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Comparison of Carbonaceous Compounds Emission from the Co-Combustion of Coal and Waste in Boilers Used in Residential Heating in Poland, Central Europe

Marianna Czaplicka, Justyna Klyta *, Bogusław Komosiński, Tomasz Konieczny and Katarzyna Janoszka

Institute of Environmental Engineering Polish Academy of Science, 34 M. Sklodowskiej-Curie St,
41-819 Zabrze, Poland; marianna.czaplicka@ipispan.edu.pl (M.C.); boguslaw.komosinski@ipispan.edu.pl (B.K.);
tomasz.konieczny@ipispan.edu.pl (T.K.); katarzyna.janoszka@ipispan.edu.pl (K.J.)
* Correspondence: justyna.klyta@ipispan.edu.pl; Tel.: +48-32-271-64-81 (ext. 111)

Abstract: In this study, the effect of the addition of waste on the emissions from coal co-combustion was investigated. Coal was co-combusted with different additions of medium-density fiberboard and polyethylene terephthalate plastic (10 and 50%), in a low-power boiler (18 W). Polycyclic aromatic hydrocarbons, phenols, alkylphenols, phthalates, and biomass burning markers emissions were determined. Gas chromatography, coupled with a mass spectrometry detector, was used to analyze these compounds in particulate matter and gas phase, after extraction and derivatization. The emissions of polycyclic aromatic hydrocarbons were the highest among all the compounds determined. The total emission of these compounds was 215.1 mg/kg for coal, and 637.7 and 948.3 mg/kg for a 10 and 50% additive of polyethylene terephthalate plastic, respectively. For the 10 and 50% additive of medium-density fiberboard, the total emission was 474.2 and 464.0 mg/kg, respectively. The 50% addition of PET also had the highest emissions of phenols (638.5 mg/kg), alkylphenols (246.5 mg/kg), and phthalates (18.1 mg/kg), except for biomass burning markers, where the emissions were the highest for the 50% addition of medium-density fiberboard (541.3 mg/kg). In our opinion, the obtained results are insufficient for the identification of source apportionment from household heating.

Keywords: household heating; co-combustion; coal with waste; polycyclic aromatic hydrocarbons; levoglucosan; alkylphenols; phenols; phthalates

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1. Introduction

Sustainable development requires a clean, safe and sufficient energy supply. Nevertheless, in many regions of the world (e.g., China, Czech Republic, Poland, and Turkey), domestic combustion in coal stoves is a popular heating method [1–3]. Coal, biomass, or fuel mixtures are most often used as fuel in coal stoves and coal-fired power plants [4–6]. Unfortunately, the co-combustion of coal with waste materials, such as plastics and waste tires, is also observed in coal stoves and coal-fired power plants [7,8].

Atmospheric aerosol generated by the combustion of various fuels in stoves reduce visibility, absorb and disperse solar radiation, influence the formation of cloud nuclei, and affect human health [9]. The type of fuel as well as the types of boiler used affect emissions, old-type boilers emit more harmful and dangerous compounds than modern-type and pellet burners [10]. In addition to the type of boiler and fuels, emissions are affected by the combustion condition, the condition of the chimney, the maintenance and quality of the boiler, and the user operator [11,12].

In the combustion processes of solid fuels or their mixtures, significant amounts of organic compounds, such as volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), phenols, and aliphatic compounds are emitted to the atmosphere as a result of incomplete combustion [13–17]. PAHs can naturally occur in coal and coal combustion fly ashes [18–20]. An increase in the emission of pollutants, including organic pollutants, to the atmosphere, is observed in the case of the co-combustion of coal with waste materials such as plastics, biomass processing waste, or waste tires. Yee et al. [21] and Yu et al. [22] indicated that phenols and their derivatives that are emitted from combustion processes are involved in the formation of secondary organic aerosol (SOA), due to the reaction of phenols in the excited state and carbonyl and/or hydroxyl radicals.

Phenols and their derivatives are mainly formed during the thermolysis of macromolecules containing an oxygen atom in their structure, at 600–800 °C. Previous studies have indicated that phenols can be formed by the reaction of phenolic radicals with free H radicals, or by breaking the aryl ether bonds present in fuels during combustion (Figure 1) [23–25].

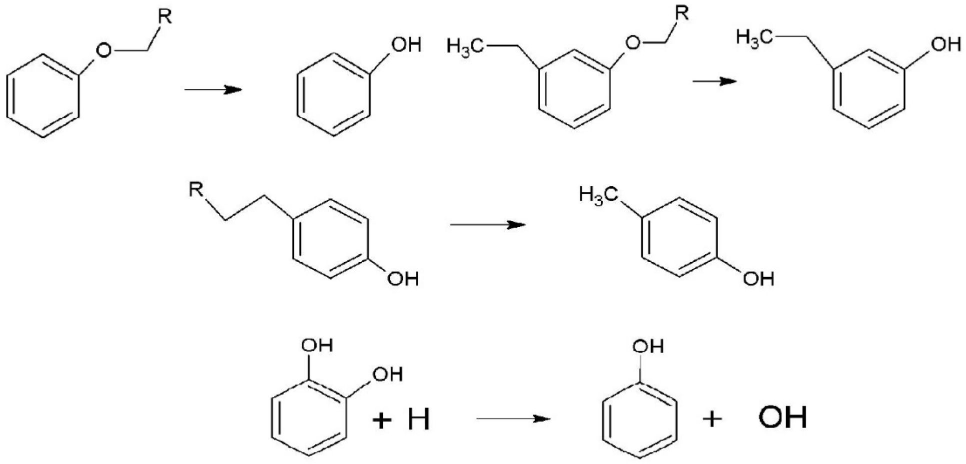


Figure 1. Formation mechanism of phenols [26].

The thermolysis of plastics produces alkylphenols, such as nonylphenols, bisphenol, and octafenols, among others. These compounds are characterized by high water solubility, low vapor pressure, and a low Henry's law, so they have been determined in both the solid and gas phases [23,26]. Alkylphenols may be harmful to humans and wildlife, through estrogenic effects on their health [27]. Studies of carbon thermolysis processes have shown that one group of compounds formed in these processes are phthalates [28]. Since phthalates have low solubility in water, and low volatility, these compounds have only been determined in the particulate phase. Phthalates are produced on a large scale, mainly as plasticizers in resins and polymers, and are used in toys, food packaging, personal care products, pharmaceuticals, paints, and varnishes. Phthalates can have a negative impact on human health, by affecting the endocrine and immune systems. These compounds are suspected of increasing the incidence of asthma and allergies. Phthalates are not physically bound to polymers, thus they can be easily released from plastics and leach into the environment [29,30]. It is known that coal and biomass combustion processes emit thermolysis products of cellulose, hemicellulose, and lignin, present in fuels such as levoglucosan, mannosan, and galactosan [31–33]. These compounds are mainly formed in the temperature range from 400 °C to 600 °C. The mechanism of their formation has been described in detail by Zhang et al. [33]. PAHs are formed during the incomplete combustion of fossil fuels (petroleum, natural gas, and coal) at high temperatures, and from burning vegetation. Some PAHs are believed to be carcinogenic and/or mutagenic, therefore they are more investigated than any other organic class [34].

Organic compounds can occur in both the gaseous and particulate phases, and the partitioning between the phases is influenced by the residence time of the combustion gases in the combustor, the dilution factor of the flue gases, and the vapor pressure of the organic substances, among other factors. In many publications, emission factors (EF) of numerous pollutants have been reported for various fuels, under specific combustion conditions [35–38].

Polyethylene terephthalate plastic (PET) is the third most widely used polymer in Europe, after polyethylene (PE) and low-density polyethylene (LDPE). PET is used to produce synthetic fibers in the textile industry, and for food beverages (for bottle manufacturing), electronics, automotive parts, houseware, sheets, and films [39]. The world plastic production in 2017 was 348 million tons, of which European production accounted for 19%, and PET bottles have become common in everyday life [40]. PET is mainly composed of carbon, hydrogen, and oxygen, and has an energy value that is similar to that of coal (the heating value of PET is 21.81 MJ/kg compared to that of domestic heating coal (28 MJ/kg)), so it may be an ideal candidate as an additive for combustion and for improving the utilization of low-rank coal [41–44]. Tomsej et al. [45] mentioned that, during the heating season, there is a decrease of 15–25% in municipal waste collection from villages and suburbs in the Czech Republic, and there are no accurate data on the percentage of plastic combustion in households. Medium-density fiberboard (MDF) is a type of composite wood product made of wood chips and particles, combined with binders and other resins, hardened into sheets. MDF is mainly used for furniture, construction, packaging, and flooring [46,47]. MDF from furniture production, such as sawdust and offcuts, can be incinerated in boilers. The incineration of these products can result in the emission of harmful compounds, such as phenols and their derivatives, ketones, aldehydes, carboxylic acids, and their esters, dibenzodioxins, and dibenzofurans, amines, and other organic compounds [48].

The co-combustion of waste, such as plastic material in domestic boilers, is not only a problem in Poland, but also in the Czech Republic, Lithuania, Hungary, Romania, and other countries of Central and Eastern Europe [45,49,50], and in South American countries, for example, Chile [51]. Therefore, it is important to know the composition of the emissions of the organic compounds, from the point of a view of the environment, human health, and information campaigns about the harmfulness of such combustion.

The aim of this study was to present the effect of the addition of medium-density fiberboard (MDF) and polyethylene terephthalate (PET) plastic on the emission of PAHs, phenols, alkylphenols, phthalates, and selected monosaccharides, under conditions of co-firing with coal in a household furnace. The study was conducted at 10% and 50% PET and MDF, by weight of the mixtures burned.

2. Materials and Methods

2.1. Experimental Section

The tests were conducted on a test stand equipped with an 18 kW boiler with 85% efficiency, a self-contained fuel feeder, an air heater installation for heat recovery, with flue gas and dust sampling points and a control and measuring apparatus system. The control and measurement system consisted of the following: controllers for controlling and monitoring the combustion process, an Itron CF 55 boiler heat capacity meter, an Emiotest gravimetric dust meter, dust aspiration probes with internal filtration, an S-type downpipe with an Emiotest 2598 recorder. The boiler specifications are shown in Table 1. Due to the type of fuel used for the study, especially the waste PET and MDF pellets added to the fuel, these mixtures were combusted on a fixed grate positioned above the feed hopper grate.

Dust from the exhaust was separated on Whatman Grade QMA quartz filters with a diameter of 50 mm. The mass of the extracted dust was determined by weighing the filter with a microbalance before and after measurement.

Table 1. Boiler specifications.

Parameter	Unit	Value
Boiler output	kW	18
Boiler heating surface	m^2	1.7
Efficiency	%	85–85.9
Average steady-state performance	h	48
Maximum water temperature	°C	95
Maximum operating pressure	MPa	0.1
Required minimum flue gas draught	Pa	16
Tank capacity	m^3	0.16

2.2. Fuel Characteristics

The bituminous (eco-pea) coal used in the experiment came from the Kazimierz Juliusz mine. Proximate, ultimate and moisture analysis were analyzed according to the European standard methods as follows: ISO 1171:2010: solid mineral fuels—determination of ash; ISO 609:2010: solid mineral fuels—determination of carbon and hydrogen—high-temperature combustion method; ISO 334:2013: solid mineral fuels—determination of total sulfur; and the Eschka method: ISO/FDIS 1928: solid mineral fuels—determination of gross calorific value. The results obtained are shown in Table 2.

Table 2. Chemical and technical analysis of coal and co-combustion materials in the dry state.

Assay	Content/Assigned Value		
	Coal	MDF	PET
	(% weight (% *w*/*w*))		
Ash	3.95	0.97	14.56
Carbon	78.39	51.42	60.11
Hydrogen	4.19	6.12	8.02
Sulphur	0.60	<0.03	0.14
Oxygen (different)	16,82	42.43	31.72
	(J/g (MJ/kg))		
Combustion heat	30.41	19.25	25.57
Calorific value	29.51	17.92	23.85

2.3. Sample Collection

The samples of particulate matter were collected on 50 mm Whatman Grade QMA quartz filters using an Emiotest dust meter in accordance with PZ-Z-2-04030-07:1994. The air flow rate was 1 m^3, and the sample collection time was 20 min. The gas-phase samples were collected in three scrubbers using an aspirator ASP3II in accordance with the accredited proprietary test procedure. First and second scrubber were contained 100 mL of absorbing solution (deionized water). For analysis the absorbing solutions were combined.

2.4. Determination of Particulate Organic Compounds in the Gas and Solid Phase

The concentrations of the PAHs, (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene), biomass burning markers (levoglucosan, mannosan and galactosan), selected esters of phthalic acids (dimethyl phthalate, diethyl phthalate, dibuthyl phthalate, butyl benzyl phthalate, di-(2-ethylhexyl) phthalate, di-n-octyl phthalate) and selected alkylphenols as markers of the thermal degradation of plastics (4-tert-octylphenol, 4-nonylphenol, bisphenol A) were extracted from the dust and determined. The concentration of the PAHs, phenols, (phenol, o-cresol, p-cresol and m-cresol) and selected alkylphenols was determined in the gas phase. The conditions of the sample preparation and GC-MS analysis of the selected compounds were set according to the methods described by Janoszka et al. [52] for biomass burning markers, as well as according to the methods of Czaplicka et al. [53] for the PAHs, Czaplicka and Kaczmarczyk [54] for the phenols, Jaworek and Czaplicka [55] for the esters of phthalic acid, and Li et al. [56] for the selected alkylphenols. The samples testing procedures are presented in Figure 2.

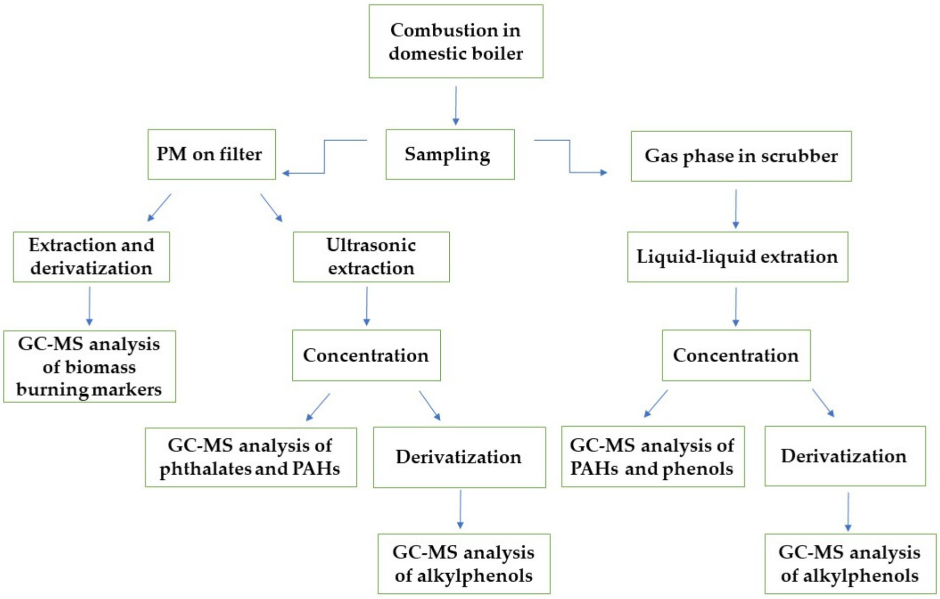


Figure 2. Samples testing procedure.

The limit of detection (LOD) was in the range 0.005–0.02 µg/mL for PAHs, 0.04–0.06 µg/mL for phenols, 0.003–0.02 µg/mL for alkylphenols, 0.01–0.05 µg/mL for phthalates and 0.002–0.004 µg/mL for biomass burning markers. The limit of quantification was in the range 0.015–0.06 µg/mL for PAHs, 0.12–0.18 µg/mL for phenols, 0.009–0.06 µg/mL for alkylphenols, 0.03–0.15 µg/mL for phthalates and 0.006–0.012 µg/mL for biomass burning markers. The precision expressed as a relative standard deviation was equal to 13% for PAHs, 14% for phenols, 11% for alkylphenols, 17% for phthalates and 19% for biomass burning markers.

3. Results

Significant variation in the physicochemical properties of the combusted mixtures resulted in the significant differences in the emissions of the determined groups of organic compounds. Due to technical reasons, GC-MS analyses were not performed for the combustion of PET and MDF alone.

3.1. Phenols

The emissions of phenols from coal co-combustion with wastes were in the range of 257.1 to 638.5 mg/h (Table 3). As expected, the highest emissions were obtained for the combustion with a 50% addition of PET, while the lowest emissions were for the combustion with a 50% addition of MDF. Among the phenols, the highest emission had phenols in the range of 99.9 to 351.5 mg/h.

Table 3. Emission factors of phenols (mg/h).

Compound	Coal	Coal + 10% PET	Coal + 50% PET	Coal + 10% MDF	Coal + 50% MDF
phenol	150.5	158.6	351.5	101.6	99.9
o-cresol	77.2	79.9	104.6	52.1	51.2
p,m-cresol	172.1	172.2	182.4	107.8	106.0
total	399.8	410.8	638.5	261.5	257.1

3.2. Alkylphenols

The emissions of alkylphenols to the solid phase were in the range of 1.5 to 10.6 m/h for coal combustion with the additives tested, and for the gas phase, they were in the range of 4.0 to 235.9 mg/h (Table 4). The highest alkylphenol emissions were obtained in the gas phase for the co-combustion with the 50% PET additive. Bisphenol A had the highest emission among all the determined alkylphenols, and was in the range of 0.69 to 10.1 mg/h for the PM phase and 1.1 to 234.8 mg/h for the gas phase.

Table 4. Alkylphenol emission factors (mg/h).

Compound	Coal + 10% PET		Coal + 50% PET		Coal + 50% MDF		Coal + 10% MDF	
	PM	Gas Phase	PM	Gas Phase	PM	Gas Phase	PM	Gas Phase
4-tOP	0.38	0.14	0.30	0.61	0.28	2.9	0.16	2.2
4-nNP	0.13	0.30	0.21	0.48	0.54	1.2	0.35	0.72
BPA	9.5	21.1	10.1	234.8	0.69	3.2	0.97	1.1
total	10.0	21.5	10.6	235.9	1.5	7.3	1.5	4.0
Grand total		31.5		246.5		8.8		5.5

4-tOP: 4-tertoctylphenol; 4-nNP: 4-nonylphenol; BPA: bisphenol A.

3.3. Phthalates

The results show that the phthalate emission factors vary from 2.23 mg/h to 18.14 mg/h, depending on the mixture combustion composition. Coal combustion had the lowest phthalate emission factors. The addition of 10% PET to the feedstock resulted in a twofold increase in the rate of this group of compounds, while the highest emission of 18.14 mg/h was found for the 50% addition. For the addition of the MDF panels, the phthalate emission factors were higher compared to those obtained when burning coal, but lower compared to the results obtained when burning the PET coal mixture, and they were 3.28 mg/h and 5.32 mg/h for the 10% and 50% MDF addition, respectively (Table 5).

Table 5. Phthalates emission factors (mg/h).

Compound	Coal	Coal + 10% PET	Coal + 50% PET	Coal + 10% MDF	Coal + 50% MDF
DMP	0.76	0.66	2.21	0.96	0.98
DEP	<0.05	<0.05	0.10	0.10	<0.05
DBP	0.25	0.22	4.5	0.44	0.52
BBP	0.23	<0.05	<0.05	1.4	3.0
DEHA	<0.05	0.15	<0.05	<0.05	<0.05
DEHP	0.78	4.9	9.4	0.15	0.22
DOP	0.19	0.50	2.0	0.28	0.64
total	2.2	6.4	18.1	3.3	5.4

DMP: dimethyl phthalate; DEP: diethyl phthalate; DBP: dibutyl phthalate; BBP: butyl benzyl phthalate; DEHA: bis-(2-ethylhexyl) adipate; DEHP: di-(2-ethylhexyl) phthalate; DOP: di-n-octyl phthalate.

3.4. Biomass Combustion Markers

During coal combustion, the emission factor of the determined monosaccharides was 4.4 mg/h (Table 6), the addition of plastics resulted in higher emissions of these compounds, compared to sole coal combustion. During coal co-combustion with 10% PET addition, the emission factor increased two-fold and was 9.6 mg/h.

Table 6. Biomass burning markers emission factors (mg/h).

Compound	Coal	Coal + 10% PET	Coal + 50% PET	Coal + 10% MDF	Coal + 50% MDF
levoglucosan	2.6	6.2	10.3	191.8	514.8
mannosan	1.3	2.4	6.0	8.3	24.1
galactosan	0.57	1.0	2.6	1.8	2.4
total	4.4	9.6	18.9	201.9	541.3
LG/MN	2.1	2.6	1.7	23.0	21.4
LG/(MN+GA)	1.4	1.9	1.2	18.9	19.5

LG: levoglucosan; MN: mannosan; GA: galactosan.

In comparison, the 50% addition of PET resulted in about a four-fold increase in emissions, to 19 mg/h, compared to coal combustion. An even greater increase in the emission factor was observed for the MDF additive. The emission factor of monosaccharides was 202 mg/h for 10% and 541 mg/h for 50% MDF addition, respectively.

3.5. Polycyclic Aromatic Hydrocarbons

The results obtained show significant variation in PAHs emissions, depending on the mixture burned. The emission factors for 17 PAHs are shown in Table 7. The total emission factors for PAHs ranged from 215.1 mg/h to 948.3 mg/h, depending on the fuel used. The highest emission factors were found for burning coal with a 50% addition of PET. The lowest emission factors were found for burning coal only. The total emission factors for burning coal with a 10% and 50% addition of MDF were at a similar level (474.2 and 464.0 mg/h), and lower than for burning coal with PET (937.7 and 948.3 mg/h).

Table 7. PAHs emission factors (mg/h).

Compound	Coal		Coal + 10% PET		Coal + 50% PET		Coal +10% MDF		Coal +50% MDF	
	PM	Gas	PM	Gas	PM	Gas	PM	Gas	PM	Gas
naphthalene	0.40	3.7	1.9	19.7	1.7	117.4	0.19	43.8	0.63	44.1
acenaphthylene	0.49	7.8	0.75	31.7	1.1	123.1	0.10	52.3	0.17	34.8
acenaphthene	0.07	0.49	0.42	4.2	0.39	5.3	0.08	9.3	0.24	11.8
fluorene	0.48	1.9	1.6	8.0	5.0	17.3	0.43	34.8	2.6	21.0
phenanthrene	5.4	5.2	9.4	27.2	100.4	56.9	0.73	67.0	3.8	60.4
anthracene	3.2	1.2	8.2	8.3	60.6	34.8	0.86	42.9	1.5	58.8
fluoranthene	24.6	0.39	53.3	3.4	70.6	4.6	11.0	5.9	4.8	8.6
pyrene	24.7	0.36	77.5	3.4	97.9	4.9	17.3	5.7	8.3	8.8
benzo(a)anthracene	22.7		85.1		52.5		35.5		30.3	
chrysene	18.0		63.8		31.3		26.1		24.5	
benzo(b)fluoranthene	23.3		60.2		31,7		34.8		42.0	
benzo(k)fluoranthene	11.7		25.2		21.3		16.4		17.2	
benzo(a)pyrene	19.4		49.0		45.1		27.1		32.0	
indeno(1,2,3-c,d)pyrene	19.1		42.2		22.1		20.9		23.0	
dibenzo(a,h)anthracene	3.7		9.1		6.7		1.9		3.7	
benzo(g,h,i)perylene	6.9		25.6		19.5		8.7		11.0	
benzo(j)fluoranthene	10.0		18.6		16.3		10.5		10.2	
total	194.1	21.0	531.7	106.0	584.0	364.3	212.5	261.7	215.8	248.2
grand total		215.1		637.7		948.3		474.2		464.0

The combustion of coal with the PET additive was characterized by higher emissions of PAHs to the solid phase (531.7 and 584.0 mg/h) than to the gas phase (106.0 and 364.3 mg/h).

4. Discussion

4.1. Phenols

The results obtained show that the emission factor of phenols during coal combustion was 400 mg/h, and was similar to the results obtained by Kong et al. [26], during the pyrolysis of bituminous coals. The addition of 10% PET to the combusted mixture resulted in a slight increase in the emissions of this group of compounds, while the 50% PET addition increased phenol emissions to 638 mg/h.

The high emission rate of phenolic compounds during the combustion of coal, with 50% PET, is most likely related to the much higher content of oxygen-containing structures in the coal with the PET mixture, compared to coal only. On the other hand, the combustion of the coal mixture with the MDF additive was characterized by an emission factor of 260 mg/h, independent of the proportion of this additive in the mixture. The results indicate that the addition of MDF waste to coal, at 10% and 50%, caused a reduction in the emissions of this group of compounds compared to coal combustion. This phenomenon can be explained by the different combustion kinetics of coal-only use and its mixing with biomass. Gil et al. [57] indicate that the coal combustion process consists of one stage at 315–615 °C, while for biomass and coal/biomass mixtures, the process consists of two or three independent stages, respectively. Furthermore, Gil et al. [57] point out that the chemical reactions determine the combustion process in the first stage, while diffusion mechanisms are more important in the second stage.

Independent of the combustion conditions, phenol was the dominant compound in this group in all cases, accounting for between 38% and 50% of the phenols determined, depending on the fuel combusted. Figure 3 shows the percentage contribution of individual phenols to total phenol emissions. Except for coal combustion with 50% PET addition, the share of phenol in the determined group of compounds was 38–39%. The addition of 50% PET resulted in an increase in the proportion of phenols to 55%.

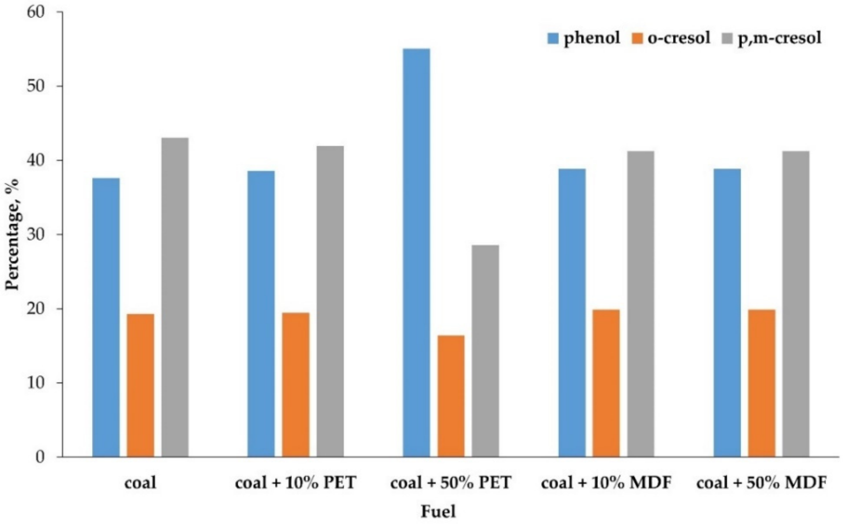


Figure 3. Percentage of individual phenols in total emission of phenols.

4.2. Alkylphenols

The obtained results indicate that the emission factors of the determined alkylphenols, in the case of the combustion of the mixture of coal and MDF panels, were 5.4 mg/h for the 10% addition of MDF and 8.8 mg/h for the 50% addition of this waste, respectively (Table 4). However, in the combustion process with the PET addition, the emission factors of this group of compounds were much higher, and amounted to 31.5 and 246 mg/h for the 10% and 50% addition of this waste, respectively.

It should be noted that, due to the low vapor pressure of these compounds, the gas phase was the dominant phase in all cases. For coal combustion with 10% PET addition, 68% of the alkylphenols were present in the gas phase, while the proportion of compounds in the gas phase increased to 95% with a 50% addition of this waste (Figure 4). A different relationship was found for the combustion of a mixture of coal and MDF. A total of 82% and 72% of the determined alkylphenols were found in the gas phase, depending on the addition of 10% and 50% MDF, respectively. Bisphenol A was the dominant alkylphenol in the combustion of the coal–waste mixture. The share of bisphenol A in the group of compounds determined varied in a range up to 68%, depending on the mixture combusted.

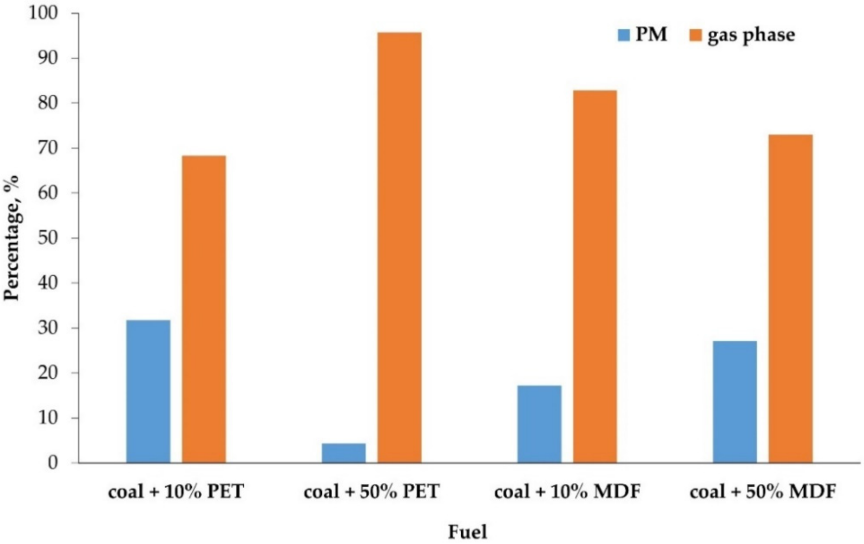


Figure 4. Percentage distribution of alkylphenols across the studied phases.

Similar results for alkylphenols were obtained by Salapasidou et al. [58], where nonylphenol and bisphenol A had the highest emissions of all the tested alkylphenols.

4.3. Phthalates

The results also indicate that the composition of the determined phthalates varies depending on the fuel combusted. During the combustion of coal mixtures with PET additives, the predominant phthalate was di(2-ethylhexyl) phthalate (DEHP), which accounted for 34% of the determined group of compounds for coal combustion, 76% for the 10% PET additive, and 51% for coal with 50% PET (Figure 5). The second phthalate, with the second highest emissions, was DBP (DEHP > DBP > DMP > DOP). Similar results for phthalates were obtained by Růžočková et al. [29], for particulate matter in the heating season (DEHP > DBP > DINP > DEP), and Ma et al. [59] also reported phthalates in particulate matter from China (DEHP > DIBP > DBP). In turn, Salapasidou et al. [58] obtained the phthalate emission profile of DEHP > DBP > BBP in PM_{10} samples in Greece. This prevalence of DEHP concentration may be due to its common use as a plasticizer, therefore it could be considered as a marker of plastic co-combustion in domestic boilers. In contrast, when coal was combusted with the addition of MDF panels, the highest emissions in this group of compounds were found for butyl benzyl phthalate (BBP), which were 41 and 55% for the 10 and 50% MDF addition, respectively. The highest concentration of BBP in the PM samples from domestic garbage combustion was obtained by Li et al. [60]. Of note, in this study, the authors did not report what the component of the domestic garbage was. The phthalate concentration profile was BBP > DNOP > DEP. BBP is used as a plasticizer in PVC products, e.g., as a laminate for MDF [61]. The highest emissions of this compound may come from these products, therefore it could be considered as a marker for the co-combustion of waste in household boilers.

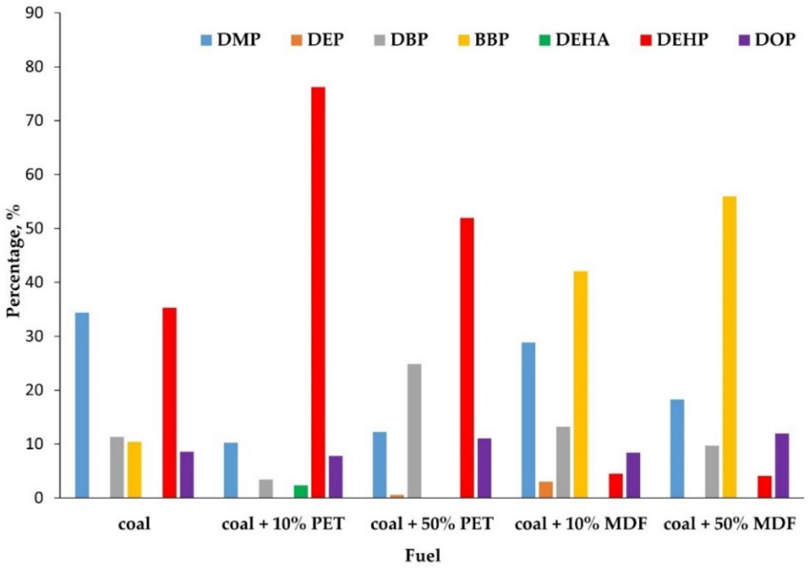


Figure 5. Percentage of individual phthalates in total emission of phthalates.

4.4. Biomass Combustion Markers

In all the presented cases, levoglucosan was the dominant monosaccharide, but its share in the determined compounds varied depending on the fuel combusted. During coal combustion, it accounted for 58% of the determined compounds, while, in the case of mixtures with a PET additive, its share ranged from 65% at 10% of the additive to 54% at 50% of the additive. In contrast, 95% of levoglucosan was found in the case of coal and MDF co-combustion (Figure 6).

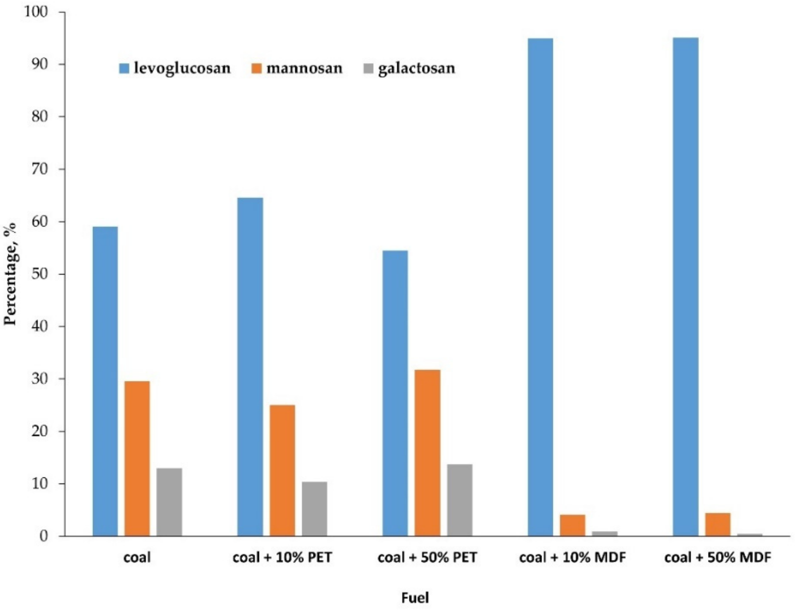


Figure 6. Percentage of individual monosaccharides in total emission of monosaccharides.

MDF is mainly composed of cellulose and lignin, and its combustion leads to the formation of significant amounts of formaldehyde, carboxylic acids, and monosaccharides [62].

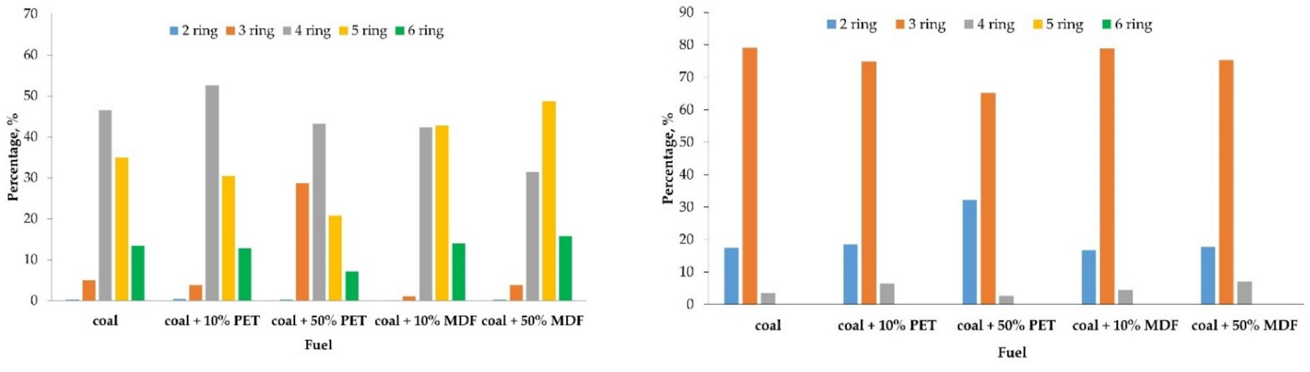
Many authors use the relationships between different monosaccharides as indicators to identify emission sources [63–65]. Most commonly, the ratio of levoglucosan to mannosan (LG/MN), and levoglucosan to the sum of mannosan and galactosan (LG/(MN+GA)), is determined for this purpose. The results of the presented studies showed that in the case of coal combustion, LG/MN was 2.1, while in the case of coal combustion with a PET addition, it ranged from 1.7 (50% PET addition) to 2.6 (10% PET addition). A significant increase in this ratio was found when burning coal with the MDF additive; the LG/MN ratio, in this case, ranged from 21 to 23, depending on the proportion of MDF (for 50 and 10%, respectively) fraction, and was 10 times higher compared to the combustion of coal. Nevertheless, the LG/(MN+GA) relation in the case of coal was 1.4, and was at a similar level to the values obtained in the case of the combustion of a coal/PET mixture. Therefore, significantly higher values for this ratio were found for the combustion of coal/MDF mixtures, which were at the level of 19.

4.5. Polycyclic Aromatic Hydrocarbons

The combustion of plastic emits PAHs [45], which was confirmed by the results of this study, in which the highest emissions were obtained for the 50% addition of PET. The difference in the emissions of the individual PAHs, with between a 10% and 50% addition of PET, may be due to the different combustion conditions. The particulate emissions from the co-combustion of coal with a 50% addition of PET were dominated by more-volatile phenanthrene, anthracene, fluoranthene, and pyrene, which may indicate a lower flue gas temperature than for the 10% addition of PET. A similar relationship was obtained by Tomsej et al. [45], for the combustion of PET with wood, which may indicate the formation mechanism of these compounds during PET combustion. An increase in the emissions of eight lighter PAHS (from 106.0 to 364.3 mg/h), with a decrease in the emissions of semi- and non-volatile PAHs (from 230.0 to 162.6 mg/h), may indicate a higher temperature during coal co-combustion with a 50% addition of PET than for a 10% addition [66].

A completely different relation was observed for the combustion of coal with the MDF additive, where the emission to the gas phase was slightly higher than to the PM phase. These emissions consisted of eight lighter PAHs (from naphthalene to pyrene). The combustion conditions must have favored the formation of more-volatile PAH, which may indicate a higher temperature during the combustion of coal with MDF than for that- with the PET additive.

The particulate emissions of the PAHs, from the combustion of coal with different additions, were composed mainly of four-ring PAH (31.4–52.6%) and five-ring PAH (20.7–48.7%). Whereas, the gas emissions of the PAHs were composed mainly of three-ring PAH (65.2–79.1%) (Figure 7). The co-combustion of coal with wastes resulted in the formation of the significantly more carcinogenic four–six-ring PAHs, which confirmed the harmfulness of these wastes for the environment and human health.



(**a**) (**b**)

Figure 7. Composition of PAH emissions in relation to ring numbers: (**a**) PM; (**b**) gas phase.

5. Conclusions

The emission factors of gaseous and particulate pollutants from the combustion of coal with different additions of PET and MDF, in a domestic boiler, were compared. The emission factors of organic compounds depend on the coal–waste mixture. The combustion of PET with coal is illegal in various countries; however, in some regions of the world, it still takes place, so it is essential to know the compounds emitted to the air during combustion in households. The co-combustion with 50% PET was characterized by the highest emissions of PAHs, phenols, alkylphenols, and phthalates among all the tested additives.

As PAHs are formed during the incomplete combustion of coal, the addition of waste can affect the combustion mechanism. This was shown by the increased PAHs emissions at 50% PET addition, compared to coal only and coal with 10% PET. The MDF additive increased the PAHs emissions relative to coal alone, but this effect was lower than for that with the PET additive. Given the material composition of MDF (mainly lignin and cellulose), an increase in the concentration of levoglucosan and its isomers, relative to coal and coal with PET, is obvious. The obtained results for the biomass burning markers correspond to the published data, in which levoglucosan is the dominant compound among the determined monosaccharides anhydride. Every class of organic compounds can be characterized by one compound that can be found in a predominant concentration in flue gasses, as follows: among phenols: phenol; alkylphenols: bisphenol A; biomass burning markers: levoglucosan; phthalates for PET: DEHP, for MDF: BBP.

Despite the limitations of the conducted research, such as burning in one type of stove, and the lack of various combustion conditions (different operators, different mixtures, different temperatures), the obtained results allowed for the preliminary identification of combustion products. After further study, these compounds could be treated as markers for the identification of the combustion in households.

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