



Research article

Chemometric analysis of air pollutants in raw and thermally treated coals – Low-emission fuel for domestic applications, with a reduced negative impact on air quality

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ABSTRACT

The emission of pollutants into the air during the combustion of solid fuels in households is still a significant problem in many European Union countries, including Poland. These emissions are a significant source of many air pollutants formed during incomplete combustion and has been identified as one of the leading environmental risk factors for these populations. One of the solutions is to utilise thermally processed solid fuels. This article discusses the concentrations of pollutants emitted as a result of the combustion of conventional fuels and new low-emission fuel in out-of-class heaters. To gain better insight into the relationships between fuel type and flue gas quality, chemometric methods and variance analysis were used. Principal component analysis confirmed that the fuel type significantly influences the level of dust emissions and the total organic carbon and sum of polycyclic aromatic hydrocarbons in the dust. Clustering analysis identified how the concentrations of polycyclic aromatic hydrocarbons correlate with the amounts of dust and total organic carbon and showed that this correlation is proportional to the size of the molecule and consequently the number of aromatic rings. The use of low-emission fuel as a solid fuel in households, as our analyses have shown, can reduce the concentrations of dust, total organic carbon and polycyclic aromatic hydrocarbons by up to 50 times, thereby reducing air pollutants in cities.

1. Introduction

One of the serious problems in Poland is poor air quality, which contributes to lowering the standard of living and health problems of society. It is a consequence primarily of the so-called low emissions. According to the ranking by the European Environmental Protection Agency, of the top 10 cities with the worst air quality in Europe, four cities are in Bulgaria and six in Poland. "Low emissions" are generated mainly by the transport sector and in the heating season (late autumn, winter, early spring) by the individual heating sector, which is dominated by coal-fired heating devices. Hard coal itself is not a worse fuel than heated oil or gas. However, it is a more complex fuel, the combustion of which can be categorised as highly efficient with low emissions, but it requires the use of technologically advanced and thus expensive equipment. A temporary solution to this problem may be to create a fuel based on hard coal, the combustion of which will not cause visible, excessive emissions of pollutants even in the case of out-of-class boilers. These heating devices still constitute almost 80% of the heating

infrastructure in Poland and are characterised by manual fuel feeding and a counter-current combustion process. They are stoves and tiled stoves of almost unchanged construction for 200 years. Introduction of such fuel will result in an immediate improvement in the air quality and thus will allow for a time-consuming and costly process of replacing worn-out heating devices with new, low-emission combustion techniques.

Research on reducing harmful emissions resulting from the combustion of solid fuels in households has been widely conducted (Krümal et al., 2019) in China (Akhmetshin et al., 2020; Li et al., 2016, 2020; Sun et al., 2018; Wang et al., 2016; Yan et al., 2020) and other countries. There are three main directions of such research:

- application of smokeless fuels analogous to the LEF presented in this article (Das et al., 2019; Liu et al., 2018; Sumbane-Prinsloo et al., 2020; Tian et al., 2018);
- introduction of additives to fuels, usually in the form of liquid solutions (Junga et al., 2020; Yao et al., 2020);

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List of abbreviations

PAH	polycyclic aromatic hydrocarbon
VOC	volatile organic compound
PCA	principal component analysis
LEF	low-emission fuel
HC	hard coal
CM	coal mud
Bio	wood biomass
LEF	low-emission fuel

- application of newer generation ovens (Lai et al., 2019; Liu et al., 2018; Wang et al., 2016).

As a consequence of household solid fuel combustion, persistent organic pollutants (Kim Oanh et al., 2002; Liu et al., 2008) are produced, which consist of polycyclic aromatic hydrocarbons (PAHs) as well as polychlorinated derivatives of dibenzo-p-dioxins, di-benzofurans, and biphenyls. These are non-volatile organic compounds with proven harmful effects on human health. Large amounts of gaseous compounds are also released: volatile organic compounds (VOCs) and nitrogen, sulfur and carbon oxides. According to the PN-EN 303-5:2012 (BS EN 303-5:1999, 1999) standard, the classification of heater quality is based on measurements of dust, VOCs and carbon monoxide (CO). Measurements of persistent organic pollutants are no longer required since they correlate quite well with the dust concentration. This assumption, on which the mentioned standard is based, will be discussed in this article.

Both sampling and laboratory analysis of persistent organic pollutants are very time-consuming. The most important analytical techniques include high-performance liquid chromatography and gas chromatography (Guimarães et al., 2013; Helmig, 1999; ISO 11338, 2003; Peltonen and Kuljukka, 1995) which require a well-equipped laboratory. Therefore, despite their high toxicity and negative health effects, measurements of POPs are not required by the regulations on emission standards (Commission, 2000).

One of the objectives of the research and analyses presented in this article was to confirm that the emission reduction resulting from the utilisation of smokeless fuel obtained from the thermal conversion of hard coal is statistically significant. Another objective was to determine if other factors such as the low class of the heating devices that are used significantly affect the emissions provided that low-emission solid fuel is used. The last objective was to evaluate and describe the interrelationships existing between the examined variables.

As mentioned earlier, studies using thermally processed coals have already been carried out. However, most of them focused on the emission of gaseous compounds such as CO, CO₂, NO_x, SO₂, VOC and PM_{2.5}. The results presented in this study cover a much wider analytical range, broadening the above list of the examined analytes with the determination of 13 PAHs. In addition to this extension of the scope of analysis, the presented studies were performed for a larger number of emitters and a total of four different solid fuels, including: wood biomass (Bio), hard coal (HC), coal mud (CM) and low-emission fuel (LEF) obtained during the thermal conversion of hard coal, resulting in a low emission fuel. Finally, the presented research concerns 179 outdoor tests carried out under the real conditions in which furnaces and other heating devices powered by solid fuels are operated daily.

2. Materials and methods

2.1. Solid fuels

Four types of solid fuels were utilised in the research: hard coal (HC), coal mud (CM), wood biomass (Bio) and low-emission fuel (LEF). All

samples of solid fuels were analysed for their physicochemical properties using analytical methods standardised and accredited by the Polish Centre for Accreditation. The parameter ranges characterising the fuels are presented in Table 1. Low-emission fuel is produced on the basis of hard coal, which is coked at 800 °C. As a result of this process, volatile components are removed to a 10 times lower level than the input material.

2.2. Combustion tests

Combustion tests were conducted at five locations in Poland. In each of them, 4 to 10 apartments were selected, the owners of which agreed to conduct tests using their heating devices. The boilers used in the test were strongly exploited and required manual fuel filling. At least two measurement series varying in fuel were conducted for each boiler, with low-emission fuel tests carried out at all locations. In each series, three complete measurements of pollutants present in the flue gas were performed. Altogether, 179 experiments were conducted.

The tests focused on measurements of pollutants emitted into the air during the combustion of classical solid fuels (wood biomass, hard coal, coal mud) and low-emission fuel. The combustion tests were conducted during days with similar external temperatures, which guaranteed a similar heat demand and thus similar boiler operation characteristics. The boiler was under constant supervision of ICHPW staff. All tested boilers manually fed. At the beginning of the test, the boiler was fired up and brought to a steady state (appropriate layer of embers in the furnace). The sample was replenished once every hour by adding a fresh portion of fuel directly onto the ember layer. On-line measurements and

Table 1
Parameters of the utilised solid fuels.

Parameter	Unit	HC	MC	Bio	LEF	
Moisture content	W _r ^t	%	2.0 ÷	22.2 ÷	5.4 ÷	3.6 ÷
		wt/ wt	14.2	30.9	15.5	13.4
Ash content on a dry basis	A ^d	%	1.21 ÷	6.2 ÷	0.31 ÷	4.66
		wt/ wt	12.22	16.0	3.14	7.51
Volatile component content on a dry basis	V ^d	%	30.8 ÷	28.38	81.1 ÷	2.8 ÷
		wt/ wt	37.6	÷ 29.3	85.6	4.8
Volatile component content on a dry and ash-free basis	V ^{daf}	%	31.3 ÷	30.58	82.4 ÷	3.0 ÷
		wt/ wt	42.8	÷ 34.3	85.9	5.1
Higher heating value	Q _s ^d	MJ/ kg	28.2 ÷	29.1 ÷	19.3 ÷	29.2
			34.5	32.7	22.4	32.3
Lower heating value	Q _i ^d	MJ/ kg	27.13	28.1 ÷	17.9 ÷	28.9
			÷ 33.5	31.7	20.0	32.0
Total sulfur content on a dry basis	S _t ^d	%	0.19 ÷	0.39 ÷	0.021	0.31
		wt/ wt	1.56	0.46	÷ 0.042	0.43
Ash sulfur content on a dry basis	S _A ^d	%	0.043	0.10 ÷	0.020	0.24
		wt/ wt	÷ 0.383	0.31	÷	0.36
Flammable sulfur content on a dry basis	S _C ^d	%	0.01 ÷	0.14 ÷	0.020	0.00
		wt/ wt	1.37	0.33	÷	0.13
Carbon content on a dry basis	C _t ^d	%	70.5 ÷	73.0 ÷	49.2 ÷	86.3
		wt/ wt	85.8	82.6	55.0	90.3
Hydrogen content on a dry basis	H _t ^d	%	4.08 ÷	4.21 ÷	5.58 ÷	0.97
		wt/ wt	4.73	4.53	6.10	1.23
Nitrogen content on a dry basis	N ^d	%	1.08 ÷	1.09 ÷	0.14 ÷	1.35
		wt/ wt	1.51	1.22	2.39	1.56
Oxygen content on a dry basis	O _d ^d	%	6.14 ÷	4.93 ÷	38.6 ÷	2.51
		wt/ wt	12.59	7.80	43.7	4.05

sample collection for dust and PAH analyses were carried out during the stable boiler operation period, i.e., between successive fuel loads.

Flue gas samples for analysis were taken continuously at the measuring point located in the chimney. For this purpose, a system consisting of a heated probe with a ceramic filter, a heated pipe and a gas conditioning system were used. The exhaust gas sample for determining the concentration of dust and organic pollutants was collected by means of a system consisting of a probe connected to a heated dust separator, a cooler, a system of tubes containing XAD-2 resin and active coal and a gas aspirator.

2.3. Analytical methods

2.3.1. Oxides of carbon (CO, CO₂), nitrogen (NO_x) and sulfur (SO₂)

Flue gas samples were drawn directly from the smoke duct via the heated transfer line to ensure that no water condensation occurred. Analysis of CO, CO₂, NO and SO₂ was conducted with a mobile gas analysis system provided by Siemens. The system consists of ULTRA-MAT 23 (based on an IR detector) and Oxymat 61 (based on a paramagnetic sensor) analysers. The first analyser enables the measurement of four compounds: carbon monoxide (CO, range: 0.05 ÷ 5% v/v - by volume), carbon dioxide (CO₂, range: 0.25 ÷ 25% v/v - by volume), sulfur dioxide (SO₂, range: 10 ÷ 1000 ppmv - by volume) = 0.001 ÷ 0.1% v/v - by volume) and nitrogen monoxide (NO, range: 10–1000 ppmv - by volume). The second analyser is responsible for the analysis of O₂ concentrations in the range of 0.1–25% v/v - by volume.

2.3.2. Dust and PAHs

The sampling system consisted of a probe, heated particle filter, condenser and tubes with sorption material (XAD-2 resin and activated carbon). A sample of 60 Ndm³ was passed through the system at a flow rate of 2 Ndm³/min. The particle filter, condensate and sorption material were transferred to the laboratory for further analysis.

The particle filter was weighed and extracted with acetone and methylene chloride to remove tar. Sorption materials were combined and extracted with methylene chloride. The above extractions were carried out in an automatic extractor DIONEX AS1. The condensate was extracted manually with methylene chloride. All extracts were concentrated under reduced pressure to obtain 1 ml of solution. Then, the samples were analysed by gas chromatography to measure the amount of PAHs. Finally, solvents were completely removed, and the residual tar was weighed. The mass of dust was calculated as the difference between the filter mass increment and the appropriate mass of tar.

Gas chromatography: TRACE gas chromatograph (Thermo-Scientific) with a flame ionisation detector (FID) and capillary column with poly(5%/phenyl 95% methyl) siloxane stationary phase (Rxi-5 30 m × 0.25 mm × 0.25 μm). Carrier gas: helium at a constant flow rate of 1 ml/min. Temperature programme: 90 °C → 12°/min → 280 °C (25 min). Qualitative analysis: comparison with 18 PAH standard mixtures. Quantitative analysis: internal standard method with TFM and 9,10-DFA as references.

2.4. Chemometric methods

2.4.1. Cluster analysis (CA)

Cluster analysis (CA) is one of the most frequently used chemometric methods, apart from principal component analysis (PCA). It allows the separation of homogeneous subsets of objects in multidimensional data when there are no prerequisites to formulate a priori hypotheses, and it is a preliminary method in the search for correlations between the analysed data. The prerequisite for the analysis of multidimensional data is their standardisation, for example, with the standard normal variation (SNV) method. The method groups parameters (variables) and observations in terms of their mutual similarity or dissimilarity. A number of distance measures are calculated, assuming that the objects next to each other are similar. The most frequently used distance

measures are Chekhovian, Euclidean, Euclidean Square and Urban (Manhattan). Finally, the linkage criteria must be chosen to determine if two data sets are sufficiently similar to be combined into a cluster. Examples of clustering methods are single-linkage, complete-linkage, weighted average linkage and Ward's method. The final CA result can be visualised as a matrix of distances or a dendrogram.

2.4.2. Principal component analysis (PCA)

Principal component analysis (PCA) is a chemometric technique that, similar to CA, allows the study of relationships between variables in a multidimensional data space. These two techniques are frequently combined to achieve a better view of data correlations. Similar to CA, PCA requires that the input data be pre-standardised. This allows for the analysis of data sets whose components differ in terms of units, as is the case in the analysis of experimental data in environmental protection, material science, as well as in the analysis of solid fuels, biomass and methods of their processing. The purpose of this analysis, as the name suggests, is to extract the main components. Calculations are conducted iteratively. The first component represents the factors that have the greatest influence on the variability of experimental data. Subsequent components are calculated according to the orthogonality principle and describe relations unexplained by the previous components. Therefore, each subsequent component explains a smaller amount of variance of the analysed data set. PCA results are usually visualised as a three-dimensional plot where the main axis represents the three main components and data variances are shown as appropriate vectors.

2.4.3. Analysis of variance (ANOVA)

ANOVA is a statistical method that enables the study of mutual relationships between independent variables. Its purpose is to examine whether one of the examined variables has an impact on other measured variables. The general idea of the variance analysis is to compare the variability among a group of observations from each of the populations (SSB) and within the group (SSE). If the inter-group variation is large compared to the intra-group variation, the classifying variable has an impact on the test variable. A "large" variation is understood to be a value such that the test statistics will be in the rejection area.

The SSB and SSW can be calculated by the following equations:

$$SSB = n \sum_{i=1}^k \sum_{j=1}^n (\bar{x}_i - \bar{x})^2 = \frac{\sum (\sum x_{ij})^2}{n} - \frac{(\sum \sum x_{ij})^2}{kn}$$

$$SSW = \sum_{i=1}^k \sum_{j=1}^n (x_{ij} - \bar{x}_i)^2 = \left(\sum \sum x_{ij} \right)^2 - \frac{\sum (\sum x_{ij})^2}{n}$$

ANOVA uses the variance equality, whereby the total variation in test variable Y (SST) is the sum of the intergroup variation (SSB) caused by the classifying variable and the intragroup variation (SSE) caused by random factors. The test statistic is the following quotient of the variance:

$$F = \frac{SSB/(r-1)}{SSE/(n-r)}$$

where n is the total sample size and r is the number of classes for variable X.

The F statistic is the ratio of the total between-group variance to the within-group variance and is compared with critical values to prove the hypothesis of mutual dependency.

The above statistics have a distribution F with (r-1/n-r) degrees of freedom. The values of these statistics increase as the difference between the SSB and SSE increases. Therefore, if the SSB exceeds the critical value for the appropriate distribution F_{r-1/n-r}, the zero hypothesis must be rejected in favour of the alternative hypothesis. It can then be concluded (with an appropriate risk of error I type) that at least two averages in the groups differ, which in turn indicates an impact of the

classification variable X on the study variable Y.

Compared to other simpler methods of data analysis (e.g., Student's t-tests, non-parametric methods), ANOVA is not restricted to only two levels (groups); it also allows analysis of the simultaneous influence of several factors.

3. Results and discussion

A series of statistical analyses were conducted to study the relationship between the fuel type and the pollutants emitted during combustion. The first step in the investigation of mutual relationships between experimental data was to perform cluster analyses (CAs) based on the Euclidean distances. The data with the highest mutual similarity are characterised by the shortest distances, close to 0. The results are visualised in Fig. 1. The cluster analysis provided the opportunity to group the analysed data according to the fuel from which the exhaust gases were generated. In Fig. 1 (right), the groups of fuels used are shown as follows: LEF - low-emission fuel, HC - hard coal, Mix – hard coal and coal mud, Bio - biomass. The analysis showed that the examined parameters can be divided into three groups. The first (green) is a set of parameters defining the composition of exhaust gases: concentrations of carbon oxides (CO, CO₂), nitrogen oxide (NO) and sulfur dioxide (SO₂). The second group of parameters (blue), which show very strong similarity to each other, consists of dust, total organic carbon (TOC) and 13 PAHs with four or more condensed rings. Low-molecular-weight PAHs (two and three rings) form the third group (red). This group is characterised by the greatest homogeneity. The similarities of parameters within this group are in the range <-0.1; 0.3>.

Significantly increased concentrations of acenaphthene, phenanthrene, fluorene and acenaphthene were observed in several samples collected during hard coal and coal mud combustion (mixed group - first yellow group from the top). The maximum values of these compounds were 6420 ppm, 13,880 ppm, 5200 ppm and 5791 ppm for anthracene, phenanthrene, fluorene and acenaphthene, respectively. This group included several samples from biomass and low-emission fuel combustion (3 each for both types of fuel, Fig. 2). It can be assumed with a high

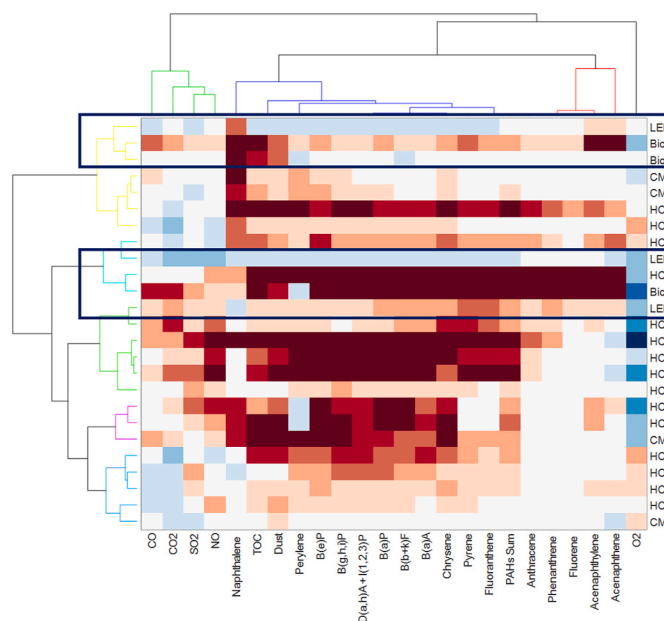


Fig. 2. Clustered heat map for the tested exhaust gas parameters (27 observations- Mix).

degree of certainty that the reason for the high concentrations of PAHs in the case of biomass and low-emission fuel combustion was the low-class heating devices. The high concentrations may also be associated with uncleaned chimneys, in which soot and tar may have been deposited. This assumption will be analysed in the future using ANOVA. The second and third most homogeneous groups are shown in blue and green (respectively LEF and LEF/Bio). Similarly, as in the previous case, the highest concentrations of the examined parameters (belonging to these groups) were observed for hard coal combustion and coal mud. However, as seen in Fig. 1, the vast majority of these groups consist of low-

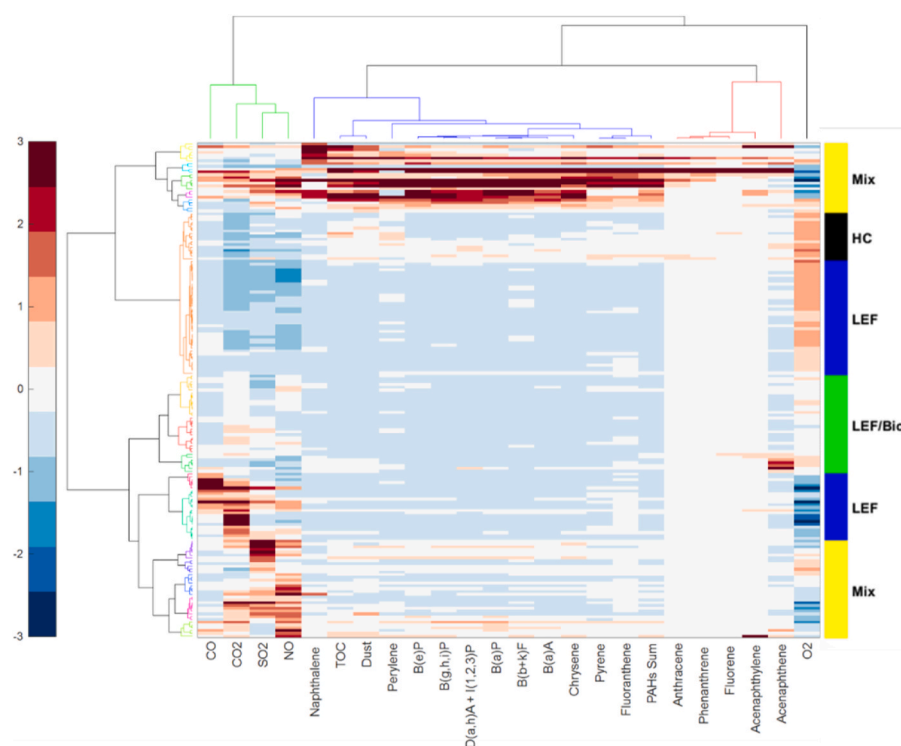


Fig. 1. Clustered heat map for the tested exhaust gas parameters (179 observations).

emission coal and biomass, whose combustion under the tested conditions emitted exhaust gasses with significantly lower concentrations of the tested compounds than hard coal and coal mud combustion (the darker the colour is, the higher the concentrations of the tested parameters).

Another group indicated by cluster analysis is the group described by the concentration of CO₂, CO, SO₂ and NO in the flue gas (green group). This group also splits the whole data set into two subgroups depending on the oxygen level in the exhaust gas. The first group is characterised by lower concentrations of PAHs and mentioned oxides in the flue gas stream with a high concentration of oxygen in the flue gas, i.e., approximately 15% on average. In the case of the second group, increases in the concentrations of CO₂, CO, SO₂ and NO and PAHs relative to those in the first group are observed, while the concentration of oxygen in the flue gas decreases to an average of 7%. Several factors may influence such a result, including the class and quality of the boiler, its design and the method of its expansion. This division is presented in more detail in Fig. 3.

Regardless of the amount of oxygen in the flue gas in the case of biomass and low-emission fuel, PAHs were significantly lower and more homogeneous than in the case of hard coal and coal mud combustion. To confirm the links between the variables, a major component analysis (PCA) was conducted. The analysis was extended with respect to the physicochemical properties of the utilised fuels. The obtained results are visualised in Fig. 4.

Three main components were identified. For each of the components, which are a linear combination of measured parameters, and for firers, three principal components are visualised as a separate axis in Fig. 4. The highest levels of significance in the first component (PC1) are related to the physicochemical properties of the examined fuels: volatile matter (V^{daf}, V^d), elemental composition (carbon C^{d_t}, sulfur S^{d_t}, nitrogen N^{d_t}, hydrogen H^{d_t}, oxygen O^{d_t}) and heating values (Q^{d_t}, Q^{d_s}). The well-known correlations of the heat value and other fuel properties can be observed: a positive correlation with the carbon content and negative correlations with hydrogen, oxygen and volatile matter. The first component divides the analysed experiments into three groups that correspond to the utilised fuel types. The highest PC1 values < 0,35 ÷ 0,5> correspond to data obtained from the combustion of wood biomass (Bio), medium values < 0,25 ÷ 0,05> characterise hard coal and coal mud (HC and CM), and the lowest values < 0,00 ÷ -0,1> correspond to low-emission fuel (LEF).

The second component (PC2) describes the exhaust gas composition. The well-known negative correlation between the concentrations of oxygen (O₂) and carbon oxides (CO, CO₂) can be observed. An important observation is the independence of these parameters from the type of fuel described by PC1.

The highest levels of significance obtained for the third component

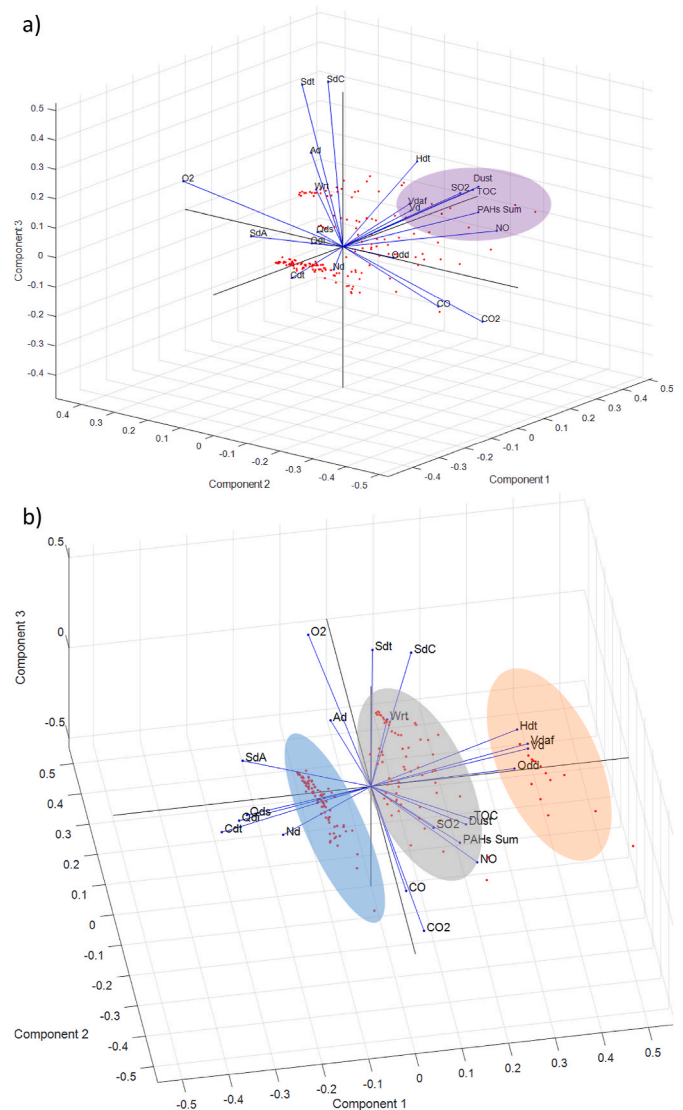


Fig. 4. Principal component analysis (PCA) plot of multivariate variation among 179 tests in terms of 41 measured variables.

(PC3) are the contents of sulfur (S^{d_t}, S^{d_c}) and ash (A^d) in fuel as well as the concentration of sulfur dioxide (SO₂) and, to a lesser extent, the concentration of nitrogen oxide (NO).

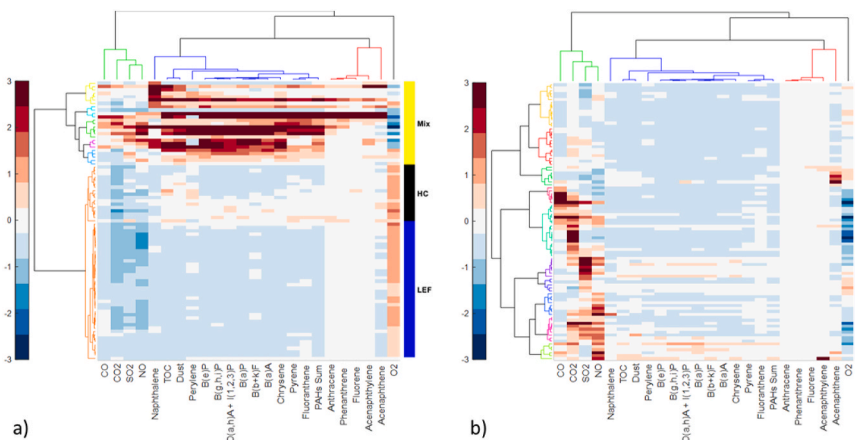


Fig. 3. Clustered heat map for the (a) group with 15% oxygen concentration and (b) group with 7% oxygen concentration in the exhaust gas.

Parameters that describe the emission of dust, TOC (total organic carbon) and sum of PAHs were positively correlated with PC1 and PC3 and negatively correlated with PC2. Moreover, all three parameters seem to be directly proportional to each other. To further investigate their mutual dependencies, a separate PCA was conducted (Fig. 5). The analysis included only parameters related to exhaust gas composition and a single parameter that describes fuel: volatile matter.

New components were identified. PC1 was observed to be dependent on the concentrations of PAHs with four and more condensed rings, dust and TOC. PC2 was described by oxygen and carbon oxide concentrations. PC3 was described by the concentration of low-molecular-weight PAHs, with the exception of naphthalene, whose vector separated from that of other organic compounds.

Based on the results of the principal component analysis and taking into account the variables with the greatest impact on the first and third main components, i.e., sum of PAHs (PC1) and total sulfur content (PC3), it was possible to identify the fuels that were significantly characterised by the lowest emissivity. Based on the results of the principal component analysis and taking into account the variables with the greatest impact on the first and third main components, i.e., sum of PAHs (PC1) and total sulfur content (PC3), it was possible to identify the fuels that were significantly characterised by the lowest emissivity. This group includes biomass, a small amount of hard coal and coal mud (only 2 samples) and 99% of the tested samples of smokeless fuel. Only in one case were higher emission results than in the other cases of using smokeless fuel obtained. This was because the exhaust gas sample was taken directly after switching the firing in a boiler to new smokeless fuel. Therefore, it can be assumed that this result was influenced by the pollutants remaining in the unclear chimney.

The CA and PCA provided convergent and complementary information about the mutual dependencies of the measured parameters. The most important are correlations between concentrations of dust, PAHs and TOC in exhaust gas and volatile matter present in the fuel. The high content of volatile components in the fuel increases the turbulence of the combustion process, which in turn increases the release of fine dust. The dust is also responsible for the high released amounts of low-molecular-weight hydrocarbons (TOC). PAHs, as low-volatile compounds, are easily adsorbed on the dust surface and are transported through the exhaust gas in this form, resulting in their positive correlation with the dust content, TOC and volatile component content.

To perform quantitative analysis, a correlation analysis was performed, and Pearson coefficients were determined. The results are

visualised in Fig. 6, and numerical values are presented in Table 2.

On the basis of the research conducted, it is clear that the utilisation of solid fuels previously subjected to the thermal conversion process (thermally processed) reduces the amount of pollutants emitted during their combustion. To determine these differences, two-factor variance analysis (2-way ANOVA) was conducted, which indicated the impact of the fuel used during combustion as well as the type of heating device. The analysis of variance indicated that the fuel itself had no statistically significant impact on the emission of CO₂ or CO, and the heating device in which the combustion process was carried out had an impact on CO₂ and CO emissions. These differences result from the amount of air supplied to the combustion chamber: an insufficient amount causes incomplete combustion of the fuel, thus contributing to the increase in emissions. The largest amount of oxygen in the flue gas, and thus the smallest amount of carbon monoxide in the examined flue gas, were characterised by samples collected during the combustion of solid fuels in tiled stoves and ovens. The quality of the fuel used for individual heating had a significant impact on the emission of sulfur oxides and nitrogen oxides, while the heating device itself in this case also had a statistically significant impact on the emission value. The lowest concentrations of these pollutants were recorded for the combustion of wood and smokeless fuel in tiled stoves and ovens.

Apart from fluorene, both the type of fuel and the type of heating device had a statistically significant impact on the values of the examined parameters. The lowest values of naphthene, acenaphthene, and anthracene were found for smokeless fuel and biomass, with values of 20.37 vs. 230.08 ppm, 38.18 vs. 90.03 ppm, and 23.19 vs. 49.43 ppm (smokeless fuel vs biomass), respectively. It should be mentioned that the concentrations of PAHs in the case of hard coal and coal mud combustion were approximately 10 times higher.

Fig. 7 presents a simple variance analysis that describes the differences between major air pollutants and the type of combusted fuel. The reduction in the concentrations of the main pollutants is clearly visible with the switch to low-emission fuel.

It is important to mention that the mechanism of PAH formation is different when burning coal-based fuels and when burning biomass (Han et al., 2020). In the case of biomass, aromatic hydrocarbons are produced in secondary reactions of gaseous products. This process is therefore strongly dependent on the residence time of the flue gases in the hot zone of the stove/boiler. In the case of coal-based fuels (hard coal, low-emission fuel, coal mud), aromatic hydrocarbons are formed as a result of the thermal cracking of the organic compounds that make

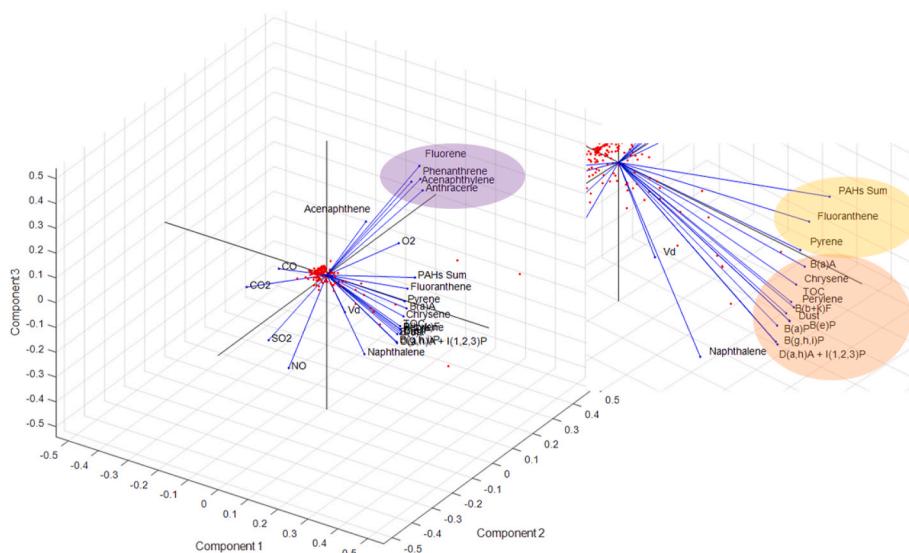


Fig. 5. Principal component analysis (PCA) plot of multivariate variation among 179 tests in terms of PAHs, dust, TOC, carbon and nitrogen oxides and volatile matter (V^d).

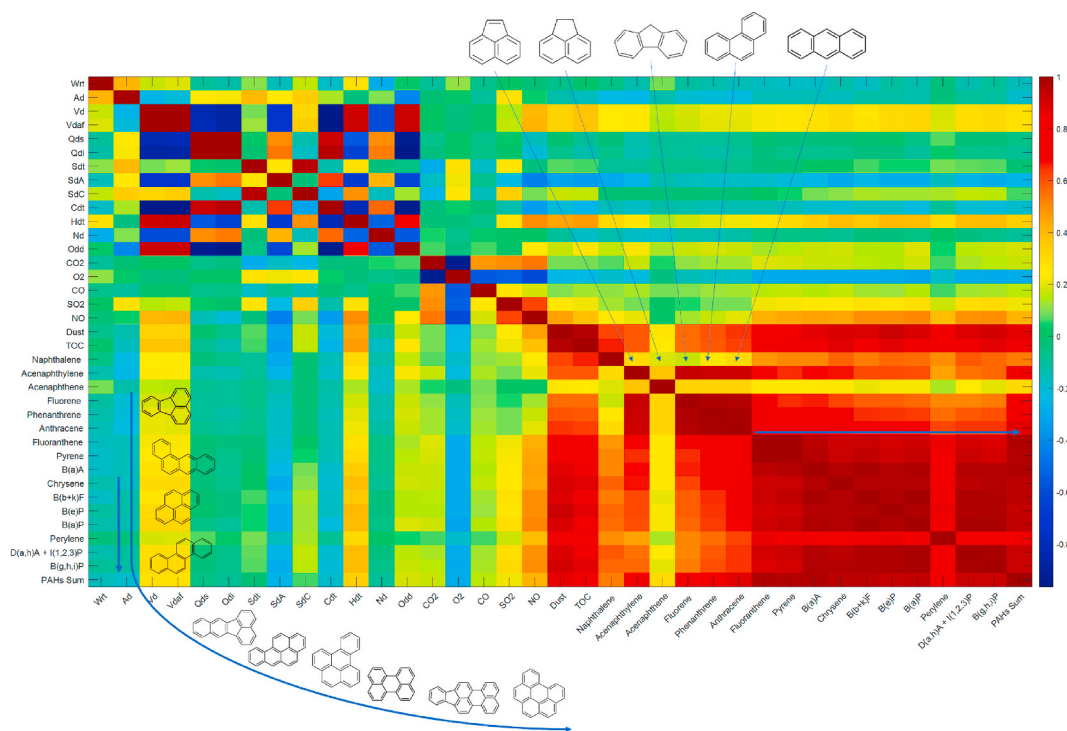


Fig. 6. Correlation heat map of all studied variables.

Table 2

Pearson coefficients for the most significant relationships between the variables.

Variable A	Variable B	Pearson coefficient
Dust	TOC	0,97
Dust	benzo(a)anthracene, chrysene, benzo(e)pyrene, benzo(a)pyrene, benzo(g,h,i)pyrene	0,80 ÷ 0,90
Dust	fluoranthene, pyrene, perylene, dibenzo(a,h)anthracene	0,80 ÷ 0,90
Dust	remaining PAHs	0,60 ÷ 0,80

up their structure, i.e., in the solid phase. Therefore, the thermal pre-treatment of hard coal makes it possible to remove the vast majority of PAHs in a controlled way, which in turn reduces PAH emissions during combustion.

4. Conclusions

As mentioned in the introduction, studies using thermally processed coals have already been carried out. The data available in the literature mainly focuses on the emission of gaseous compounds such as CO, CO₂, NO_x, SO₂, VOC and PM_{2.5}. The results presented in the present study cover a much more comprehensive analytical range. In addition to pollutants such as CO, CO₂, NO_x, SO₂, VOC and PM_{2.5}, the contents of the 13 PAHs were examined and compared in one comprehensive field study. Moreover, the presented research concerned four different solid fuels, wood biomass (Bio), hard coal (HC), coal mud (CM) and low-emission fuel (LEF) obtained in the process of the thermal conversion of hard coal, resulting in a low-emission fuel. As mentioned in the introduction of this article, the aim of the present paper was to confirm that the reduction in emissions resulting from the use of smokeless fuel obtained from the thermal conversion of hard coal is statistically significant. The present study clearly showed that the combustion of thermally processed fuel significantly decreased the emission of harmful substances. Regardless of the fuel being compared (Bio, HC, MC), the

concentration of contaminants from smokeless coal was reduced several times, and the composition of flue gases was much more homogeneous.

An interesting division of PAHs into two groups was observed: the first group consisted of two- and three-ring compounds, and the second group contained compounds with four or more condensed aromatic rings. The first group was characterised by a lower correlation with dust and VOC concentrations and weaker correlation with the content of volatile components in fuel (V^d). The concentrations of these compounds were therefore less dependent on both the turbulence of the combustion process and fuel type. This was a certain deviation from the dependence of tar substances on the amount of dust on which the PN-EN 303-5:2012 standard is based. Fortunately, compounds from this group are also characterised as low health hazards (Nisbet and LaGoy, 1992).

There was also virtually complete independence between the concentration of emitted pollutants and the amount of moisture contained in the fuel. Thus, there was no significant dust emission during the drying process of the fuel in the furnace. The temperature of the process was also too low to lead to the decomposition of organic compounds and the formation of VOCs and PAHs.

The results of analytical tests and the use of both statistical and chemometric methods confirmed the effectiveness of smokeless fuel to reduce PAH and dust emissions. Therefore, the use of solid fuels by individual users for heating purposes does not have to be the main source of low emissions, especially in winter. The use of cleaner coal technologies such as the production of solid smokeless fuels can be a transitional element on the way to decarbonisation, especially for regions where solid fuels are the main source of heat in households.

Authorship contributions

Maciej Chrusasik: Conception and design of study, acquisition of data, analysis and/or interpretation of data, Drafting the manuscript, revising the manuscript critically for important intellectual content, writing - review & editing, Approval of the version of the manuscript to be published. Marcin Sajdak: Conception and design of study, analysis and/or interpretation of data, Drafting the manuscript, revising the manuscript critically for important intellectual content, Approval of the

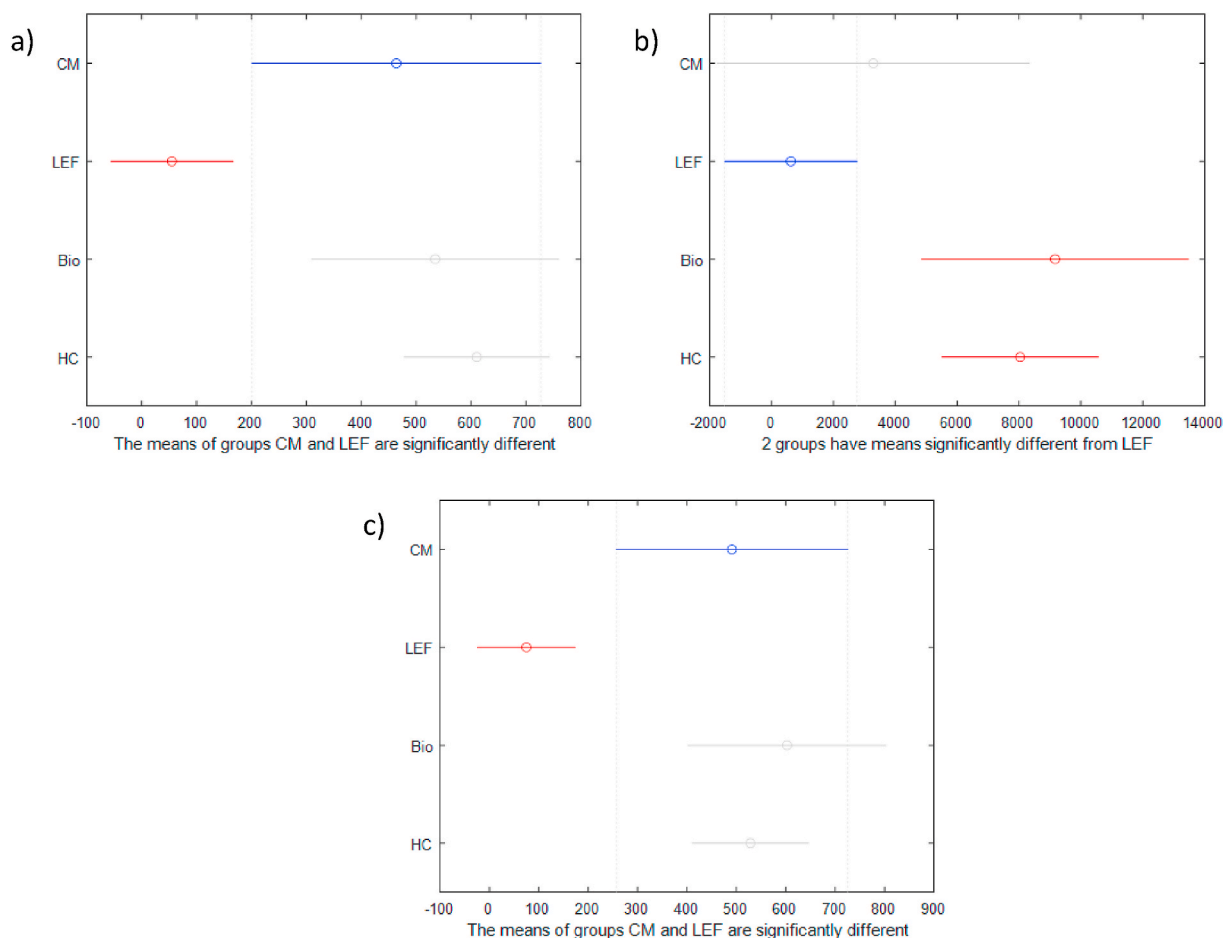


Fig. 7. The impact of the fuel type on the change in the exhaust gas content: a) dust, b) sum of PAH, c) TOC.

version of the manuscript to be published. Roksana Muzyka: acquisition of data, analysis and/or interpretation of data, Drafting the manuscript, revising the manuscript critically for important intellectual content, writing - review & editing, Approval of the version of the manuscript to be published. Małgorzata Pogoda: acquisition of data, writing - review & editing, Approval of the version of the manuscript to be published.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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