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The Impact of Additives on Gaseous Pollutants from the Combustion of Various Solid Fuels

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Abstract: This article compares the emission of gaseous pollutants such as CO_2, CO, NO, SO_2, and HCl emissions from the combustion of the selected most popular solid fuels in a low-power boiler. The process was carried out under controlled conditions on a laboratory stand equipped with a Moderator Unica Vento Eko 25 kW boiler. Solid fuels were selected for comparison, such as hard coal with granulation above 60 mm, hard coal with a granulation of 25–80 mm, hard coal with a granulation of 8–25 mm, wood pellets, and mixed firewood. The experiment was carried out in two stages. In stage 1, previously selected solid fuels were combusted under controlled repeatable conditions, while simultaneously measuring gaseous components in the exhaust gases in real time. On the other hand, the second stage involves the combustion of the same fuels under the same conditions with combustion additives that modify the combustion process in terms of reducing the emission of pollutants. At the same time, in the second stage, gaseous components in the exhaust gas were also measured in real time. The experiments carried out have shown that, in addition to the additive, a testing system should be used to assess the profitability and improve the efficiency of energy production and distribution after using a given additive for fuel combustion. Implementation of the use of solid fuel activators on a common scale should also entail research on the emission of dioxins and furans, which may be emitted in increased amounts under the influence of some components contained in combustion modifiers.

Keywords: solid fuels; combustion; air pollution; combustion additives; gaseous emissions

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1. Introduction

Conventional methods of burning solid fuels both in home and industrial conditions are organized sources of emissions of damaging elements into the atmosphere [1,2]. The reasons for their occurrence are diverse and can be divided into three groups, shown in Figure 1. The first group consists of raw material causes, which result from the fact that fuels have elements and compounds that, because of combustion, are transformed into harmful compounds emitted along with exhaust gases.

The second group includes pollutants resulting from incomplete combustion. The third group consists of by-products of the combustion process [3].

The amount of pollutant emissions from low-power boilers changes depending on the class of combusted fuel. According to research by Du [4], burning coal resulted in significantly higher CO_2, CH_4, and SO_2 emissions than burning wood. On the other hand, burning wood in gasification furnaces caused much higher emissions of PM2.5, EC, and OC. It was found that studies on more emission sources should be conducted to determine the difference between wood and coal combustion because the emissions depend on many factors, fuel properties, etc. [4]. On the other hand, studies carried out by the Chen research group [5] concerning CO, CO_2, SO_2, OC, EC, PM2.5, and PM10 emissions during cooking and heating with the use of various fuels produced from biomass proved that the use of wood briquettes for cooking and charcoal for space heating resulted in 28%, 24%, and 25%

reductions in CO, PM10, and PM2.5 emissions, respectively, when comparing the use of firewood for cooking and space rewarming [5].

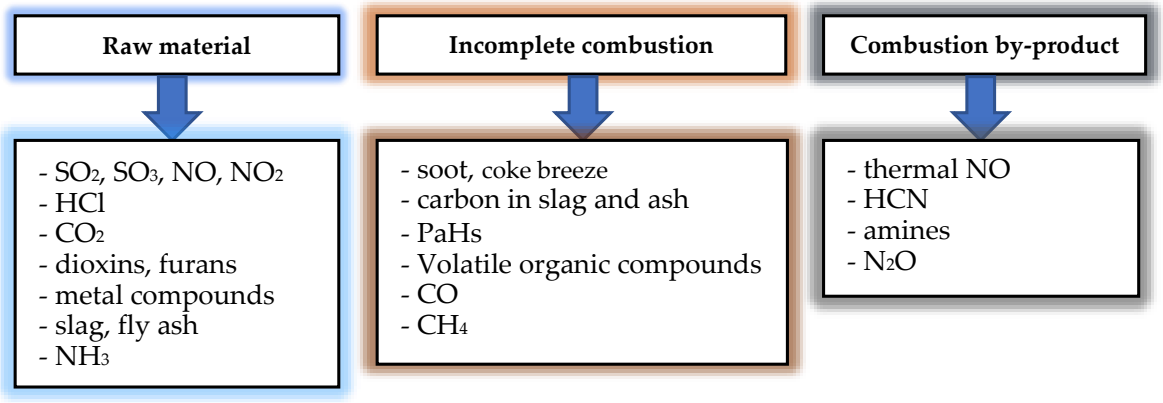


Figure 1. Causes of emissions from combustion in low-power boilers.

Attempts to solve the problems related to the incomplete combustion of fuels and the emission of pollutants into the atmosphere have been made over the last twenty years. Scientific research developed numerous additives with different chemical compositions and dosing techniques [6,7]. Initially, introducing sodium chloride, NaCl, was believed to positively affect the hard coal combustion process. In 1994, Borisovna patented a discovery involving periodically dosing sodium chloride in hard coal combustion. It determined the best dose at about 7–8 g of sodium chloride per m^2 of the boiler. The result was an increase in the efficiency of heating installations, a reduction in CO and NO_x emissions to the atmosphere, and the possibility of reducing the coefficient of excess air in the exhaust gases. Additionally, a 12% reduction in heat losses was recorded [6].

Additives for the combustion of solid fuels are used to reduce pollutant emissions or combustion losses and remove and burn soot formed in the combustion process. An effective way to remove soot is to introduce a combination of oxidizing agents into the furnace. The thermal decomposition of mineral salts, such as nitrates(V) or manganates(VII), occurs at high temperatures. Oxygen, formed in situ, is highly reactive, making it possible to oxidize the soot at low temperatures. The advantage of in situ oxidation based on potent oxidizing compounds is the generation of a large volume of gases due to the decomposition of a small amount of the introduced substance. The resulting gas penetrates the surface of the temperature exchanger even in places where the cleaning mechanism is very burdensome [7]. When burning wood biomass, additives are also used. They refer to a group of mineral deposits or chemical compounds that can change the chemical composition of ash, reduce the content of problematic compounds, and increase the melting point of ash in biomass burning processes [8]. The modifiers for the combustion of solid fuels are fed in two ways: by mixing with the fuel before combustion, e.g., by granulating the fuel with additives or by mixing the modifiers with the fuel transported by the conveyor, and by introducing them into the burner in the form of powder or solutions employing installed spray systems [8].

According to available sources, additives for the burning of solid fuels work in two ways. The first method of action is the chemical reactions of fuel components with additives; fuel components that melt at low temperatures are converted at high melting points. The second is based on physical adsorption. During the combustion of fuel with a combustion additive, vapor condensation occurs; molten ash is finer, while solid particles, i.e., aerosols, can be captured by spongy additive elements with a large surface area and transported by combustion techniques [8–11].

In connection with the above information and the not fully explored topic of gaseous pollutant emissions into the atmosphere as a result of the burning of solid fuels with various types of combustion additives, it was decided to compare the emissions of CO_2,

CO, NO, SO_2, and HCl from the combustion of the selected most popular solid fuels in a low-voltage-power boiler with and without the use of combustion additives. The following solid fuels were selected for comparison: hard coal with a granulation above 60 mm, hard coal with a granulation of 25–80 mm, hard coal with a granulation of 8–25 mm, wood pellets, and mixed firewood. Four different combustion additives were selected based on the different compositions given in the specification. The results of this work allowed us to determine and evaluate the impact of combustion additives of various compositions on the emissions of gaseous pollutants from the combustion of solid fuels. In addition, the basic properties of the selected solid fuels were examined, and their impact on the above-mentioned gaseous pollutants was assessed.

2. Materials and Methods

2.1. Feedstock for Combustion Processes

The five most popular solid fuels were selected for experimental research, i.e., hard coal with a size of more than 60 mm, hard coal with a granulation of 25–80 mm, hard coal with a granulation of 8–25 mm, wood pellets with a diameter of 6 mm (according to the ENplus A1, ENplus A2, EN B, and DINplus standards, wood pellets should have a diameter of between 6 and 8 mm), and mixed firewood. Solid fuels for testing were purchased in a generally accessible specialist shop. Table 1 presents the basic parameters characterizing the selected fuels, which were provided by the producers of the selected solid fuels.

Table 1. Characteristics of selected fuels.

Type of Fuel	Granulation [mm]	Calorific Value [MJ/kg]	Moisture [%]	Volatile Content [%]	Ash Content [%]	Total Sulfur Content [%]
hard coal with a grain size above 60 mm	60–200	23–25	<19	>35	Max 7	Max 0.5
hard coal with a granulation of 25–80 mm	25–80	26	9	no data	5	0.6
hard coal with a granulation of 8–25 mm	8–25	26	0–15	no data	0–10	0–0.08
wood pellets	6	18	6.6–8.8	no data	0.8–1.1	0.01
mixed firewood	100–300	15	12	no data	0.4	no data

Source: own study based on information from the manufacturer.

2.2. Characteristics of Selected Solid Fuels

Analysis of the elemental composition of solid fuels was performed using the CHN628 analyzer by LECO (Lakeview Ave, USA). The content of carbon and hydrogen in dry biomass was determined by the high-temperature combustion method with the detection of infrared radiation (IR). The nitrogen content was determined by the calorimetric method according to PN-EN ISO 16948:2016, where, according to the requirements of the analysis, 0.1 g of the sample was weighed. The sulfur content was determined by high-temperature combustion with IR detection, where, according to the PN-EN ISO 16994:2016 standard, 0.3 g of the sample was weighed.

2.3. Fuel Additives

Four publicly available solid fuel modifiers were selected for the research in stage 2, which consisted of the combustion of solid fuels with additives. Due to the protection of the rights of producers and their personal data, trade names and information from

the packaging are not provided. The elemental analysis for this work was performed independently. Combustion additives were named with the following ordinal numbers: 1, 2, 3, and 4. In the course of chemical analyses, the following elements were determined in the composition of the selected combustion additives: calcium Ca, sodium Na, magnesium Mg, potassium K, aluminum Al, silicon Si, iron Fe, copper Cu, chromium Cr, zinc Zn, carbon C, chlorine Cl, sulfur S, phosphorus P, and nitrogen N.

The content of the metals calcium Ca, sodium Na, magnesium Mg, potassium K, aluminum Al, iron Fe, copper Cu, chromium Cr, and zinc Zn was determined using an ICP-MS Agilent 8800 spectrometer (Agilent, Santa Clara, CA, USA). Before proceeding with the composition analysis, they were mixed in a ball mill using pots and balls made of zirconium oxide. Homogenized samples of additives for the combustion of solid fuels were dissolved in distilled water, and then appropriately diluted before analysis. The ICP-MS spectrometer (Agilent, Santa Clara, USA) was calibrated using standards with the certified content of all determined elements.

Total carbon was determined using an Analytik Jena TOC multi NC 3100 analyzer (Analytik Jena, Jena, Germany), which was equipped with a solids attachment. From the samples of the additives for burning solid fuels after homogenization, about 10 mg was weighed out for analysis. Sample weights in porcelain boats were manually introduced into the high-temperature chamber of the apparatus, and the carbon content was read from the calibration curve. The calculations were carried out with the use of the software provided with the apparatus. The TC content in the test sample was measured by burning the sample in an oven at 850 °C, where pyrolysis and oxidation of the sample took place. Carbon dioxide as a product of complete combustion was directed to the NDIR infrared detector, which was used to determine the concentration of CO_2.

Silicon, phosphorus, and sulfur in samples of solid fuel combustion additives were determined using an X-ray fluorescence spectrometer TXRF S2 PICOFOX (Brucker, Berlin, Germany). For this purpose, the samples homogenized in the mill were slurried with 25 mg of the sample in 2.5 mL of Triton X-100 non-ionic surfactant. Then, 10 µL of the suspension was applied to an acrylic glass disc and analyzed using the software attached to the TXRF spectrometer.

Total nitrogen was determined using a HACH 6000 DR spectrophotometer (Hach Lange GmbH, Düsseldorf, Germany). For this purpose, stock solutions were prepared by weighing 100 mg of samples of additives for the combustion of solid fuels, which were dissolved in 100 mL of distilled water. The instructions for the HACH total nitrogen, 5–40 mg/L cuvette tests (cat. no. LCK 238) were then followed, using appropriate dilutions of the stock solution.

Chlorine was determined using a DIONEX ICS-5000+ ion chromatograph (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an EGC III KOH eluent generator, an IonPac AS18 (Waltham, MA, USA) anion exchange column, an ASRS 300 suppressor (Waltham, MA, USA), and a conductivity detector. For the determination of chlorine ions, stock solutions were prepared by dissolving 100 mg of a sample of a given fuel combustion additive in 100 mL of 2M HNO_3.

2.4. Combustion Process

The experimental studies concerned selected five types of solid fuels, which were combusted in laboratory conditions in the Low-Emission Combustion Technologies stand, which is the equipment of the Department of Agricultural and Food Engineering and Environmental Development of the Białystok University of Technology. The stand was equipped with a Moderator Unica Vento Eko 25 kW boiler with an automatic feeder, equipped with a manual and retort grate and an MCA10 flue gas analyzer by Dr. Fodisch (Dr Fodish, Markranstädt, Germany). The Unica Vento Eko boiler is a classic boiler, very often used in individual heat sources in Poland. The boiler used was a device with a transverse circulation chamber, operating with top combustion. The cubic exchanger consisted of a chamber with a self-cleaning retort furnace, above which there was a flue

gas deflector. Additionally, it had a retort furnace door and a loading door (for alternative fuel), which enabled the combustion of fuels such as firewood or coal with sizes above 60 mm [12].

Each time, 20 kg of each fuel was burned, maintaining the same combustion conditions, i.e., the flue gas temperature and the temperature of the feed water (at the exit from the boiler), which was about 70–80 °C, and at the return not less than 50 °C. The settings of the fuel mass stream and air blowing into the combustion chamber were selected by the boiler controller in the fuzzy logic mode [12,13]. The installed fuzzy logic controller also controlled the exhaust gas temperature in such a way that the fuel was burned optimally. The type of fuel combustion was selected in the controller. In stage I, each of the selected fuels was combusted three times in three successive days. At the same time, the concentration of waste products in the exhaust gases was measured. However, in stage II, the same fuels were combusted with each of the 4 selected fuel combustion additives, while the exhaust gas composition was measured at the same time. Each combustion experiment was conducted for 5 h. Measurements from the first and last hour were discarded. The results were averaged after stabilization, i.e., 3 h in the middle of the total time of the combustion process.

2.5. Exhaust Composition Measurements

Exhaust gases were collected during the in situ combustion process and analyzed for the presence of carbon monoxide CO, carbon dioxide CO_2, nitrogen oxide NO, sulfur dioxide SO_2, hydrogen chloride HCl, and oxygen O_2 by the MCA10 analyzer with a sampling period of 20 s. In total, approximately 540 results were obtained for individual measurement meters within 3 h. The results were averaged (arithmetic mean) and used in part of this article. The results were displayed online and archived on a tablet. The measuring principle of the MCA10 was based on infrared photometry. A broadband light source was used as the radiation source. The content of individual exhaust gas components was calculated by recording the unattenuated and attenuated light intensity in the absorption wavelength of the sample component. Thanks to an additionally installed cell with zirconium dioxide, it was possible to measure the molecular oxygen content in the exhaust gas. The analyzer gave the contents of CO_2 and O_2 in percent, and the others, i.e., CO, NO, SO_2, and HCl, in mg/m^3. The content of the tested compounds in the CO_2, CO, NO, SO_2, and HCl exhaust gases was normalized to 10% of the O_2 oxygen content according to the formula [14,15]:

$$Z_{s2} = \frac{21 - O_2'}{(21 - O_2'') \times Z_{s1}} \left[\%,\ \mathrm{mg/m^3}\right] \quad (1)$$

where:

Z_{s1}—the actual content of the chemical compound in the exhaust gas [%, mg/m^3];
Z_{s2}—the content of a chemical compound in the flue gas for a given oxygen content [%, mg/m^3];
O_2'—the set oxygen content in the exhaust gas [%];
O_2''—the actual oxygen content in the exhaust gas [%].

The excess air coefficient λ was calculated on the basis of the formula used for technical calculations [15]:

$$\lambda = \frac{21.5}{21.5 - O_2''} \ [-] \quad (2)$$

where:

λ—the excess air coefficient;
O_2''—the actual oxygen content in the exhaust gas [%].

3. Results and Discussion

3.1. Analysis of the Elemental Composition of Selected Fuels

The results of the analysis of the primary composition of the tested solid fuels are represented in Table 2. In the case of mixed firewood, the analysis of the elemental composition was carried out separately for the bark and the middle in the form of wood fibers.

Table 2. Elementary composition of the tested solid fuels.

Solid Fuels		Carbon	Hydrogen	Sulfur	Nitrogen	Oxygen *	Chlorine
		[%] in Working Condition					
mixed firewood	tree bark	49.50 ± 0.20	5.58 ± 0.003	0.455	0.84 ± 0.06	43.60	0.034
	middle	50.81 ± 0.12	6.11 ± 0.03	0.461	0.14 ± 0.08	42.41	0.019
pellets		51.54 ± 0.06	6.28 ± 0.01	0.441	0.05 ± 0.01	41.70	0.008
hard coal with a granulation of 8–25 m		68.38 ± 0.44	5.02 ± 0.06	0.502	0.65 ± 0.06	25.44	0.015
hard coal with a granulation of 25–80 mm		72.44 ± 0.17	5.81 ± 0.10	0.569	0.79 ± 0.06	20.04	0.012
hard coal with a grain size above 60 mm		69.05 ± 0.17	4.59 ± 0.03	0.902	0.69 ± 0.08	25.10	0.014

* Parameter calculated based on other measurements.

The elemental configuration of biomass and coals used in power generation is qualitatively the same, but differences exist in the proportions of individual elements and chemical compounds. On average, biomass contains about four times as much oxygen, twice as much carbon, and less sulfur and nitrogen. The consequence of this composition is a high content of volatile parts [16]. Carbon, hydrogen, and oxygen are the main components of solid fuels. During combustion, carbon and hydrogen, through exothermal reactions, are oxidized to carbon dioxide CO_2 and water vapor H_2O, so their content positively affects the fuel's combustion heat. In contrast, oxygen content has a adverse effect, as it is a source of weight in combustion processes [17]. According to Hardy and Kordylewski [18], hard coal should contain 75% to 97% elemental carbon, 2% to 6% hydrogen, 1% to 18% oxygen, 0.5% to 2% nitrogen, and 0.2% to 2% sulfur.

Our research (Table 2) allowed us to conclude that the highest content of the element carbon was present in hard coal with a granulation of 25–80 mm (72.44%), while the lowest was in firewood bark (49.50%). In pellets, the carbon content was 51.54%, while in the wood–fiber composite measure, it was 50.81%. Hard coal with a granulation of 8–25 mm had a carbon content of about 68.38%, while hard coal with a granulation of 60 mm had a carbon content of about 69.05%. The carbon content expresses a considerable degree of coalification, especially in the C/O and C/H ratios. This parameter behaves inversely proportional to the content of volatile parts. With the degree of coalification, the content of the element C increases; for example, for lignite, it is 58–77%, and for hard coal, it is already 76–93% [19].

The hydrogen content (Table 2) of the solid fuels tested ranged from 4.59% in hard coal with a granulation > 60 mm to 6.28% for pellets. In contrast, the hydrogen content of the other coals was 5.08% and 5.81%, respectively, for hard coal with a granulation of 8–25 mm and coal with a granulation of 25–80 mm. In the case of firewood, the hydrogen content of the bark was 5.58%, while that of the wood fiber agent was 6.11%. According to the available data, as the degree of carbonization increases, the hydrogen content decreases, and hard coal averages 1.5–5.8% [19]. The tested hard coals, in terms of hydrogen content, were within the specified range. The oxygen content (Table 2) of the solid fuels analyzed ranged from 20.04% (hard coal with a grain size of 25–80 mm) to 43.60% (mixed firewood

bark). The pellets contained about 41.70% oxygen, while the wood fiber composite agent contained 42.41%. The other hard coals, i.e., hard coal with a granulation of 8–25 mm and a granulation >60 mm, contained 25.44% and 25.10% oxygen, respectively. A significant difference in oxygen content was noted between biomass fuels, i.e., pellets and firewood, and stone coals of different granulations. In biomass fuels, the oxygen content was almost twice as high as in hard coal.

Among the solid fuels tested, high nitrogen contents (Table 2) were obtained successively for mixed firewood bark (0.84%), hard coal with a granulation of 25–80 mm (0.79%), hard coal with a granulation > 60 mm (0.69%) and hard coal with a granulation of 8–25 mm (0.65%). Lower nitrogen contents were recorded in pellets (0.04%) and wood fiber middlings (0.14%). According to Obernberger and colleagues [17], the lowest nitrogen content is found in coniferous wood (0.1% nitrogen) and deciduous wood (0.1% nitrogen) without bark. The highest content is found in wood bark (0.3–0.5% nitrogen) [17,20].

During combustion processes, the nitrogen in the fuel is almost completely converted into the nitrogen gases N_2 and NO_x [21]. Nitrogen oxides, communally raised to as NO_x, are formed in all burning processes, mainly as nitrogen monoxide (NO), with smaller amounts of nitrogen dioxide (NO_2) and nitrous oxide (N_2O) [22]. According to Glarborg [23,24], in the case of fuels with low N content, nitrous oxide is formed by the oxidation of nitrogen N_2 in the air dosed by the burning processes. In contrast, in fuels with much higher nitrogen content, the oxidation of fuel-bound nitrogen is the dominant source of nitrogen oxides. Only a negligible amount of N is incorporated into the ash. NO_x emissions increase as the nitrogen content of the fuel increases. In addition, air supply, furnace geometry, combustion temperature, and the type of combustion technology used are the main variables affecting NO_x formation [21,22]. According to Janicki [25], the nitrogen content of wood pellets is 0.12–0.13%.

In the available literature, it has been found that the increased content of chlorine and sulfur in solid fuel has an adverse effect on increasing the corrosion rate of heating equipment during the coal combustion process [26,27]. It has to also be observed that the high content of sulfur and chlorine in solid fuels, during their thermal decomposition, leads to increased emissions of, among other things, the highly harmful sulfur oxides SO_x and HCl [28]. The Cl content of woody biomass is generally very low. An example is bark-free wood, which contains about 0.01% chlorine [17]. According to Hardy and co-workers [18], Wasilewski and Hrabak [29] and Ren and co-workers [30] claim that during combustion, the chlorine contained in biofuels mainly forms HCl, molecular chlorine Cl_2, or alkali metal chlorides (KCl, NaCl). In the fuels studied (Table 2), the chlorine content ranged from 0.008 (pellets) to 0.034% (mixed firewood bark). In firewood, in the middle part, which is composed of wood fibers, the chlorine content was 0.034%. In the case of stone coals, the chlorine content was similar, regardless of the coal granulation (8–25 mm—0.015%, 25–80 mm—0.012%, >60 mm—0.014%).

The sulfur content of the solid fuels selected for the study ranged from 0.441% in pellets to 0.902% for hard coal with a granulation > 60 mm. In contrast, mixed firewood yielded 0.455% bark and 0.461% wood fiber agent, respectively. The remaining coals were characterized by a sulfur content of about 0.5%. Sulfur, which is limited in biomass, is oxidized during combustion mainly to sulfur (IV) oxide SO_2 (and in small amounts also to sulfur (VI) oxide (SO_3)) and forms alkalis and sulfates [17]. According to Yanik and colleagues [31], and Ren and colleagues [30], SO_x emissions from woody biomass combustion are usually not important. Obernberger [17] states that SO_x problems can be estimated when the sulfur concentration in biomass exceeds 0.2% by weight. In the case of the fuels analyzed, this will be of great importance, since all of the fuels, including biomass, exceeded a sulfur content of 0.2% by weight. The importance of sulfur is not mainly due to SO_x but its role in corrosion processes. According to Król [32], high concentrations of SO_x in the flue gas contribute to the sulfidation of alkali and alkali metal chlorides by lowering the flue gas temperature and releasing chlorine [32].

3.2. Analysis of the Elemental Composition of Combustion Additives

Table 3 analyses the elemental components of four solid fuel combustion additives available on the Polish market. The elemental analysis determined the type and mass percentage composition of the chemical elements included in the substance under study, i.e., the fuel combustion additive. The elemental analysis, however, did not make it possible to determine the structure—that is, how chemical bonds interconnect the atoms. Based on manufacturer data, it was determined that the combustion activators are mostly minerals and inorganic salts.

Table 3. Elemental composition of the selected 4 additives for the combustion of solid fuels.

Element/Number of Additives	D1	D2 Content%	D3	D4
Al	0.97	-	-	-
C	9.48	0.71	0.95	0.58
Ca	18.98	-	4.15	-
Cl	-	26.73	32.03	37.52
Cr	-	-	-	0.12
Cu	-	0.30	12.96	0.23
Fe	0.46	0.54	0.20	0.59
K	2.80	20.80	0.50	0.07
Mg	10.14	8.1	-	-
N	-	10.48	2.22	5.09
Na	12.84	18.18	17.35	24.18
P	1.07	0.68	-	-
S	0.86	10.61	5.58	26.11
Si	4.72	-	1.99	-
Zn	-	-	-	3.15

Based on an analysis of the composition of the nominated combustion additives (Table 3), it was found that three of the four additives had a high chlorine content by weight composition. The highest amount of elemental chlorine, as much as 37.52% by weight, was obtained in Additive No. 4, Additive No. 3—32.03% chlorine by weight—and Additive No. 2—26.73%. In Additive No. 1, the analysis did not yield a significant proportion of chlorine in the composition. The next element determined in significant amounts in the three solid fuel activators was sodium. It was present in all selected substances that were combustion additives. The highest amount of Na was recorded in Additive No. 4 and amounted to 24.18% by sample weight. In the case of Additive No. 2, sodium accounted for 18.18% by weight; in the combustion Additive No. 3 composition, sodium occupied 17.35% by weight of the substance. In contrast, in Additive No. 1, it accounted for 12.84%. From the group of alkali metals, potassium was also present in the tested additives. The highest amount of potassium by weight was determined in Additive No. 2 (20.80%). Potassium was also present in the other three fuel combustion activators, but in much smaller amounts: in Additive No.—2.80%, in Additive No. 3—0.50%, and Additive No. 4—0.07%. Another element in the composition of all selected additives was sulfur. Sulfur was determined in the highest amount in Additive No. 4 and accounted for 26.11%, followed by 10, 61% in Additive No. 2. Additive No. 3 had 5.58%, while Additive No. 1 had less than 1% (0.86%). The next non-metal that was determined in significant percentages in three of the four additives analyzed was nitrogen. The highest amount of elemental nitrogen by weight was found in Additive No. 2 and amounted to 10.48% by weight of the additive sample; in Additive No. 4, nitrogen was determined at 5.09% by weight. Nitrogen was also present in the composition of Additive No. 3 and accounted for 2.22% of the weight of the additive. In addition to nitrogen and sulfur from the non-metal group, carbon C was present in the composition of each additive, with the highest amount recorded in Additive No. 1, which was 9.48% by weight. In the other three additives, the percentage of carbon was lower compared to Additive No. 1: Additive No. 2—0.71%, Additive No. 3—0.95%,

and Additive No. 4—0.58%. Another non-metallic element in Additive No. 1 and Additive No. 2 composition was phosphorus P. The phosphorus content in Additive No. 1 was 1.07%, while in Additive No. 2 it was 0.68%. Silicon, as a representative of semi-metals, was present in two additives, No. 1 and No. 3. In Additive No. 1, it accounted for 4.72% by weight of the additive, while in Additive No. 3, it accounted for 1.99% by weight.

The other elements detected in the composition of the combustion modifiers were metals such as calcium Ca, magnesium Mg, aluminum Al, iron Fe, copper Cu, zinc Zn, and chromium Cr. Calcium was present in Additive No. 1 and Additive No. 3, accounting for 18.98% and 4.15% of the activator's weight, respectively. Magnesium was present in Additive 1 and Additive 2, accounting for 10.14% and 8.01%, respectively. Iron was present in all solid fuel activators. The highest iron content was recorded in Additive No. 4 and amounted to 0.59% by weight. In Additive No. 2, the iron content was 0.54%, while in Additive No. 1 and No. 3, 0.46% and 0.20%. Another metal in the three selected solid fuel combustion modifiers was copper. It was most abundant in Additive No. 3—12.96% by additive weight. In Additives No. 2 and 4, the copper content was 0.30% and 0.23%, respectively.

Aluminum was present in Additive 1, with a content of 0.97%. On the other hand, zinc and chromium were still found in Additive 4. The content of these elements was 3.15% and 0.12%, respectively. Many researchers [33–36] have researched inorganic catalysts affecting coal combustion. They have found that they are most often found in the form of additives (e.g., metal oxides such as MnO_2, CaO, CeO_2, $Fe2O_3$, CuO, and ZnO) and alkali metal compounds (e.g., $NaNO_3$, $NClO_4$, KNO_3, $KClO_3$, and K_2CO_3) [37–40]. These additives help improve carbon decomposition [41,42]. Metal oxides in the combustion process decompose and accelerate carbon combustion due to the release of molecular oxygen. It should be noted that the catalyst's efficiency depends on the coal's burnable carbon content [43]. During salt decomposition, oxides are formed that act as active oxygen carriers to promote the catalytic burning of coal. Active oxygen at higher temperatures forms an active center, and the carbon around it burns faster. In addition, the resistance on the surface of the coal particles is reduced due to the holes created during combustion; thus, oxygen diffusion into the fuel molecule is increased [40]. This mechanism allows direct contact between oxygen and coal, which consequently improves the rate of coal combustion and, at the same time, lowers the ignition temperature of coal. Various researchers have studied the effects of alkali metal salts, alkaline earth metals, rare earth metals, and transition metals on the combustion of coal [38,42,44–46]. The data obtained indicated a decrease in ignition temperature and, at the same time, an increase in the burn rate due to the introduction of combustion additives. It has been established that catalytic combustion is more efficient, so catalysts have been and continue to be successfully used in many industries for burning coal and other fuels [38]. Based on studies, the addition of catalysts to coal combustion can affect the following:

- An increase in reactivity due to a reduction in flash point and a growth in the rate of combustion [34];
- Improving the combustion of unburned coal in ash and accelerating the release of heat from coal [35];
- Reducing CO emissions and pollutants in the exhaust such as NO_x, SO_2, CO, and PM [47,48].

3.3. Emission of Gaseous Components

In technological research, where the process of combustion of solid fuels was controlled, exhaust gas components such as CO_2, CO, SO_2, NO, and HCl were measured. Figures 2–6 show the average values of concentrations of the selected five exhaust gas components during combustion: hard coal with a grain size above 60 mm, hard coal with a grain size of 25–80 mm, hard coal with a grain size of 8–25 mm, wood pellets with a granulation of 6 mm, and mixed firewood. All the values of the selected exhaust gas

components were calculated for 10% oxygen content in the exhaust gas with reference to the Ecodesign Directive.

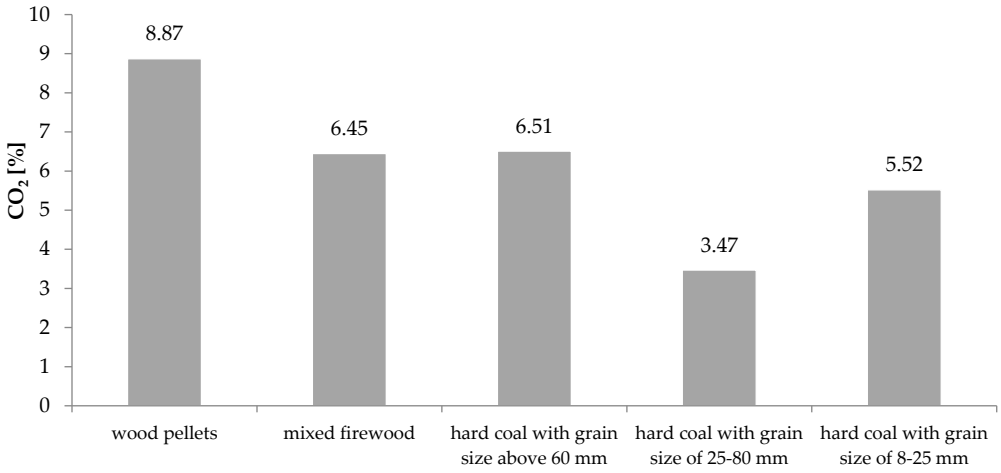


Figure 2. Carbon dioxide CO_2 emissions from the combustion of the tested solid fuels.



Figure 3. Carbon oxide CO emissions from the combustion of the tested solid fuels.

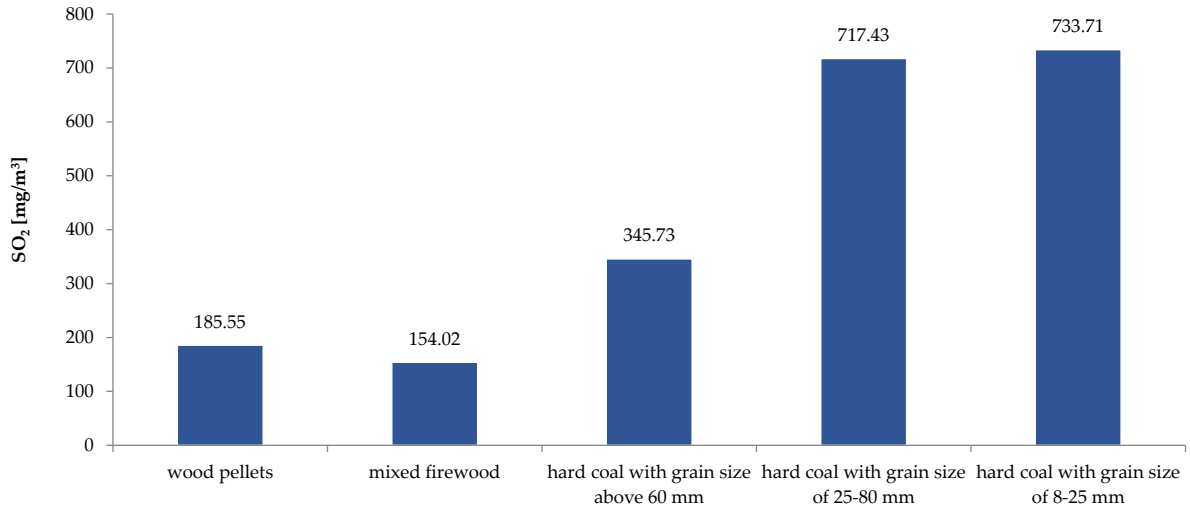


Figure 4. Emission of sulfur dioxide SO_2 from the combustion of the tested solid fuels.

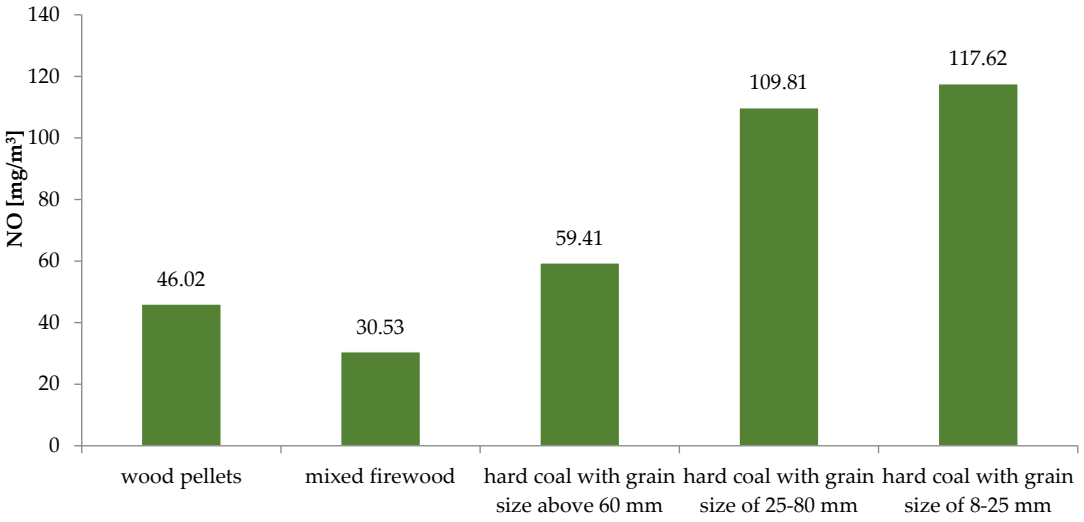


Figure 5. Emission of nitric (II) oxide NO from the combustion of the tested solid fuels.

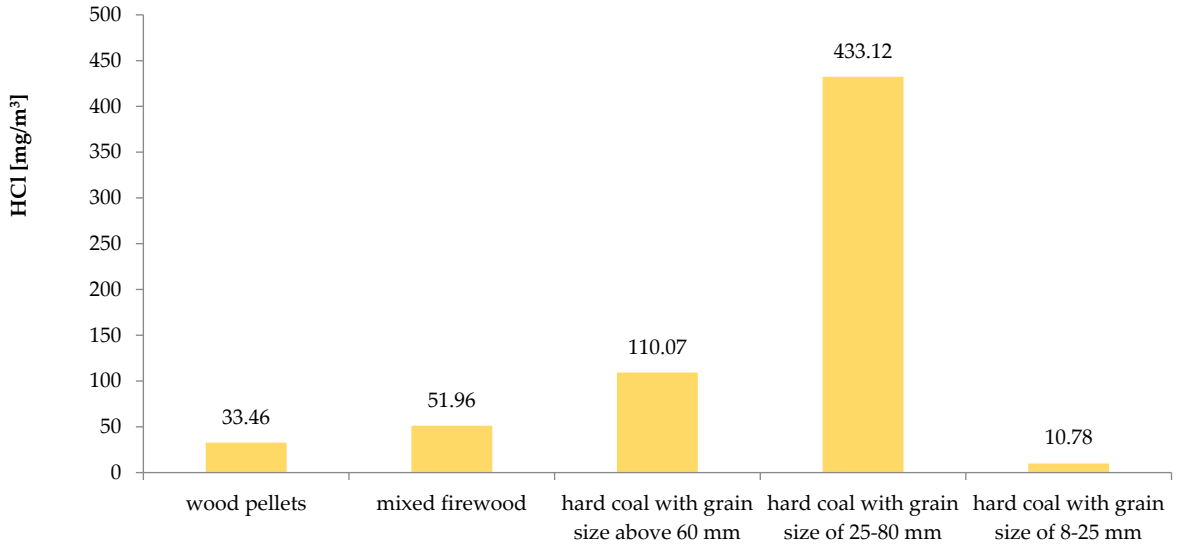


Figure 6. Emission of hydrogen chloride HCl from the combustion of the tested solid fuels.

The conducted research on the release of carbon dioxide due to combustion (Figure 2) shows that the highest emissions were characteristic for 6 mm pellets—8.87%—and the lowest were found for hard coal with a granulation of 25–80 mm (3.47%), which, among all the tested fuels, had the highest moisture content (22.75%). The Rokni research group [49] found that differences in CO_2 emissions for different types of solid fuels arise due to differences in the size of individual fuel particles and due to differences in the content of elemental carbon in the fuel [49]. As a result of the use of hard coal of various granulations, which had a very similar elemental carbon content, it can be concluded that different oxygen contents and possibly different mechanical and chemical factors cause burn out (unburning).

In combustion processes, attention is paid to the share of carbon monoxide in exhaust gases as an indicator of the presence of substances such as soot, hydrocarbons, dioxins, and furans [50]. However, when loaded manually, the CO standard is 700 mg/m^3 for both fuel types. The average value of CO emissions obtained for the combustion of the tested solid fuels is presented in Figure 3.

The highest CO emission value occurred during the combustion of hard coal with a granulation of 25–80 mm, which amounted to 5528 mg/m^3 on average (Figure 3). Literature sources report that at low CO_2 content in exhaust gas, there are obstacles related to the oxidation of CO to CO_2, and the combustion process may be unstable [51]. Ciupak's

research group [52] researched the impact of hard and brown coal fragmentation and moisture in the combustion process. Their results proved that an increase in hard coal moisture of 10% causes a three-fold increase in CO emissions for the wetted fuel concerning the CO emissions for unmodified fuel. For wetted hard coal, CO emission values of about 3000–4000 mg/m^3 were obtained [52]. As part of our own research, similar values were seen when burning mixed firewood (average 4217 mg/m^3). On the other hand, in the case of 6 mm pellets and hard coal with granulation >60 mm, the CO emissions were around 2500–2600 mg/m^3. The lowest reference emissions were found in the case of the combustion of hard coal with a grain size of 8–25 mm (2402 mg/m^3). Research conducted by Mustafa et al. [53] noted that the amount of CO was lower at higher temperatures. Increased carbon monoxide emissions show the risk of incomplete combustion. Literature sources show that the purpose of combustion is to convert fuel into heat, during which the carbon contained in the fuel is oxidized to CO_2. If the conversion is not ideal (for example, due to low temperature, oxygen deficiency, low turbulence, and the short residence time of exhaust gases in the furnace), the combustion process leads to the partial combustion of the fuel and the formation of intermediate products [54].

As part of our own research, sulfur(VI) dioxide in exhaust gases was also analyzed. Figure 4 shows the share of SO_2 in the gases produced due to the combustion of the tested fuels. It was noted that exhaust gases with the highest content of sulfur dioxide came from the combustion of 25–80 mm hard coal and 8–25 mm hard coal, where concentrations of 717.43 mg/m^3 and 733.71 mg/m^3 were recorded, respectively. These coals, alongside hard coal with a grain size above 60 mm, are characterized by a high sulfur content in their composition. According to research by Ravichandran and Corscadden [55], SO_x emission depends principally on the sulfur content in the combusted fuel. The lowest emission of SO_2 in our own research was characteristic for biomass, i.e., 6 mm pellets, and mixed firewood, which emitted 185.55 mg/m^3 and 154.02 mg/m^3**.** These fuels were characterized by a much lower content of sulfur alone in their composition compared to hard coal of various granulations.

Another analyzed exhaust gas was nitric(II) oxide. Figure 5 shows the concentration of NO in exhaust gases generated from the combustion of the tested solid fuels. The maximum concentration of nitric oxide was standardized by the Ecodesign directive at 200 mg/m^3. The largest allowable limit is marked with a red line in Figure 4.

The highest emission of nitrogen(II) oxide was recorded in exhaust gases from the combustion of 8–25 mm hard coal and 25–80 mm hard coal. Its concentration was 117.62 mg/m^3 and 109.81 mg/m^3. On the other hand, the lowest emission level was achieved when burning mixed firewood, which amounted to an average of 30.53 mg/m^3. In the case of 6 mm pellets, an average of 46.02 mg/m^3 was recorded, and in the case of hard coal > 60 mm, the NO emission level was 59.41 mg/m^3. All five selected solid fuels did not exceed the conditions required by the Ecodesign directive during combustion, and the emission was lower than NO < 200 mg/m^3. According to Yang et al. [56], the NO_x emissions in this nitrogen oxide are closely reported to the nitrogen content in the mass of combusted fuel. In the case of the tested fuels, the highest content of nitrogen (Table 2) was found in 25–80 mm hard coal, which also translated into higher NO emissions compared to other fuels. According to the available literature, nitrogen and sulfur content in the elemental composition is lower in wood biomass than in the case of coal fuels [57]. Wielgosiński's research group [58] saw that NO emissions decreased with increasing combustion temperature and decreasing airflow rate. According to the authors, this results from transformations in the NO synthesis process under these conditions. On the other hand, Williams et al. [59] believe that controlling NO_x emissions through stoichiometric control decreases their emissions, which applies principally to compounds released during the combustion of volatile fuel parts.

The last exhaust gas analyzed was hydrogen chloride. Figure 5 shows the share of HCl in the exhaust gases generated from the combustion of the tested fuels. Chlorine contained in biomass (Table 2) is primarily released in the form of hydrogen chloride HCl during combustion [30], which may further react with other components of exhaust

gas, resulting in the creation of dioxins [59]. Król [32] supplies the limit value of HCl emissions based on German standards, which does not exceed HCl < 5 mg/m^3. In our own research, the highest concentration of HCl in the exhaust gas was recorded during the combustion of hard coal with a grain size of 25–80 mm, and it was 133.12 mg/m^3. The lowest emission of HCl was noticed in burning 8–25 mm hard coal, i.e., at the level of 10.78 mg/dm^3. To compare hydrogen chloride emissions from the combustion of solid fuels, Dołżyńska and Obidziński [60] burned hard coal—Big Fire eco-pea coal with a granulation of 8–25 mm—and obtained HCl emissions of about 8.76 mg/m^3.

In stage V, during the combustion of solid fuels with combustion modifiers, the concentrations of selected fume components, such as CO, CO_2, SO_2, NO, and HCl, were analyzed. Figures 7–11 show the average concentration values of selected exhaust gas components during the combustion of the tested solid fuels: hard coal with cube sizes above 60 mm (cube), hard coal with granulation of 25–80 mm (nut), hard coal with granulation of 8–25 mm (eco-pea coal), pellets with a granulation of 6 mm, and mixed firewood with 4 additives, which have been characterized in Section 3.2. All values of gaseous pollutants were calculated for the content of 10% oxygen in the exhaust gas with reference to the Ecodesign Directive.

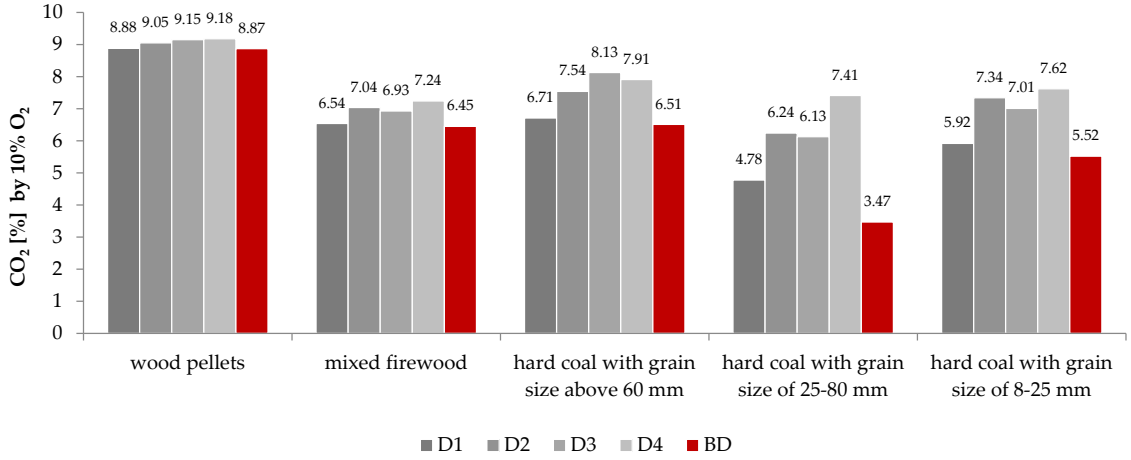


Figure 7. CO_2 emission in the combustion process of fuels with added activators, D1—additive number 1; D2—additive number 2; D3—additive number 3; D4—additive number 4; BD—without additive.

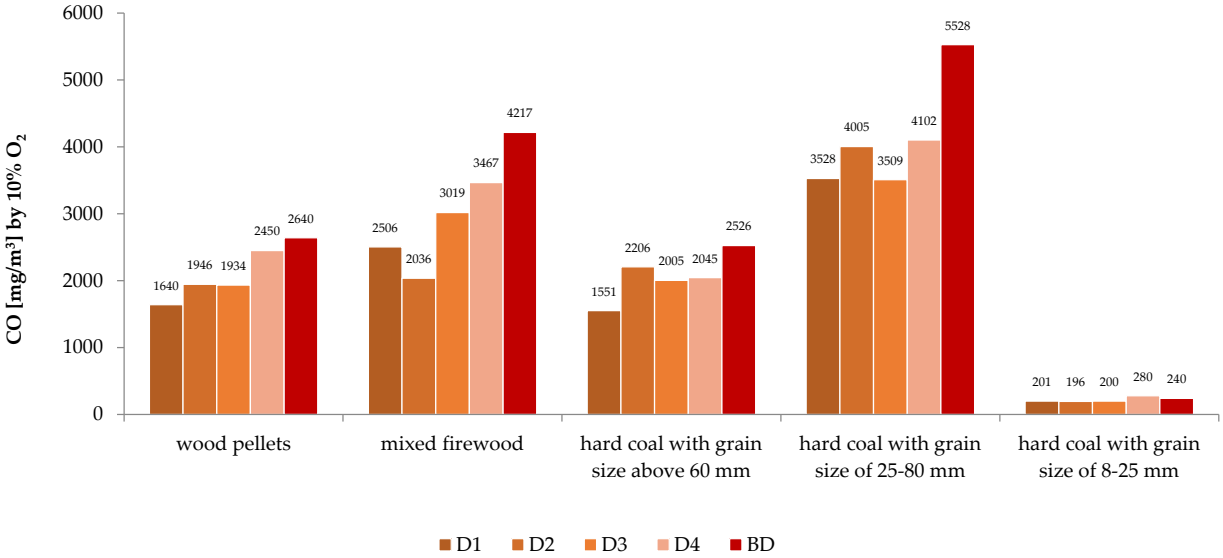


Figure 8. CO emission in the combustion process of fuels with added activators, D1—additive number 1; D2—additive number 2; D3—additive number 3; D4—additive number 4; BD—without additive.

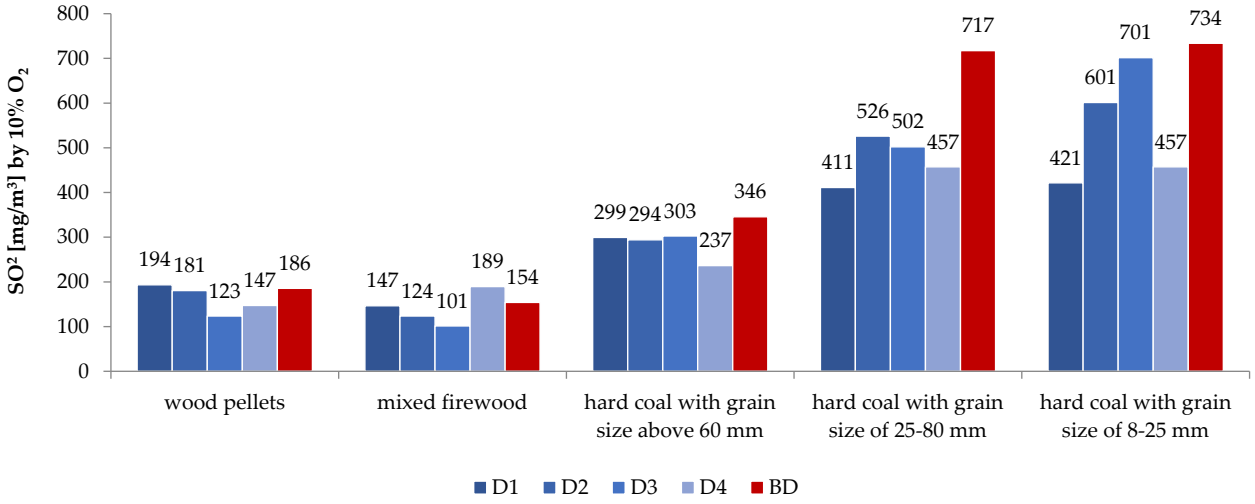


Figure 9. SO_2 emissions in the combustion process of fuels with added activators: D1—additive number 1; D2—additive number 2; D3—additive number 3; D4—additive number 4; BD—without additive.

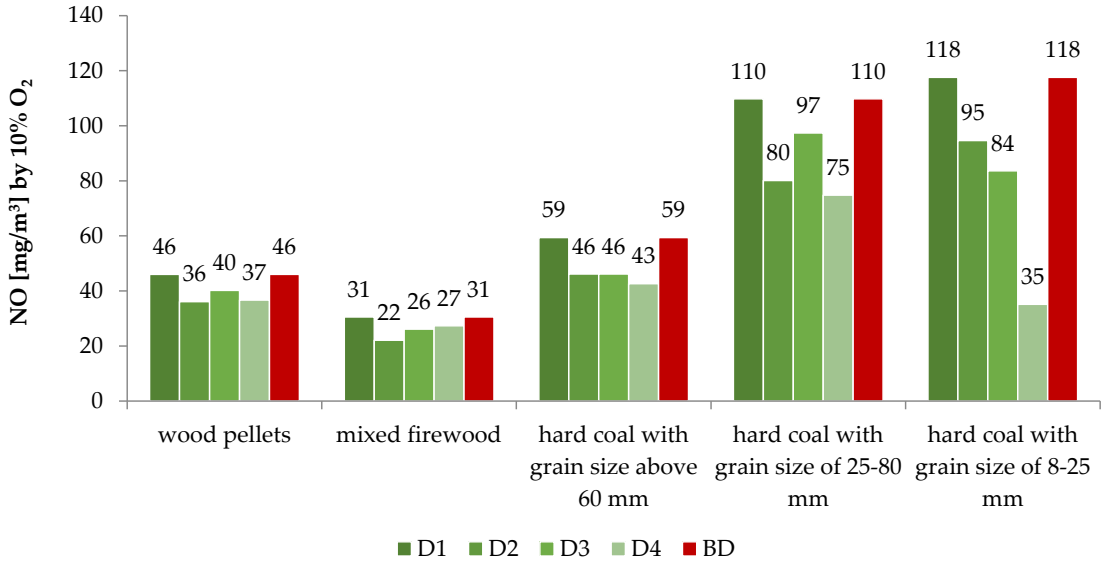


Figure 10. NO emissions in the combustion process of fuels with added activators: D1—additive number 1; D2—additive number 2; D3—additive number 3; D4—additive number 4; BD—without additive.

Figure 7 shows the concentration of CO_2 in the exhaust fumes generated during the combustion of the tested fuels. The highest concentration was found in the case of burning 6 mm pellets. Comparing the emissions from the combustion of 6 mm pellets with additives to CO_2 emissions without additives, it was found that there was an increase in CO_2 emissions in the exhaust after using all four selected combustion modifiers. The most considerable difference was 0.31% in the case of Additive No. 4 and the most minor—0.01%—in the case of applying Modifier No. 1. The opposite situation was seen when burning mixed firewood. Higher CO_2 emissions were obtained here using combustion activators than wood combustion without additives. In the combustion of hard coals of various granulation, significantly higher CO_2 emissions were achieved concerning the combustion of coal fuels without additives. Additives for burning solid fuels increased CO_2 emissions more in the case of coal burning than wood biomass, i.e., 6 mm pellets and mixed firewood.

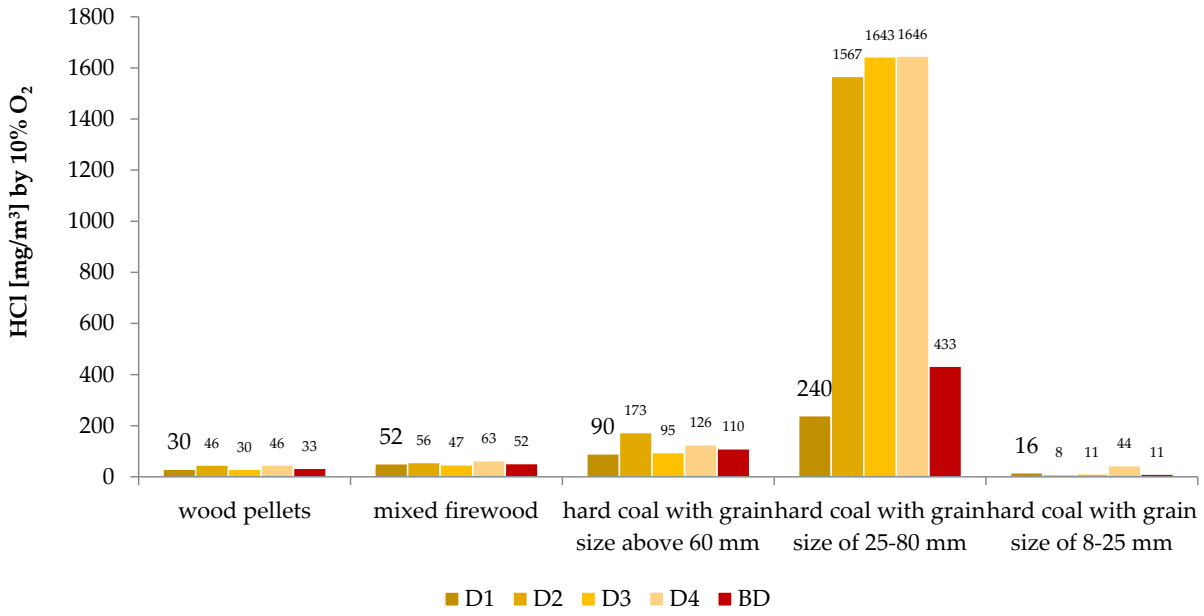


Figure 11. HCl emissions in the combustion process of fuels with added activators: D1—additive number 1; D2—additive number 2; D3—additive number 3; D4—additive number 4; BD—without additive.

Increasing CO_2 emissions during the burning of solid fuels is a desirable effect of using fuel additives. As a result of the use of combustion modifiers that contain copper and chlorine compounds, the balance of the combustion effect is shifted towards the formation of a smaller amount of carbon(II) monoxide in favor of carbon(IV) dioxide [6,7]. In addition, it is known that copper and its compounds accelerate the Deacon reaction, which is the basis for the stage related to the de novo synthesis of polychlorinated xenobiotics. However, under combustion conditions in central heating boilers, it is not recommended to use additives with copper and chlorine salts, as they cause the formation of dioxins and furans. Combustion modifiers that have oxidants, most often potassium nitrate or sodium nitrate, less often form potassium chlorate [61]. Additives No. 2, No. 3, and No. 4 used in the experiment for fuel combustion contained copper, and Additive No. 3—12.96% contained most of it. On the other hand, chlorine was contained in the same fuel combustion additives: No. 2, No. 3, and No. 4. Chlorine occupied the most significant amount, within 37.52% of the mass of the additive, in the case of modifier No. 4. This fuel additive in the case of most combusted fuels, i.e., 6 mm pellets, mixed firewood, 25–80 mm hard coal and 8–25 mm hard coal, increased CO_2 emissions compared to the emissions of fuel combustion without additives.

The CO emissions generated during the burning of solid fuels with the use of the four selected fuel additives are shown in Figure 8. The CO emissions were reduced for most solid fuels after using all selected combustion additives. The most considerable differences in the reduction in CO concentration after using combustion additives were noted in exhaust gases during the combustion of mixed firewood and hard coal, 25–80 mm.

A decrease in carbon monoxide emissions is associated with increased carbon dioxide emissions as the CO/CO_2 balance shifts in fuel combustion. According to Tic and Tic [62], the decrease in the concentration of CO in the exhaust gas after using combustion modifiers is associated with lower losses during incomplete combustion. Tic and Tic [62] evaluated solid fuel activators such as a mixture of salts containing Cu, Na, Mg, and NH_4^+ and a mixture of Ca and NH_3 salts for hard coal combustion. A significant reduction in CO emissions in the combustion process was achieved in a modifier with Cu, Na, Mg, and NH_4^+. In turn, the effect of individual cations such as NH_4^+, Na^+, Cu^{2+}, and Mg^{2+}, and mixtures of these cations in amounts of 25, 15, 50, and 10% were assessed by Tic's research group [63]. Researchers achieved the most significant decrease in CO concentration of

about 10% in the exhaust gas after using the Cu^{2+} cation. The average CO emission values obtained in our own research for the combustion of the tested solid fuels with combustion activators exceed the permissible level of CO emissions following PN EN-303-5:2012 and the Ecodesign Directive.

Figure 9 shows the concentrations of SO_2 generated in the combustion of solid fuels using combustion modifiers. The most significant decrease in SO_2 emissions was found in the combustion process of hard coals of various granulation with the addition of activators, compared with the tests without their participation. In the case of burning wood biomass, no significant reduction in SO_2 emissions was recorded. Only in the case of the combustion of 6 mm pellets after applying Additives No. 3 and 4 did the concentration of SO_2 decreased slightly, and in the case of mixed firewood after applying Additives No. 2 and No. 3, SO_2 emissions were lower than when burning fuel without the fuel additive.

Differences in the decreases in emissions during the combustion of hard coal with granulation > 60 mm were as follows: Additive No. 1 decreased by 14%, Additive No. 2—15%, Additive No. 3—13%, and Additive No. 4—32%. The SO_2 emissions were best reduced by Additive No. 4, which had a significant amount of chlorine in its mass composition. In the case of other hard coals, a significant reduction in SO_2 emissions was recorded. During the combustion of 25–80 mm hard coal, the decrease in SO_2 concentration in the exhaust gas compared to the sample without additives was as follows: Additive No. 1—43%, Additive No. 2—27%, Additive No. 3—30%, and Additive No. 4—37%. In the case of hard coal with a granulation of 8–25 mm, the reduction of SO_2 emissions was as follows: Additive No. 1—43%, Additive No. 2—18%, Additive No. 3—5.5%, and Additive No. 4—38%. The Tic research group [64] showed the most significant percentage decrease (7.5%) in SO_2 emissions after using a hard coal combustion process modifier in the form of a mixture of cations: NH^{4+}, Na^{+}, Cu^{2+}, and Mg^{2+}.

The concentrations of nitrogen oxide NO in exhaust fumes are shown in Figure 10 in the combustion process of the selected five solid fuels with fuel additives. It was found that the use of Additive No. 4 caused the most significant decrease in NO concentration in exhaust fumes. Comparing the emission of NO in exhaust gases from biomass fuels and hard coal of various granulations, it was noted that fuel additives reacted with coal fuels, the combustion of which emitted a higher concentration of NO than in the case of biomass. In the case of 6 mm pellets, the effect of the additive reduced emissions by an average of 11–22%, and in the case of mixed firewood by 10–30%. On the other hand, in coal fuels, additive No. 4 in the case of hard coal > 60 mm reduced emissions by 28%, for hard coal with a grain size of 25–80 mm by 32%, and hard coal with a grain size of 8–25 mm by 71%. Yu et al. [64] also conducted observations of NO_x in exhaust gases. They noticed that adding ammonia as a combustion modifier resulted in higher concentrations of this gas in the exhaust. According to research by Tic and Tic [62], the combustion of hard coal with a granulation of 0–20 mm and a combustion modifier composed of both Ca and NH_3 causes a decrease of several percent in the NO concentrations of the exhaust gas.

The HCl emissions generated during the combustion of solid fuels with the use of the selected four fuel additives are shown in Figure 11. A slight increase in the concentration of hydrogen chloride in the exhaust gas was seen after the use of three out of four additives for the combustion of solid fuels, i.e., Additives No. 2, No. 3, and No. 4. This can be explained by the fact that chlorine occupied a significant mass share in the composition of the listed additives.

4. Conclusions

The analysis of exhaust gases in solid fuel combustion conducted as part of this experiment proved that the emissions of such exhaust gas ingredients as SO_2, NO, and HCl depend on the sulfur, nitrogen, and chlorine content in the combusted solid fuel. On the other hand, the emission of carbon monoxide CO depends on the level of humidity of the solid fuel. It was noticed that using fuel additives and essential solid fuels increases CO_2 emissions regardless of the fuel type. Combustion modifiers intensified CO_2 emissions to a

greater extent during the combustion of coal fuels than wood biomass, i.e., 6 mm wood pellets and blended firewood. The CO emissions were reduced after using combustion additives for all solid fuels selected for the tests. The most significant differences in reducing CO emissions in exhaust gases were recorded after using additives when burning mixed firewood and 25–80 mm hard coal. The decrease in carbon monoxide emissions is associated with increased carbon dioxide emissions as the CO/CO_2 balance shifts in fuel combustion. Shifting the CO/CO_2 balance towards increasing carbon dioxide emissions is an environmentally beneficial effect. This proves that a given fuel is burned to a greater extent. In turn, the most significant reduction in nitrogen oxide NO emissions was observed after using combustion additive No. 4 for the combustion of all selected fuels. Comparing the NO emissions in exhaust gas from coal-based biomass fuels, it was noted that the fuel additives reacted with all coals. Their combustion resulted in an increase in NO emissions compared to biomass. SO_2 emissions after the use of fuel additives were also reduced. The greatest decrease in SO_2 emission was found in the burning process of hard coal of various granulation with the addition of activators, compared with the tests without their participation. In the case of burning wood biomass, no significant reduction of SO_2 emissions was noted. The opposite situation was seen in the case of HCl emissions. A insignificant increase in the concentration of hydrogen chloride in the exhaust gas was found after using three out of four tested additives for the combustion of solid fuels, marked with numbers 2, 3, and 4. It can be explained by the fact that chlorine occupied a significant mass share in the additives' composition.

Currently, solid fuels are commonly used by various groups of users to produce heat and electricity. To reduce the refusal impact of exhaust gases on the earth, many catalysts have been developed to reduce the nuisance of burning a given fuel. The oxidation of tar products and soot at the location of their creation, i.e., in the central heating boiler, destroys many by-products resulting from incomplete burning of coal and other solid fuels, which are carcinogenic, mutagenic, and toxic. In addition to carbon monoxide, PAHs and solid particles in the form of soot should be mentioned here. An essential benefit of limiting soot pollution is minimizing the danger of its ignition in chimney ducts, which cuts the cause of fires and damage to structural divisions of buildings. In addition, its accumulation on the walls of an installation reduces the chimney draft, which makes it difficult to discharge exhaust gases from the burning chamber and increases the concentration of toxic carbon monoxide in the exhaust gases.

The experiments showed that apart from the additives themselves, a control and supervision technique should be used to evaluate the profitability and upgrade the efficiency of energy production and distribution after using a given fuel additive. Implementing solid fuel activators on a large scale should also entail research on the emission of dioxins and furans, which may be emitted in increased amounts under the influence of some components contained in combustion modifiers.

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