labelled internal standard of anthracene. All compounds demonstrated linearity in the range of 0.03–10 mg·l⁻¹ with a regression coefficient ≥ 0.998 . LOD (limit of detection) and LOQ (limit of quantification) for each PAH are listed in Table 1. Combined standard uncertainty for each PAHs was calculated from the relative standard deviation of 7 measurements of standards with low and high concentrations. A combined standard uncertainty multiplied by 2 (estimated uncertainty of 95% confidence) was lower than 15% for each PAH. The correlations and variance of concentrations within the measured PAHs were performed for pyrolysis oil and pyrolysis wax by principal component analysis (PCA). Statistical evaluation was calculated and projected in script software R, version 4.0.0.

Quantitative analysis of PAHs in pyrolysis wax

The GC-MS method used for the quantitation of PAHs in pyrolysis oil was also applied to the determination of PAHs in pyrolysis wax. PAHs had to be extracted from the wax product, therefore, the spike recovery of the procedure was evaluated for each compound. The recovery calculated as the difference between spiked wax and

Table 1. Limit of detection (LOD) and limit of quantification (LOQ) for individual PAHs

PAH	LOD (mg·l ⁻¹)	LOQ (mg·l ⁻¹)
Acenaphthene	0.009	0.030
Acenaphthylene	0.006	0.020
Anthracene	0.009	0.029
Benzo[a]anthracene	0.014	0.048
Benzo[a]pyrene	0.010	0.034
Benzo[b]fluoranthene	0.010	0.032
Benzo[g,h,i]perylene	0.011	0.037
Benzo[k]fluoranthene	0.011	0.037
Chrysene	0.008	0.028
Dibenz[a,h]anthracene	0.003	0.010
Phenanthrene	0.008	0.026
Fluoranthene	0.006	0.019
Fluorene	0.007	0.023
Indeno[1,2,3-c,d]pyrene	0.009	0.030
Naphthalene	0.017	0.057
Pyrene	0.007	0.023

wax ranged between 81% for indeno[1,2,3-cd]pyren up to 144% for benzo[a]pyrene.

Risk assessment approach for PAHs

The evaluation of PAHs risk assessment follows the concept presented by Nisbet et al., 1992. Toxicological properties of a group of chemicals with similar properties can be expressed with potency equivalency factors similar to the toxic factors used for dioxin-like compounds (Agency for Toxic Substances and Disease Registry, 2022). In the calculation of risk assessment for PAHs according to toxicity equivalency factors, the benzo[a]pyrene (BaP) is used as the surrogate compound classified with TEF(BaP) equal to 1. It means the compound has the highest toxic (carcinogenic) potency whereas 0 marks noncarcinogenic PAHs. The total equivalency quantity related to benzo[a]pyrene (TEQBaP) is then calculated as the sum of TEF(BaP) multiplied by individual PAHs concentrations as shown in Eq. 1. The value of TEF(BaP) for individual PAH was used as suggested in literature (Nisbet et al., 1992), where 1 is for benzo[a]pyrene and dibenz[a,h]anthracene, 0.1 for benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-c,d]pyrene, 0.01 for anthracene, benzo[g,h,i]perylene, chrysene, 0.001 for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene. Concept of toxic equivalency quantity calculation by using the toxic equivalent factor was also used for other pyrolysis products (Hu et al., 2020; Che et al., 2019; Zhang et al., 2021).

$$TEQ(BaP) = \sum_{i=1}^k c_i \cdot TEF(BaP) \quad (1)$$

where: TEQ(BaP) – the toxicity equivalency quantity related to benzo[a]pyrene; c_i – the concentration of an i^{th} compound;

$TEF(BaP)_i$ – a toxic equivalency factor related to benzo[a]pyrene of an i^{th} compound; and k – the number of compounds in TEQ(BaP) calculation.

RESULT AND DISCUSSION

Process yields

The distribution of gas, oil, wax and char in the pyrolysis products is shown in Table 2. Most of the yielded material could be detected in the form of oil except for PVC where the composed substances were in the gaseous phase and char, which agrees with early published data (Williams and Williams, 1997; Scott et al., 1990). The highest yield of pyrolysis oil was observed for PS. The amount of the released gas was higher for the 5P mixture pyrolyzed at 700 °C compared to 500 °C. This corresponds well with the literature describing increasing amounts of gases and decreasing oil yields with increasing temperature (Li et al., 1999; Scheirs and Kaminsky, 2006; Hernández et al., 2007).

PAHs in pyrolysis oil

The variance of PAHs concentrations in pyrolysis oil shows the relative similarity of investigated material groups and it is presented in Fig. 2a. In the case of pyrolysis oil, the certain specification can be observed for groups PS, PVC; and HDPE, 5P (700 °C), LDPE and independently PP. The overall data groups can be described as noticeable heterogenous. The content of PAHs in the pyrolysis oil is shown in Table 3 (the concentration is expressed as milligrams of PAHs per liter of the oil). The highest concentration was found in PVC, where the total sum of all PAHs was 22 470

Table 2 The basic parameters of the pyrolysis procedure along the distribution of yielded material (mass of 300 g; a heating rate of 10 °C min⁻¹; N₂ flow rate of 10 l⁻¹; and pyrolysis time of 4 h)

Input material	Temperature (°C)	Condensation temperature (°C)	Product distribution (wt. %)			
			Oil	Wax	Char	Gas
PVC	450	300, -10, -10	8.5	8.3	16.6	66.6
PP	450	300, -10, -10	67.9	20.9	2.6	8.6
PS	450	300, -10, -10	87.9	10.0	0.1	2.0
HDPE	500	300, -10, -10	45.7	41.4	0.0	12.9
LDPE	500	300, -10, -10	49.6	38.9	0.3	11.2
5P 500 °C	500	300, -10, -10	55.1	20.8	2.1	22.0
5P 700 °C	700	200, -10, -10	48.9	2.3	1.7	47.1

Table 3. Concentration of individual PAHs in pyrolysis oil in mg·l⁻¹

PAH	PVC	PP	PS	HDPE	LDPE	5P (500 °C)	5P (700 °C)
Acenaphthene	1300	9.0	0.42	13	20	27	65
Acenaphthylene	1.0	0.26	0.17	3.6	6.4	4.4	92
Anthracene	430	13	12	0.99	4.5	25	74
Benzo[a]anthracene	85	20	0.65	0.25	4.0	10	29
Benzo[a]pyrene	12	16	0.33	< LOQ	3.0	2.7	12
Benzo[b]fluoranthene	8.5	6.7	0.25	< LOQ	1.2	1.3	5.5
Benzo[g,h,i]perylene	3.6	6.2	< LOQ	< LOQ	2.2	1.4	5.7
Benzo[k]fluoranthene	9.6	8.1	< LOQ	< LOQ	1.3	1.3	6.2
Chrysene	220	30	0.29	0.34	5.0	17	35
Dibenz[a,h]anthracene	3.8	5.6	< LOQ	< LOQ	0.99	0.71	3.6
Phenanthrene	2300	17	24	3.6	17.0	99	230
Fluoranthene	110	7.9	4.5	0.71	2.9	8.2	23
Fluorene	2900	25	20	9.2	20	81	210
Indeno[1,2,3-c,d]pyrene	1.8	3.9	< LOQ	< LOQ	1.4	0.59	3.7
Naphthalene	15000	63	170	58	92	570	1700
Pyrene	85	9.5	0.82	0.64	3.6	9.5	34.2
SUM	22470.3	241.2	233.4	90.3	185.5	859.1	2 528.7

mg·l⁻¹, whereas the lowest concentration was in HDPE (90 mg·l⁻¹). The total concentrations of selected PAHs in the investigated groups of plastic decreased as follows: PVC > 5P (700 °C) > 5P (500 °C) > PP > PS > LDPE > HDPE. Low-containing-aromatic-rings PAHs, meaning two or three benzene rings (mostly naphthalene, phenanthrene, fluorene and acenaphthene), were the most abundant group for each pyrolysis oil. The highest concentration for each PAH corresponded to the presence of naphthalene (maximum value of 15 000 mg·l⁻¹ in PVC). This agrees with the findings by Zhou et al., 2015, who reported similar major compounds in PS and PVC pyrolysis oil.

Looking in detail at the 5P plastic mixture, the concentration of PAHs increased with increasing pyrolysis temperature. There was also an increase in all individual PAHs with higher temperature. The total sum of all PAHs increased from 859 mg·l⁻¹ (5P 500 °C) to 2529 mg·l⁻¹ (5P 700 °C), which is in good agreement with early published data for plastics (Williams and Williams, 2010; Onwudili et al., 2009). The concentration of individual PAHs was used to calculate the total equivalency quantity related to benzo[a]pyrene TEQ(BaP) as shown in Eq. 1. For the pyrolysis oil, the concentration used for the calculation was expressed in mg·l⁻¹. TEQ(BaP) value of PAHs calculation for pyrolysis oil in mg·l⁻¹ was 54.5 (PVC) > 26.1 (PP) > 23.5 (5P, 700 °C)

> 6.0 (5P, 500 °C) > 5.1 (LDPE) > 0.8 (PS) > 0.1 (HDPE). The TEQ(BaP) in case of plastic mixture 5P increased with temperature from 6.0 mg·l⁻¹ (5P, 500 °C) to 23.9 mg·l⁻¹ (5P, 700 °C). Benzo[a]pyrene contributed most to TEQ(BaP) calculation in almost all pyrolysis oils with the value 16 mg·l⁻¹ for PP, which gave 61% contribution, 12 mg·l⁻¹ 5P (700 °C) 51%, 3.0 mg·l⁻¹ LDPE 59 %, 2.7 mg·l⁻¹ 5P (500 °C) 44% and 0.33 mg·l⁻¹ PS 38%. In pyrolysis oil from PVC, naphthalene is the highest contributor (15 mg·l⁻¹, 28%) followed by benzo[a]pyrene (12 mg·l⁻¹, 22%).

PAHs in pyrolysis wax

Similarly, as in the case of the pyrolysis oils, the content of PAHs in pyrolysis waxes was non-uniformly distributed among the investigated types of plastic materials (Fig. 2b). The similarity can be described within the groups PP, PS; and LDPE, 5P (500 °C), 5P (700 °C) on a lower scale. The overall data groups can be described as noticeable heterogeneous. The concentrations of PAHs for pyrolysis wax are presented in Table 4 (the concentration is expressed as milligrams of PAH per kilogram of the wax). The highest total sum of PAHs was observed for PVC (15481 mg·kg⁻¹) and the lowest for HDPE (12 mg·kg⁻¹). The sum of concentrations among the selected groups of waxes from plastics decreased as

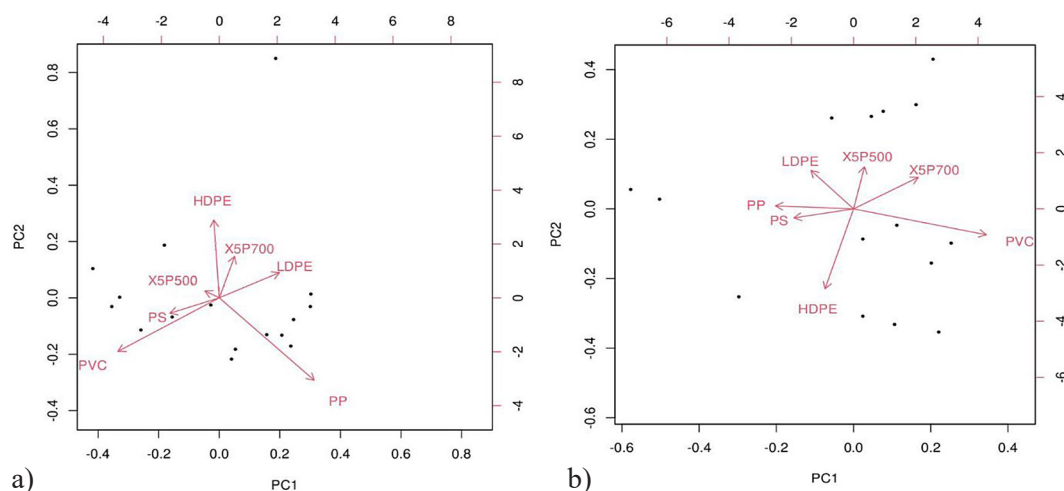


Figure 2. Results of a principal component analysis (PCA) based on clr-transformed data of PAHs concentrations in (a) pyrolysis oil and (b) pyrolysis wax loading values of the respective similar groups of elements. PP – polypropylene; PVC – polyvinylchloride; PS – polystyrene; LDPE – low-density polyethylene; HDPE – high-density polyethylene; X5P500 – mixed plastics 5P pyrolyzed at 500 °C; X5P700 – mixed plastics 5P pyrolyzed at 700 °C

Table 4. Concentration of individual PAHs in pyrolysis wax in $\text{mg}\cdot\text{kg}^{-1}$

PAH	PVC	PP	PS	HDPE	LDPE	5P (500 °C)	5P (700 °C)
Acenaphthene	52	< LOQ	< LOQ	< LOQ	0.58	< LOQ	2.7
Acenaphthylene	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	6.1
Anthracene	2500	1.5	3.0	< LOQ	1.6	6.1	35
Benzo[a]anthracene	1700	1.7	2.0	< LOQ	3.3	51	160
Benzo[a]pyrene	760	2.5	1.8	1.4	4.3	62	160
Benzo[b]fluoranthene and benzo[k]fluoranthene	790	2.1	2.9	< LOQ	6.9	38	130
Benzo[g,h,i]perylene	300	5.0	1.0	5.1	4.9	62	97
Chrysene	2200	2.2	8.4	< LOQ	3.5	67	210
Dibenz[a,h]anthracene	250	2.6	1.5	< LOQ	1.7	17	48
Phenanthrene	3600	3.4	34	< LOQ	6.2	18	120
Fluoranthene	1300	1.4	6.1	0.80	8.0	11	56
Fluorene	360	1.2	3.1	< LOQ	1.1	2.2	15
Indeno[1,2,3-c,d]pyrene	160	2.2	< LOQ	1.8	2.5	24	65
Naphthalene	9.3	3.5	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
Pyrene	1500	2.7	< LOQ	3.0	17	36	160
SUM	15 481.3	32.0	63.8	12.1	61.6	394.3	1264.8

follows: $\text{PVC} > 5\text{P} (700\text{ °C}) > 5\text{P} (500\text{ °C}) > \text{PS} > \text{LDPE} > \text{PP} > \text{HDPE}$. The highest concentration of the individual PAH was found for phenanthrene $3600\text{ mg}\cdot\text{kg}^{-1}$ in wax from PVC. Higher numbered ring PAHs (means 4 and more) were mostly formed in waxes from PP, HDPE, LDPE, 5P (500 °C) and 5P (700 °C). In pyrolysis wax from PVC, the group of low and higher-numbered ring PAHs was almost equal and in pyrolysis wax from PS, low-numbered rings PAHs

dominated. As in pyrolysis oils, the concentration of individual PAHs for 5P increased with increasing pyrolysis temperature. The total sum of all PAHs for 5P increased from $394\text{ mg}\cdot\text{kg}^{-1}$ (500 °C) to $1265\text{ mg}\cdot\text{kg}^{-1}$ (700 °C).

TEQ(BaP) was calculated as shown in Eq. 1 by using the concentrations in $\text{mg}\cdot\text{kg}^{-1}$. According to TEQ(BaP), the most toxic pyrolysis wax started with 1331.8 (PVC) > 247.3 (5P, 700 °C) > 91.7 (5P, 500 °C) > 7.4 (LDPE) > 5.8

(PP) > 4.0 (PS) > 1.6 (HDPE). Comparing all pyrolysis waxes the benzo[a]pyrene is the highest contributor to toxicity with contribution 760 mg·kg⁻¹ and followed by dibenz[a,h]anthracene (250 mg·kg⁻¹) in PVC. Overall benzo[a]pyrene was a compound with the highest attribution in TEQ(BaP) calculation in all individual pyrolysis waxes i.e. 760 mg·kg⁻¹ PVC, which gave 57% contribution, 160 mg·kg⁻¹ 5P (700 °C) with 65%, 62 mg·kg⁻¹ 5P (500 °C) with 68%, 4.3 mg·kg⁻¹ LDPE 58%, 2.5 mg·kg⁻¹ PP 43%, 1.8 mg·kg⁻¹ PS 45%, 1.4 mg·kg⁻¹ HDPE 88%. The TEQ(BaP) in the case of plastic mixture 5P increased with temperature from 91.7 mg·kg⁻¹ (5P, 500 °C) to 247.3 mg·kg⁻¹ (5P, 700 °C).¹

CONCLUSIONS

Pyrolysis of plastics is a constantly evolving technology sector that enables recycling of waste plastics for the production of raw polymers. However, the negative impact on human health and biotic parts of ecosystems must be considered; since the pyrolysis of plastics brings out numerous results of PAHs contents including carcinogenic benzo[a]pyrene in pyrolysis products.

Among all analyzed samples of pyrolysis oils, the highest contents of PAHs were detected for naphthalene, phenanthrene and fluorene. The concentrations of naphthalene reached more than half of total PAHs content in all groups except of pyrolysis oil from PP. In the pyrolysis wax the highest concentrations were observed for anthracene; chrysene; phenanthrene and fluoranthene, especially within the wax from PVC. High amount of benzo[a]pyrene was occurred in pyrolysis wax from model 5P mixture and PVC.

Taking the toxicity factors in account and calculating the toxicity equivalency quantity, TEQ(BaP), the highest toxic oil from the group of investigated pyrolysis oils was from PVC (54.5 mg·l⁻¹) and the lowest is from HDPE (0.1 mg·l⁻¹). Benzo[a]pyrene contributed most to TEQ(BaP) in all pyrolysis oils except for PVC, where the naphthalene was the major one not only in concentration but also in TEQ(BaP) contribution. From the pyrolysis waxes, the highest TEQ(BaP) value occurred in wax from PVC (1331.8 mg·kg⁻¹) and the lowest (1.6 mg·kg⁻¹) from HDPE. Benzo[a]pyrene was a compound with the highest contribution in TEQ(BaP) calculation in all pyrolysis waxes.

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