



Article Ignition and Emission Characteristics of Waste Tires Pyrolysis Char Co-Combustion with Peat and Sawdust

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Abstract: The pyrolysis processing of waste tires is a promising technology for obtaining products with high marginality. One of the possible methods of solid pyrolysis product utilization is its combustion for energy production, but this is complicated by poor reactivity and sulfur emissions. The combustion of char together with more reactive fuels could solve this problem. The current study is devoted to the combustion characteristics of waste tires pyrolysis carbon residue mixed with biomass: pine sawdust and peat. The oxidation characteristics in thermal analyzer conditions were found to change insignificantly. In contrast, 15 wt% of peat and sawdust additives was found to decrease ignition delay times in realistic conditions of combustion at 800 °C by 42 and 78%, respectively, while the SO₂ emissions also dropped by 73 and 52%, respectively. The extra sulfur was found to be contained in ash residue in the form of CaS and CaSO₄. While increasing peat concentration from 5 to 15 wt% was found to have almost no effect, the same increase for sawdust resulted into an almost proportional decrease in ignition delay times. The results obtained could be used for the integration of waste tires pyrolysis char mixtures with peat or sawdust into the energy sector.

Keywords: waste tires; pyrolysis char; biomass; ignition; combustion; gas-phase products; sulfur

1. Introduction

Pyrolysis is promising technology for end-of-life waste tires' utilization, which allows us to obtain different products from formed char such as inkjet, carbon black, etc. [1] However, the most simple and feasible solution for waste tire char (WTC) application with very high market capacity is still its incineration for energy production [2]. Widespread application of this solution is limited by poor combustion reactivity of WTC, comparable with anthracite [3,4] or coal pyrolysis semi-coke [3,5]. This is caused, primarily, by the low content of volatile matter (usually, lower than 10 wt.% [2]).

Possible solutions to this problem are using WTC together with other fuels with high reactivity. One of such highly reactive fuels could be liquid-phase substances such as pyrolysis oil [6,7], waste turbine lubricant [8,9], or other petrochemicals [8,10]. Such substances showed good performance in combination with anthracite [6] and filter cake [10] (byproduct of coal enrichment). In [6], the combustion characteristics of anthracite with up to 25 wt.% of a waste tire pyrolysis oil additive were determined. The minimal ignition temperatures and ignition delay times were found to decrease by up to 104 and 75%, respectively. Moreover, it was found that even 5–10 wt.% of additive resulted in the significant improvement of both ignition and emission characteristics. Similar results were



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). reported for filter cake with waste turbine oil in the composition of organic coal–water slurry [8]; 15 wt.%. of this additive decreased ignition delay time by approximately 25%. However, implementation of such solution is complicated by the very different approach to the combustion of solid and liquid fuels. Thus, the majority of such studies propose using coal-water slurry [8,9,11] or complex fuel treatment system [12], which require significant investments into power plant modification.

While solid fuels are usually less reactive compared to liquid ones, using an additive in the solid phase is simpler in terms of the equipment used. However, the ignition and combustion phenomena for solid fuels are more complex, which determined the predominantly empirical and experimental character of the corresponding studies and the lack of reliable prediction approaches. The synergetic effect occurring during such mixture combustion is usually attributed to the additional heat generated during volatile matter releasing and catalytic effect of biomass ash components [13], but its prediction is very difficult. The quite-simple mechanism for waste tires and petroleum gasification residue combustion, reported in [14], includes 11 consequent and parallel reactions. This results in quite contradictive data, published by different groups. So, in [15], the anti-synergistic effects were reported for the burnout stage of the lignite and bituminous coals mixed with torrefied cornstalk, while opposite was reported in [16] regarding biomass-plastic mixed with coal. However, the majority of studies in the field still reported some positive effects during co-combustion [16–20] expressed in the lower activation energy values or ignition and combustion indices. Still, the actual effect varied for different studies. It is widely assumed that actual processes occurring during the co-combustion of biomass with coal or char are very complex. While the major method of researching such processes is thermal analysis, studies using other equipment (such as the circulating fluidized bed in [15] or the drop tube furnace in [19]) are extremely useful.

Additionally, co-combustion of traditional solid fuels with biomass is widely assumed to permit the reduction of some anthropogenic gases emissions (for example, sulfur oxides [21,22]) compared to initial fuels. Some research, in contrast, reported an increase in some emissions. Thus, in [15,19], increases in NO_x emissions were reported. Moreover, the lower calorific value of such blends results in lower combustion temperature, which, in turn, is promote sulfur sequestration [21] and hamper thermal NO_x formation. Thus, the co-combustion of waste tire char with biomass is expected to allow for the reduction in both ignition delay times and anthropogenic gas emissions. However, lack of corresponding experimental data in this field does not allow for precise numerical evaluation of the possible characteristics of the combustion of such fuel compositions.

The current article is devoted to the study on the ignition and combustion characteristics of the WTC in composition with two widespread biomass samples—peat and pine sawdust—in different mass ratios with up to 15 wt.% additive. The study was realized using both the thermal analyzer and experimental setup with conditions close to actual energy equipment in order to formulate possible mechanism of their action.

2. Materials and Methods

2.1. Initial Sample

As the initial sample of solid fuel, a carbon residue obtained as the result of a steam pyrolysis of pelletized-to-3–4 mm spent tires of large-sized vehicles of the Belaz brand for special purposes was used. The methodology of pyrolysis was given in our previous work [23].

The obtained sample of the carbon residue was subjected to mechanical grinding (using a ball mill) with subsequent fractionation in sieves with a cell size $< 80 \ \mu m$.

Technical characteristics (calorific value, moisture, ash, and volatile matter content) were determined using standard techniques: ISO 1126: 2015 "Rubber compounding ingredients-Carbon black-Determination of loss on heating"; ISO 1125: 2015 "Rubber compounding ingredients-Carbon black-Determination of ash content"; ISO 562: 2010 "Hard coal and coke-Determination of volatile matter"; and ISO 1928: 2020 "Coal and

coke-Determination of gross calorific value". The elemental composition was defined using Vario Micro Cube CHNS analyzer (Elementar, Langenselbold, Germany). The technical characteristics and elemental compositions determined are presented in Table 1.

Table 1. Technical characteristics and elemental compositions of the waste tire pyrolysis carbon residue.

Parameter	Value	
Moisture content ^a , wt%	0.5	
Ash content ^d , wt%	15.6	
Volatile matter content ^{daf} , wt%	8.8	
Calorific value (lower), MJ/kg	27.2	
Elemental composition	n ^{daf} , wt%	
C	94.7	
Н	1.0	
Ν	0.3	
S	4.0	

^a—analytical mass; ^d—dry mass; ^{daf}—dry ash-free mass.

From comparison of the technical characteristics and elemental composition of the studied sample (Table 1) with other solid fuels, it could be seen that the obtained carbon residue was similar to oil coke [24], as well as subbituminous coal [25] with a high sulfur content [26].

Table 2 presents the elemental composition of the ash of the studied carbon residue determined via atomic emission spectroscopy using the ICAP 6300 Duo analyzer (Thermo Fisher Scientific, Waltham, MA, USA).

№	Element	Concentration, mg/kg	Relative Composition, wt%
1	Al	8833.18	1.68
2	Ba	50.14	<0.1
3	Ca	12,184.33	2.32
4	Cd	3251.61	0.62
5	Co	63.13	<0.1
6	Cr	17.14	<0.1
7	Cu	2985.25	0.57
8	Fe	4642.40	0.88
9	K	5903.23	1.12
10	Li	252.53	<0.1
11	Mg	10,119.82	1.93
12	Mn	69.68	<0.1
13	Мо	20.28	<0.1
14	Na	6802.76	1.30
15	Ni	232.26	<0.1
16	Pb	221.29	<0.1
17	Si	201,659.00	38.41
18	Sr	450.69	<0.1
19	V	24.24	<0.1
20	W	59.91	<0.1
21	Zn	267,096.80	50.88
22	Zr	24.70	<0.1

Table 2. Elemental composition of the ash residue.

Figure 1 presents SEM images of the particles of waste tire pyrolysis carbon residue obtained by scanning electron microscopy using JSM-7500F microscope (JEOL, Akishima, Japan).

The particles of the carbon residue sample were characterized by an array of spherical agglomerates with size less than 20 μ m. These agglomerates, in turn, consisted of a large number of smaller nanodispersed particles.



Figure 1. SEM image of studied carbon residue particles.

According to [27], the formation of agglomerates was associated with the occurring van der Waals forces, since the particles of the studied carbon samples were less than 1 μ m. According to [28], the formation of agglomerates could be associated with the continuous oxidation of the main elements of rubber (the rubber itself and other resin-like products formed during steam gasification), which acted as a binder during vulcanization.

As biomass additives to the carbon residue, peat (Sukhovsky deposit, Tomsk region, Russia) and pine sawdust were used. The latter was received from the timber enterprise LLC "Sibirskiy Biougol" (Belyai, Tomsk region, Russia). Before analytical studies, the samples were subjected to grinding using a cutting mill, which was followed by fractionation on sieves with 200 mkm mesh size.

Table 3 presents the technical characteristics and the elemental compositions of the biomass samples used. Moisture, ash, and volatile matter content, as well as combustion heat, were determined using ISO/FDIS 18134-3 "Solid biofuels—Determination of moisture content—Part 3: Moisture in general analysis sample"; ISO 18123 "Solid biofuels—Determination of volatile matter"; and ISO 18122: 2022 "Solid biofuels—Determination of ash content", ISO 18125: 2017 "Solid biofuels—Determination of calorific value", respectively. The elemental composition was determined in the same way as for the carbon residue sample.

Table 3. Characteristics of studied biomass samples.

Sample	Humidity, W ^a , wt%	Ash Content A^{d} , wt%	Volatile Matter Content V ^{daf} , wt%	Calorific Value Q_i^a , MJ/kg	C ^d	$\begin{array}{c} {\hbox{ Elemental }} \\ {\hbox{ Composition }}^{\rm d}, {\hbox{ wt}}\% \\ {\hbox{ d }} \\ {H}^{\rm d} \\ {N}^{\rm d} \\ {S}^{\rm d} \end{array}$			0 d
Peat	9.9	22.8	74.8	11.8	40.2	4.9	2.8	0.2	29.2
Sawdust	7.0	1.6	83.4	18.1	51.7	6.5	0.2	-	40.1

^a—analytical mass; ^d—dry mass; ^{daf}—dry ash-free mass.

The composition of the macrocomponents of the ash of peat and pine sawdust (SiO₂, SO₃, Al₂O₃, Fe₂O₃, CaO, MgO, TiO₂) were determined according to ISO/TS 16996: 2015 "Solid biofuels–Determination of elemental composition by X-ray fluorescence". To de-

termine the content of silicon (SiO₂) and sulfur oxides (SO₃) in the sample, a gravimetric (weight) method was used. The complex method was used for determination of aluminum (Al₂O₃), iron (Fe₂O₃), calcium (CaO), and magnesium oxides (MgO) content. To determine the content of TiO₂, a spectrophotometric method was used. The results of determining the elemental composition of the ash are presented in Table 4.

Table 4. Elemental composition of the ash residue of peat and pine sawdust.

6 amm 1 a			The Compos	ition of the	Main Compo	onents of As	h, %
Sample -	SiO ₂	$AL_2O_3 + TiO_2$	Fe ₂ O ₃	SO ₃	CaO	MgO	Other (K_2O , Na_2O , P_2O_5 et al.)
Peat	3.8	7.6	16.2	0.2	54.3	1.6	16.3
Sawdust	6.7	2.1	1.5	2.8	31.1	4.3	51.5

Figure 2 presents SEM images of particles of the studied samples of peat and pine sawdust obtained via scanning electron microscopy using the JSM-6000C microscope (JEOL, Akishima, Japan).



Figure 2. SEM images of the studied peat (a) and pine sawdust (b) samples.

It can be seen that both particles of peat (Figure 2a) and sawdust (Figure 2b) were characterized by an uneven surface and either a spherical or an oblong cylindrical shape. The particles of peat had a more regular form with a small number of inclusions and irregularities, while the opposite was true for sawdust. This additionally contributed to the higher reactivity of latter due to larger specific surface area and smaller diffusional resistance.

2.2. Fuel Mixtures Characteristics

A partial replacement of up to 15 wt% of carbon residue obtained by the pyrolysis of waste tires of heavy-duty equipment on pine sawdust or peat was applied. Fuel composites (carbon residue/peat or pine sawdust) were subjected to mechanical mixing with various mass ratios (5–15 wt%) to homogeneous state. The technical characteristics and elemental compositions of the studied fuel composites were determined by the calculation method using the superposition principle and are presented in Table 5. The averaged characteristics of the mixtures of two solid fuels with known mass fractions were determined using Equation (1):

$$X_{mix} = b_1 X_1 + b_2 X_2 = b_1 X_1 + (1 - b_1) X_2,$$
(1)

where X_{mix} —characteristic of the mixture; b_1 and b_2 —mass fraction of the first and second components of the mixture, respectively; X_1 and X_2 —characteristic of the first and second component, respectively.

Sample	Moisture Content W ^a , %	Ash Content A^{d} , %	Volatile Matter Content V ^{daf} , %	Calorific Value Q_i^r , MJ/kg	Elem C ^d	nental (H ^d	Compo N ^d	sition, S ^d	wt% O ^d
5% peat	1.0	15.9	12.1	26.4	73.8	1.0	0.3	3.1	5.9
10% peat	1.4	16.3	15.4	25.7	72.0	1.2	0.5	2.9	7.1
15% peat	1.9	16.7	18.7	24.9	70.3	1.4	0.6	2.8	8.3
5% pine sawdust	0.8	14.9	12.5	26.7	74.4	1.1	0.2	3.1	6.4
10% pine sawdust	1.2	14.2	16.3	26.3	73.2	1.4	0.2	2.9	8.2
15% pine sawdust	1.5	13.5	20.0	25.8	72.0	1.7	0.2	2.7	9.9

Table 5. Calculated characteristics of studied fuel composites.

^a—analytical mass; ^d—dry mass; ^{daf}—dry ash-free mass.

2.3. Thermal Analysis

Thermal analysis was used to determine the parameters of the oxidation of the studied samples. It was performed via STA 449 F5 Jupiter analyzer (Netzsch, Selb, Germany). The analysis was carried out under the same conditions at 10 °C/min heating rate in an air environment at 150 mL/min air flow rate. The experiments were performed in the temperature range 50–800 °C. The mass of the studied sample was 10 mg.

2.4. Research on Ignition and Combustion

The study on ignition and combustion was carried out using an experimental setup for solid fuel burning (Figure 3).



Figure 3. Simplified scheme of the experimental setup for solid fuel burning.

The principal scheme and detailed description of this setup are given in our previous work [6]. The studied ignition and combustion were visualized via FastCam Mini UX100 high-speed camera (Photron, San Diego, CA, USA). The reactivity of studied fuels and fuel mixtures was evaluated using ignition delay time τ_i , which was determined using these recordings.

The compositions of gas-phase combustion products (CO, CO₂, SO₂, and NO_x) were determined using a flow-through gas analyzer. The flow rate of passing gases was 3 L/min, and the frequency of the sensor's scanning was 0.33 Hz.

The experiments were carried out in identical and well-reproducible conditions at temperature (temperature in the muffle furnace) $T_G = 800$ °C.

After each measurement (in order to ensure the accuracy of measurements and complete removal of the reaction products from the furnace), the gas analyzer and the furnace was blown by air from a compressor. For each sample, at least 10 repeated experiments were carried out.

2.5. XRD Analysis of Ash Residue

XRD analysis of the ash residues obtained as a result of sample combustion (for the initial sample of carbon residue and samples containing 15 wt% of peat and pine sawdust) was carried out using the X-ray diffractometer Shimadzu XRD 7000S (CuK α -radiation). The sample of the ash residue is evenly distributed in the standard aluminum cuvette, with subsequent studying in the interval between 10 and 90 degrees and with a goniometer step of 0.02 degrees.

3. Results

3.1. Thermal Analysis

Figure 4 presents the TG and DTG profiles of the studied samples of the waste tire pyrolysis carbon residue and the fuel composites based upon it. The parameters of the oxidation, which were calculated using Figure 4 data, are presented in Table 6.

According to Figure 4, the intensive oxidation of the samples of waste tire pyrolysis carbon residue took place in the temperature range 510–636 °C (T_i and T_f , respectively (see Table 6)). Adding peat has a significant impact on the completeness of the oxidation of this mixture. So, an increase in the fraction of peat to 15% in the mixture led to an increase in the ash mass of 4.1%. The reason for this is the large ash content of the peat compared to the studied carbon residue (22.8 and 15.5%, respectively). The addition of sawdust did not have a significant effect on the completeness of its oxidation (Table 6).

It is worth noting that the addition of biomass (either peat or sawdust) results in the change in the form of the TG profiles with the more prominent low-temperature area of low-boiling components' oxidation such as hemicellulose (200-370 °C), cellulose (275–400 $^{\circ}$ C) and lignin (over 400 $^{\circ}$ C). The values of the onset of intensive oxidation were in good correspondence with the increase in the fraction of biomass in the fuel composite (Table 6). The profile of the waste tire pyrolysis carbon residue has a monomodal form with a characteristic maximum temperature of 565 °C and an oxidation rate of 9.26%/min $(T_{max} \text{ and } w_{max}, \text{ respectively})$. However, when the biomass was added, an additional peak appeared in the form of a characteristic shoulder of the main DTG profile with the appearance of obvious thermal decomposition phase in the low temperature zone. An increase in the fraction of the biomass in the composition led to a decrease in the rate of intensive oxidation in both cases (by 0.6 and 1.7%/min, respectively), which was associated with an increase in the rate of the volatile matter release in the low-temperature region. Thus, the addition of biomass to the fuel composition led to the expansion of the oxidation area to the left by 8-30 °C on average and an increase in the maximum temperature of intensive oxidation.

Table 6. Oxidation paran	neters of char and fuel co	ompositions by thermal analy	vsis.
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Component	Mass, wt%	T_{i} , °C	$T_{f'} \circ \mathbf{C}$	w _{max} , %/min	T_{max} , °C	∂ <i>m</i> , %
Char	100	-/510.3	-/635.5	9.26	565.1	91.52
	5	302.5/515.1	471.1/632.5	8.69	562.5	88.02
Peat	10	277.5/505.1	460.6/630.4	8.31	567.5	87.4
	15	272.5/502.5	452.5/635.1	7.55	570.1	86.11
	5	325/507.5	472.5/637.5	0.6/7.4	335/575	89.66
Pine sawdust	10	320.1/500.1	447.5/632	1.22/7.7	335/567.5	91.45
	15	317.5/502.5	452.5/627.5	1.87/7.5	332/570.1	90.52



Figure 4. TG (**a**,**b**), DTG (**c**,**d**), and DSC (**e**,**f**) profiles of the oxidation of the studied samples of waste tires pyrolysis carbon residue and fuel composites based on it with different contents of peat (**a**,**c**,**e**) and pine sawdust (**b**,**d**,**f**). Air flow rate—150 mL/min; heating rate—10 °C/min.

Such results are in good agreement with the literature data on the co-combustion of the char/biomass [17], char/waste [16,18], char/coal [19,20,29] or coal/biomass [15] blends. While interactions between components are widely acknowledged [15–20,29], the reasons for such behaviors are yet to be determined due to their extreme complexity. The different oxygen adsorption rates are proposed to be the possible reason by Liu Y. et al. [15]; however, no proofs were presented. The interactions between volatile matter released and solid-phase components of the fuel are considered to be the key factor of this process

because different volatile matter content and features of its releasing stage were the clearest differences between peat and sawdust behavior according to thermal analysis results.

According to the above, it should be noted that the application of biomass in the form of peat and pine sawdust did not lead to significant shifts in the temperature characteristics of the oxidation of a carbon residue. This result indicates the stable combustion, and heat transfer to the heat exchange surfaces, regardless of the fraction of the organic component in the nominal mode of equipment operation.

3.2. Ignition and Combustion

Figure 5 presents the results of the ignition time delay (τ_i) determination of the studied samples using an 800 °C heating medium in the combustion chamber.



Figure 5. The ignition delay times of the studied fuel samples at heating medium temperature $T_g = 800 \text{ }^\circ\text{C}$.

According to Figure 5 data, an increase in the content of biomass in the form of peat and pine sawdust in the fuel composite led to nonlinear reduction in the ignition delay times in comparison to the reference sample of waste tires pyrolysis carbon residue. The introduction of 5 wt% of either peat or sawdust additives resulted in a sharp drop of ignition delay time by approximately 40% from ~0.4 s to 0.24 s. The difference between peat and sawdust at such a concentration was insignificant. Further increasing peat additive concentration did not result in a strong effect on ignition delay time; the sample with 15 wt% of peat produced a smaller ignition delay time than the sample with 5 wt% by less than 5%. In contrast, increasing the concentration of the sawdust additive from 5 wt% to 15 wt% resulted in an approximated 2.5-fold decrease in the ignition delay time. Compared to the initial sample, the strongest effect was achieved when adding pine sawdust (from 44 to 78%, depending on the content). The reducing of the τ i parameter was explained by an increase in the reactivity of this mixture due to the significantly higher content of volatile substances (by 9.4 wt%), lower moisture content (by 2.9 wt%), and the higher overall ignition reactivity of sawdust (Table 5). The latter could be caused by the higher content of hemicellulose and cellulose in sawdust compared to peat, which has a high content of the less reactive lignin.

Figure 6 presents typical frames of ignition and the consequent combustion of the fuel samples. Several stages of the combustion process could be distinguished using the presented images. The first ones, which are usually distinguished in literature [30]—inert heating and moisture removal—are not presented in Figure 6. The latter stages—simultaneous releasing and combustion of volatile matter with solid carbon oxidation—took place at the moment of ignition. The ignition in this case could be characterized by the following mechanism: volatile matter (mainly consisting of substances of organic origin

such as hemicellulose, cellulose, and lignin) form a gas cloud in the vicinity of the fuel sample, which heats the fuel and thus promotes the stable fuel combustion. The results are in good agreement with the thermal analysis data (Figure 4), which revealed an additional exothermic reaction of the organic component decomposition in the low temperature zone. The glowing at the moment of ignition was localized either at the top or in the bulk of the sample. This indicated the significant contribution of both heterogeneous reactions on the sample's surface and homogeneous reactions in its vicinity. Intensity of glowing increases with time and its distribution becomes more uniform. While the contribution of gas-phase reactions near the sample surface increases with the volatile matter content in the mixture, the glowing distribution for the samples with higher content of additives was more uniform. However, this effect was quite weak.



Figure 6. Cont.



Figure 6. Images of typical stages of studied fuel ignition and combustion.

The mechanism of ignition of the samples containing peat was similar to the respective mechanism of samples containing sawdust but was characterized by the less intensive release of heat during the initial stage of thermal decomposition of fuel. This is also consistent with the thermal analysis data (Figure 4). It is also worth noting that an increase in the content of peat beyond 5 wt% in the fuel composite did not lead to a significant reduction in the ignition delay time. While the ignition delay times for samples with 5 wt% additives were quite close, and opposite was true for samples with 15 wt% additives (the ignition delay times for the sample with 15 wt% of peat were almost three times higher than those for the sample with 15 wt% of sawdust); the general features of combustion, according to video recording (Figure 6), were quite similar for all of them, indicating the major contribution of the additive in terms of enhancing reactivity without affecting general mechanism.

3.3. Gas-Phase Combustion Products

Figures 7 and 8 present the profiles characterizing the release of gas-phase combustion products (CO, CO₂, NO_x, and SO₂) of studied fuel composite samples based on the waste tires pyrolysis carbon residue and biomass additives in the form of peat and pine sawdust.



Figure 7. Dependences of the gas-phase combustion products release on time for the studied samples of waste tire pyrolysis carbon residue and fuel composites with peat additive: (**a**)—carbon monoxide; (**b**)—carbon dioxide; (**c**)—nitrogen oxide; (**d**)—sulfur oxide.



Figure 8. Dependences of the gas-phase combustion products release on time for the studied samples of waste tire pyrolysis carbon residue and fuel composites with pine sawdust additive: (a)—carbon monoxide; (b)—carbon dioxide; (c)—nitrogen oxide; (d)—sulfur oxide.

The analysis of the data presented in Figure 7 allows us to identify the significant effect of peat on the character of the gas-phase combustion product's formation. With an increase in the content of peat in the fuel composite, a decrease in the intensity of carbon monoxide formation has been observed, which corresponded to the elemental composition of the initial components—in particular, lower carbon content of both sawdust and peat in comparison with carbon residue. However, the increase in the peak concentrations of nitrogen oxides observed was connected to the intensification of the fuel composite combustion rate. Thus, an increase in the peak concentration of nitrogen oxides for waste tires pyrolysis carbon residue samples with the peat additive could be associated with the intensive formation of thermal nitrogen oxides at the initial stage of combustion.

The concentration profiles of sulfur oxide had a bimodal form with an obvious trend of reducing emissions with an increase in the fraction of biomass components. The greatest effect was achieved at the carbon residue combustion stage and was expressed in both the general narrowing of the emission range (starting from 5 wt% of peat additive) and the decreasing of the peak concentrations. Moreover, it was observed that at higher concentrations of peat additive, these effects were stronger. The reduction in concentration of sulfur oxides was caused by its binding and conservation in solid form into ash residue [22].

It was determined that the effect of pine sawdust on concentration profiles of nitrogen and sulfur oxides was very much similar to the earlier-described effect of peat. It should be noted that the profiles of gas-phase combustion products' formation in the form of carbon monoxides had a characteristic type and were in good correlation with the elemental composition of the initial components, i.e., the waste tires pyrolysis carbon residue and pine sawdust.

Table 7 presents the ratios of gross emissions of gas-phase combustion products. Here, SREF is the initial waste tires carbon residue; SMOD is a fuel composite with corresponding additive.

Table 7. The ratio of gross gas-phase combustion products' emission from waste tire pyrolysis carbon residue with and without peat and pine sawdust additives.

	Biomass Additive							
		Peat Pine Sawdu						
Fraction of Additive, %	Gas-Phase Combustion Product, S _{mod} /S _{ref}							
	СО	CO ₂	NO _x	SO_2	CO	CO ₂	NO _x	SO ₂
5	0.97	0.95	1.86	0.58	1.02	1.01	1.24	0.52
10	0.69	0.73	1.82	0.27	1.03	1.04	1.26	0.52
15	0.53	0.58	1.85	0.27	1.07	1.06	1.27	0.48

It could be seen that the effect of thermal nitrogen on overall nitrogen oxide emissions was almost independent of concentration and the type of biomass additive. An essential conclusion from the data presented is that 5 wt% additive in the form of peat and 10 wt% additive in the form of pine sawdust were optimal for producing fuel with low sulfur oxide emissions. A further increase in fuel additive was found to have a weak effect on the environmental characteristics of such fuel but, according to thermal analysis results, would cause a stronger negative effect on the energy value of the fuel composite. Similar values were reported for torrefied biomass/coal blends [15]. The change in CO emissions could be connected to different reactivities of volatile matter components. The major mechanism of SO₂ emissions reduction was attributed to lower sulfur content in biomass, despite small synergetic effects which could be attributed to interactions between ash components and gas-phase combustion products. The NO_x emissions increase is quite typical for such fuel mixtures, as is reported in [15,19], which is connected to different nitrogen contents in char and volatile matter. The same assumptions are also true for the current study.

3.4. XRD Analysis of Ash Residue

The XRD-spectra for ash formed after the combustion of the initial and modified fuel composites (with 15 wt% peat and pine sawdust additives) are presented in Figure 9. The results observed allow us to identify that the major components of ash were calcium sulfide, calcium sulfate, and zinc oxide. While Ca is widely considered to be one of the major components of ash residue of many different types of biomasses, it is usually considered to present in the form of oxide [31]. However, regarding coal-biomass blends, several instances of sulfur-containing solid-phase products in the form of CaS and CaSO₄ are present in the literature [22]. In turn, the presence of Zn in the form of ZnO is quite typical for ash of both waste tires and its pyrolysis char [1]. Despite XRD-data not allowing us to obtain a precise evaluation of each components in the form of sulfides and sulfates for fuel compositions with biomass additives. This is assumed to be the major cause of the decrease in the concentration of sulfur-containing gas-phase combustion products, albeit not the only one. A similar mechanism was earlier reported in [22] for mixtures of coal with woody biomass.



Figure 9. XRD-spectra of ash residue formed after combustion of initial waste tire pyrolysis carbon residue (red line) and fuel composite with peat (blue line) and pine sawdust (black line) additives.

4. Discussion

The complex combustion and gas-phase products emission characteristics of waste tires pyrolysis carbon residue with peat and pine sawdust additives with concentrations up to 15 wt% were determined. The thermal analysis data revealed that the oxidation characteristics of mixtures were similar to the oxidation profiles of their individual components, indicating weak interactions between components at low heating rates. This is strongly connected to low reaction rates in conditions of thermal analyzer and the low diffusional resistance of oxygen access to the surface of the sample. However, we also observed the formation of additional low-temperature stage during oxidation in the range between 250 and 400 °C, which is typical for hemicellulose, cellulose, and lignin-typical components of biomass of different types. The combustion characteristics, in contrast, revealed the strong synergetic effects between waste tire pyrolysis carbon residue and biomass additives, as expressed in the lower ignition delay time values at 800 °C heating medium—up to 78% at 15 wt% of pine sawdust additive and 44% at 15 wt% of peat additive. Possible reasons could be connected to features of oxygen adsorption to the surface of the sample during the volatile matter releasing and char combustion stages, as well as the additional heat generated by the release and oxidation of volatiles from biomass additives (peat and sawdust). While for peat, increasing the additive concentration did not result in lower ignition delay time—the difference between 5 and 15 wt% additive was less than 5%—the opposite was observed for pine sawdust—the higher concentration corresponded to the lower ignition delay time (the ignition delay time dropped by 60% from 2.2 to 0.9 s with the increase in the sawdust additive from 5 to 15 wt%). This was caused by the higher volatile matter content and calorific value of the sawdust compared to the peat. The mechanism of such behavior was proposed based on the analysis of high-speed video camera recording images. The gas-phase combustion products' concentration profiles revealed both higher peak concentrations and gross emissions of nitrogen oxides, while the opposite was true for sulfur oxide. Such behavior was attributed to the higher reactivity and combustion rate of fuel composites and the altered contribution of different factors such as nitrogen content in volatiles and char, as well as the binding of sulfur to solid components of ash residue. The latter was proved by XRD analysis results, which indicated high concentrations of calcium sulfides and sulfates in the ash residue formed after combustion. It was also observed that the most significant contribution to sample ignition, combustion, and emission characteristics was attributed to the general reactivity of the additive and its content of volatile matter. Considering different aspects of biomass additive application, 5 wt% of peat and 10 wt% of pine sawdust were recommended to be applied as additives for waste tires pyrolysis carbon residue combustion.

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