



Article Justification of the Reduction Possibility of Sulfur Oxides and Fly Ash Emissions during Co-Combustion of Coal and Waste from Woodworking Enterprises

Stanislav Yankovsky ^{1,2,*}, Anton Tolokol'nikov ¹, Alexander Gorshkov ^{1,2}, Albina Misyukova ^{1,2} and Geniy Kuznetsov ¹

- ¹ The Butakov Research Center, National Research Tomsk Polytechnic University, 634050 Tomsk, Russia; anton.tolokolnikov1@gmail.com (A.T.); asg47@tpu.ru (A.G.); adm14@tpu.ru (A.M.); kuznetsovgv@tpu.ru (G.K.)
- ² Research Laboratory of Catalysis and Conversion of Carbon-Containing Materials to Produce Useful Products, Institute of Energy, T.F. Gorbachev Kuzbass State Technical University, 650000 Kemerovo, Russia
- * Correspondence: jankovsky@tpu.ru

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Copyright: © 2021 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/). Abstract: In this work, we experimentally investigated the effect of widespread biomass (woodworking waste-pine sawdust) in the composition of mixed fuel, formed also using the widespread steam coals metalignitous (D) and lean (T), on the concentration of sulfur, nitrogen and carbon oxides in flue gases. Investigations of composite fuels with a mass of at least 5 g were carried out in a reactor with continuous recording of the composition of the flue gases formed during the thermal decomposition of the investigated fuels. Thermal decomposition of fuels was carried out in the temperature range from 293 K to 873 K. It was found that an increase in the proportion of wood components in mixed fuels based on two different coals from 10% to 50% leads to a significant decrease in the concentration of sulfur oxides from 11% to 95.8% relative to the concentration of the formation of sulfur oxides in a homogeneous coal, respectively. It was found that an increase in the proportion of the wood component in the mixture with grade D coal up to 50% leads to a significant increase in the content of calcium sulfates (45.1%) and aluminum (43.2%) in the blended fuel. The increase in the content of these salts in the ash of mixed fuels based on T coal and wood is 35.1% and 38.6%, respectively. The obtained research results allowed us to conclude that woodworking wastes are an effective addition to the coals of various deposits, which would help to reduce anthropogenic-induced gas emissions when they are co-combusting in the furnaces of power boilers.

Keywords: coal; biomass; processing waste; mixed fuel; thermal decomposition; anthropogenic oxides

1. Introduction

Fossil coal has been one of the main sources of raw materials for generating heat and electricity for many hundreds of years, along with other traditional fuels [1]. In the long term, according to statistics [2,3], the share of coal in the production of heat and electricity in the global structure of the fuel and energy complex will be (according to various estimates) from 31% (planning horizon—2040) [2] to 38% (planning horizon—2050) [3]. The key prerequisites for this are significant reserves of coal, their low cost, as well as the developed infrastructure of production, delivery, and storage. However, coal application in the energy sector is associated with significant emissions of sulfur, carbon, and nitrogen oxides, as well as fly ash [4,5] in the coal combustion products.

Numerous attempts to replace fossil fuels with alternative (renewable) energy sources [6–8], such as solar [9], wind [10], and geothermal [11], have not led to a significant change in the share of coal in the global energy balance over the past two decades [12–14]. However, many countries (primarily the European Union countries) consider biomass as a separate, environmentally friendly type of fuel [9–11]. Increased attention to the use of

biomass in the energy sector is due to the fact that the latter practically does not contain sulfur in its mineral composition and is a carbon-neutral fuel [15]. It is important to note that the world economy is largely dependent on energy prices, and therefore the use of a renewable energy source—biomass [16–18]—should have a positive impact on the energy sustainability of each individual state. In addition, it should be emphasized that only the accumulated volume of wood waste in the world is significant (from 7% to 40% of the wood processing amount per year) [19], and therefore an active search is underway for ways to effectively dispose of it and convert it into a sustainable energy source [20,21]. At the same time efforts have also been undertaken to exploit waste wood by-products towards novel composites, contributing to reduced energy input [22]. The types of biomass that have potential applications in the energy sector vary depending on the region. For example, rice husks or straw [23] are typical for the countries of the Asian region, maize [24] for North America, and palm biomass [25], grape cake [26], and olive seeds [27] are typical for southern Europe countries and the Mediterranean region.

Direct combustion of large amounts of biomass in the furnaces of high-capacity power plants is difficult due to its heterogeneity and lower calorific value relative to coal and gas [28]. In this regard, a promising direction for the effective use of biomass in the energy sector is its application as components of mixed fuels with coals; for example, organo-coal-water fuels [29,30] or solid fuel mixtures [31,32]. Biomass [33] and municipal waste [34,35] are mainly used [36] as the second component in mixed fuels [37].

It was established [5,33,34] that the most promising power engineering biomass is wood and waste from its processing—sawdust. Attempts to effectively use sawdust in the energy sector [35,38] have been made repeatedly (for example, [39,40]).

Currently, there are known examples [41,42] of boiler units designed for co-combustion of coal and biomass [43]. Analysis of the application efficiency of sawdust (or pellets based on it) as the main type of biomass in a mixed fuel shows that one of the most promising technologies is direct combustion of a mixture of crushed coal and wood in a pseudo-liquefied layer. The most striking example of such co-combustion of coal and wood waste is the 550 MW power plant [40] located in Helsinki, Finland.

To date, the results of experimental analysis of the wood biomass effect on the concentration of greenhouse gases in the combustion products of its mixture with coal have been published quite a lot (for example, [44–46]). However, the mechanisms of physical and chemical processes occurring during the interaction of the products of thermal decomposition of the main components of mixed fuels (coal and wood) have not been reliably established [29,47]. Therefore, the theoretical foundations of technologies for co-combustion of coal and biomass have not been developed.

The main problem is that analysis of gaseous combustion products in many experiments (for example, [48,49]) was carried out after the complete combustion of mixtures of dispersed coals and biomass. However, the composition of the flue gases changes quite significantly as the combustion process of the initial fuels is completed, depending on the combustion conditions. Therefore, an objective (statistically based) assessment of the composition of the pyrolysis products of coal and biomass particle mixtures at the stage of their intensive pyrolysis is important.

One of the goals of the modern power engineering development strategy is to reduce the share of coal in the global structure of heat and electricity production, largely due to the fact that direct coal combustion causes significant harm to the environment. Creation of technologies that reduce anthropogenic load on the earth's atmosphere as a result of coalfired power plants operation is one of the main tasks of the world community. A promising solution to the problem of air pollution by coal combustion products is to burn it together with biomass.

This manuscript is aimed at substantiating the mechanisms of binding of anthropogenic gases during thermal decomposition of mixed fuels based on coal and woodworking waste. A completely new installation for registration of gas-phase pyrolysis products has been developed for research. In our previous works, studies were carried out using a thermogravimetric analyzer with a mass spectrometric attachment. The weighed portions of mixed fuels for thermogravimetric analysis were no more than 20 mg. Based on the studies carried out in [50], a hypothesis was put forward about the processes that can occur during the joint thermal decomposition of wood waste mixed with coals of different grades, which contribute to the sequestration of anthropogenic gases. Thermogravimetric analysis showed a significant decrease in the temperature of the onset of thermal decomposition of mixed fuels with an increase in the proportion of woody biomass in a mixture with coal up to 50%.

Gas analysis of the thermal decomposition of mixed fuels with a weight of up to 20 mg showed a significant decrease in the formation of nitrogen, sulfur, and carbon oxides. Technical analysis of the coals showed that their composition can differ significantly when examining samples with a low mass of fuel. As a result of the analysis of the results obtained, an installation was developed for determining the ignition delay times of the composite fuels. In [51], mixed fuel pellets weighing up to 1 g were investigated in various coal/wood mass ratios. Studies have confirmed the previously obtained results on the significant effect of woody biomass on a decrease in the temperature of the onset of thermal decomposition of mixed fuels with an increase in the share of the latter in wood pellets. All studies were carried out on brown coals of various deposits.

In this work, a setup was used to study the gaseous products of thermal decomposition of mixed fuels based on thermal coal mixed with wood waste. The developed experimental setup made it possible, for the first time, to carry out uniform heating of a fuel sample weighing up to 5 g from 293 K to 873 K, continuously measure the temperature inside the reactor with fuel, and simultaneously monitor gases every 3 s.

The volume of the ash residue obtained from the results of the experiments was sufficient for an analysis of the elemental composition by various methods, in order to establish the fact of a decrease in anthropogenic gases with the formation of agglomerates of calcium and aluminum sulfates in the ash of the fuel mixtures under study. The presented manuscript is a logical continuation of earlier studies with a new approach to substantiate the processes of binding anthropogenic-induced gases during the thermal decomposition of woodworking waste mixed with coals of various grades and deposits (firewood/coal) from 10% to 50%.

2. Materials and Methods of Experimental Research

Typical coals for the energy sector were selected as the basic components of the studied mixed solid fuels: lean (T-grade coal) (Alardinskoye field, Russia) and metalignitous (D-grade coal) (Listvyazhnoye field, Russia). These coals have a relatively low sulfur content and a high calorific value, which is why they are used at large thermal power plants. Their analogues in composition and main characteristics are coals of the Hongyang, Handan, and Huaibei grades, Northern China, and San Juan in the United States [52,53]. The biomass used was crushed wood—waste from pine processing (LLC Dzerzhinskiy LPK, Tomsk, Russia). The experiments were carried out under standard conditions in the laboratory (at an air temperature of 293 K and pressure of 101 Pa).

A method for the preparation of mixed fuels has been developed. Fuel preparation was carried out before the start of experimental studies. Lumpy coal was crushed in a two-stage grinding system, consisting of a jaw crusher and disintegrator, grinding to a fraction of less than 500 microns. The milled coal was sifted through a sieve system. The particle fraction selected for the experiments ranged from 80 microns to 200 microns. Wood processing waste was previously cleaned of bark and garbage, dried for one day to remove excess moisture at a temperature of 293 K, and then also sifted to isolate particles with a fraction of 80 to 200 microns.

Proximate analysis of the initial fuel components and mixtures based on them was performed (calorific value, ash content, moisture, and volatile yield were determined) according to the methods of GOST 147-2013 (ISO 1928-2009), GOST 11022-95, GOST 27314-91

	Moisture	Ash Content,	Volatile Matter	Net Heating Value.	Elemental Composition ¹				
Fuel (Wood/Coal), %	W ^a	A ^d	V daf	Q,	С	Н	Ν	S	0
(,,,,,,,,,	wt.%			MJ/kg	wt.%				
100 D	5.83	15.76	12.36	26.20	74.20	3.60	1.60	0.1000	20.50
10 W/90 D	5.42	14.00	14.55	24.92	63.20	4.50	1.80	0.1034	30.40
25 W/75 D	5.23	11.91	38.89	24.31	60.60	4.70	1.50	0.1079	33.09
50 W/50 D	5.35	10.44	40.96	23.84	56.20	5.20	1	0.1179	37.48
100 T	5.52	18.37	24.93	25.72	84.30	6.40	2.90	0.40	6.00
10 W/90 T	5.42	14.24	26.46	25.60	53.50	4.10	1.40	0.15	40.85
25 W/75 T	5.34	13.65	28.33	25.22	52.20	4.40	1.20	0.13	42.07
50 W/50 T	5.41	11.08	39.95	24.79	51.00	4.90	0.80	0.09	43.21
100 W	5.40	0.30	80.30	21.70	58.90	6.90	-	-	34.20

performed. The results of the analyses are shown in Table 1. **Table 1.** Characteristics of fuel components and their elemental composition.

Indexes a, d, and daf are the analytical, dry, and dry-ash-free mass of the sample. ¹ In relation to the mass of a dry sample.

The results shown in Table 1 allow us to conclude that the mixing of particles of such types of coal with wood using a percentage (by weight) ratio (coal/wood of 90%/10%, 75%/25%, and 50%/50%) leads to a significant reduction in the total mass of the ash residue. This reduction is not additive in relation to the calculated ash content of the base components and mixtures formed on their basis. The actual ash content values of the mixtures of the two studied coals and wood exceed the theoretical values. For example, if we consider the processes of pyrolysis and combustion of the coal and wood mixture independently, the theoretical ash content of such fuels, for example, based on T-grade coal (with 50% share of sawdust), should be 9.34%, and based on D-grade coal with the same share of sawdust in the mixture, should be 8.03%. According to the results of the experimental studies, the ash content of such mixtures was 11.08% and 10.44%, respectively [51]. These results give grounds for the conclusion about the chemical reaction of the gaseous and solid products of the pyrolysis of coal and wood with formation of metal salts that are part of coal (calcium, aluminum) and wood (calcium).

(ISO 589-81), and GOST 6382-2001. Ultimate analysis of the initial fuel components was

Regularities in the formation processes of sulfur, nitrogen, and carbon oxides in the gaseous products of the thermal decomposition of the mixed fuels based on D and T coals and wood processing waste (pine sawdust) were experimentally investigated. Analysis of the gaseous pyrolysis products of the mixed fuels was performed using a TEST-1 gas analyzer manufactured by Boner LLC, Novosibirsk, which is part of the experimental stand. The layout of the stand is shown in Figure 1.

The experiments were carried out according to the following scheme. A fuel sample (1) weighing 5 g (discreteness of the analytical balance is 10^{-4} g) was placed in the cylindrical reactor (2). The reactor, in turn, was installed in a cylindrical heat-insulated cavity fixed at the "hot" end of a temperature-controlled air heater (3) of the LHS 61L PREMIUM brand (LEISTER, Kegiswile, Switzerland) with a capacity of 16 kW. Air was supplied to the heater using an AIRPACK supercharger (LEISTER, Kegiswile, Switzerland). The reactor with a fuel sample was heated by a stream of air heated to a temperature of 873 K during the experiment. The heating process was carried out continuously until the concentrations of the detected oxides were reduced to a minimum. After that, the reactor was cooled to room temperature (293 K). Two holes were drilled in the reactor during the preparation of the stand. The first was intended for the removal of thermal decomposition products of the studied fuel samples into the gas analyzer (4) through the channel and the filter system (5). Filtration of the gaseous products of thermal decomposition of the studied fuels and their mixtures was carried out in order to dehumidify the gases and prevent adsorption of the vapor-gas mixture on the channel walls, as well as to capture the fly ash of solid pyrolysis products at the entrance to the gas analyzer. The second technological opening was designed to control the temperature of the heated medium in the reactor using a thermocouple (6). The parameters recorded by the gas analyzer and the thermocouple were recorded and then graphically visualized using a thermocouple signal converter (7) and a laptop (10). The sensors of the above equipment were polled every 3 s. At least five experiments were conducted for each type of fuel under identical conditions (with fixed main factors) in order to minimize random errors. The experiments continued until the pyrolysis of the studied fuels and their mixtures was fully completed (the main indicator of the process is termination of the SO₂ formation process).



Figure 1. Layout of the experimental stand for determining the composition of the gaseous products of a fuel thermal decomposition. 1—fuel sample; 2—reactor with fuel sample; 3—air heater; 4—gas analyzer; 5—coarse filter; 6—channel for supplying gaseous products of fuels thermal decomposition to gas analyzer with filtration system; 7—thermocouple; 8—thermocouple signal converter; 9—communication line between thermocouple and signal converter; 10—communication line between thermocouple signal converter and laptop; 11—laptop; 12—communication line between gas analyzer and laptop; 13—output channel for gaseous products of thermal decomposition of fuel samples; 14—ventilation shaft.

3. Results and Discussion

Continuous gas analysis was performed under the conditions of heating the reactor (with a fuel sample) with hot air in the temperature range from 293 K to 873 K. In the figures, the blue line shows the temperature inside the reactor, measured continuously throughout the experiment, and the red line shows the change in the concentration of the analyzed gas. Figures 2–5 show the typical results of recording the composition of the gaseous products of thermal decomposition of D-grade coal and wood, as well as the mixed fuels prepared on their basis.

It was experimentally established that the proportion of sulfur oxides decreased by 95.8% at a wood component concentration of 50% in a mixed fuel based on metalignitous coal.

Analysis of Figure 2 allows to establish a significant decrease in the concentration of sulfur oxides in the gaseous products of the pyrolysis of mixed fuels by increasing the proportion of sawdust relative to the concentration of sulfur oxides in the flue gas of the initial coal. It was also found that a reduction in the sulfur oxides concentration is not additive, even in the absence of bound sulfur in the composition of pine sawdust. The obtained data confirm the ultimate analysis results of the ash composition of the studied fuels and their mixtures. An increase in the proportion of the wood component by 25%

in the mixture with coal also leads to a significant (93%) decrease in the concentration of sulfur oxides.

Figure 3 shows the results of determining the concentrations of nitrogen oxides in the gaseous pyrolysis products of metalignitous coal, wood, and mixed fuels based on them.





Figure 2. Changes in the concentration of sulfur oxides in the gaseous products of thermal decomposition of mixed fuels based on D-grade coal and wood with a change in the proportion of the latter in the mixture from 10% to 50%: (**a**) metalignitous coal 100%; (**b**) metalignitous coal 90%/wood waste 10%; (**c**) metalignitous coal 75%/wood waste 25%; (**d**) metalignitous coal 50%/wood waste 50%.

The change in the concentration of nitrogen oxides (Figure 3) in the composition of the gaseous pyrolysis products of mixed fuels, depending on the proportion of the wood component in the mixture, is not unambiguous. Thus, it was found in experiments that an increase in the proportion of the wood component by 10% leads to decrease in the maximum concentration of nitrogen oxides in such a mixture by 30%. However, an increase

in the share of biomass by 25% leads to an increase in the share of nitrogen oxides by 7% relative to the values obtained by pyrolysis of homogeneous D-grade coal. At the same time, the concentration of nitrogen oxides decreases by 11.3% with an increase in the proportion of the wood component to 50% relative to the concentration of the same oxides during pyrolysis of homogeneous coal. Analysis of the gaseous products of mixed fuels thermal decomposition showed that the yield of nitrogen oxides significantly depends on the temperature conditions of the thermal decomposition of the latter.



Figure 3. Cont.



Figure 3. Changes in the concentration of nitrogen oxides in the gaseous products of thermal decomposition of mixed fuels based on D-grade coal and wood with a change in the proportion of the latter in the mixture from 10% to 50%: (**a**) metalignitous coal 100%; (**b**) metalignitous coal 90%/wood waste 10%; (**c**) metalignitous coal 75%/wood waste 25%; (**d**) metalignitous coal 50%/wood waste 50%.

The results of recording the concentration of carbon dioxide in the gaseous pyrolysis products of mixed fuels based on D-grade coal and wood are shown in Figure 4.

Analysis of the composition of the gaseous thermal decomposition products (Figure 4) of mixed fuels allowed us to distinguish two stages of carbon dioxide formation. Intensive thermal decomposition of the wood component begins at the first stage (small peak). The second peak (the main peak) corresponds to the maximum rates of thermal decomposition of both fuel components (coal and wood). It was established that an increase in the concen-

tration of the wood component (Figure 4) in the mixed fuel leads to an increase in carbon dioxide in the gaseous products of their thermal decomposition. Introduction of up to 50% wood into the fuel mixture intensifies the formation of carbon dioxide by 40% relative to the obtained concentrations during thermal decomposition of homogeneous metalignitous coal. This increase in CO_2 concentration is most likely due to more intense carbon oxidation in the fuel. However, carbon dioxide emissions from the thermal decomposition of wood are generally considered to be a carbon-neutral footprint [46]. The experiments also revealed a shift in the carbon dioxide output to the lower temperature zone due to the intensification of coal thermal decomposition due to wood pyrolysis.



Figure 4. Cont.



Figure 4. Changes in the concentration of carbon dioxide in the gaseous products of thermal decomposition of mixed fuels based on D-grade coal and wood with a change in the proportion of the latter in the mixture from 10% to 50%: (**a**) metalignitous coal 100%; (**b**) metalignitous coal 90%/wood waste 10%; (**c**) metalignitous coal 75%/wood waste 25%; (**d**) metalignitous coal 50%/wood waste 50%.

The results of recording the concentration of carbon oxide in the gaseous pyrolysis products of mixed fuels based on D-grade coal and wood are shown in Figure 5.

Analysis of Figure 5 made it possible to establish a significant increase in carbon monoxide with an increase in the proportion of wood in the mixed fuel up to 50%. An increase in the area under the carbon monoxide curve confirms an increase in the yield of carbon dioxide, since most of the released oxide was oxidized to CO_2 .

The results of calculating the areas under the gas curves for metalignitous coal are shown in Table 2.

Analysis of the areas under the gas curves for D-grade coal made it possible to reliably state a significant 96% decrease in sulfur oxides in the thermal decomposition products of mixed fuels with an increase in the biomass fraction in the mixture. The difference between the maximum concentration of sulfur oxides and the area under the curve was no more than 3%.



Figure 5. Cont.

CO (ppm)

CO (ppm)



time (min) (**d**) Figure 5. Changes in the concentration of carbon oxide in the gaseous products of thermal decompo-

Figure 5. Changes in the concentration of carbon oxide in the gaseous products of thermal decomposition of mixed fuels based on D-grade coal and wood with a change in the proportion of the latter in the mixture from 10% to 50%: (**a**) metalignitous coal 100%; (**b**) metalignitous coal 90%/wood waste 10%; (**c**) metalignitous coal 75%/wood waste 25%; (**d**) metalignitous coal 50%/wood waste 50%.

Table 2. The results of calculating the areas under the gas curves for metalignitous coal.

Element	The Composition of the Mixture						
	100% Coal	90% Coal/10% Wood	75% Coal/25% Wood	50% Coal/50% Wood			
SO ₂ ,%	Delta	-48.36	-94.06	-96.12			
Meaning	6514.5	3364	387	252.6			
NO _x ,%	Delta	-19.16	-1.38	-17.32			
Meaning	34554	27,934.5	34,077	28,570.5			
CO ₂ ,%	Delta	-5.01	+22.77	+29.85			
Meaning	20,310,000	192,91500	26,299,500	28,954,260			

Table 2. Cont.

Element	The Composition of the Mixture					
	100% Coal	90% Coal/10% Wood	75% Coal/25% Wood	50% Coal/50% Wood		
CO,%	Delta	-39.29	+48.56	+70.70		
Meaning	38,671.00	23,478.00	75,183.00	131,977.00		

Figures 6–9 show the results of gaseous products analysis of the thermal decomposition of T-grade coal, wood, and the mixed fuels formed on their basis.



Figure 6. Cont.



Figure 6. Changes in the concentration of sulfur oxides in the gaseous products of thermal decomposition of mixed fuels based on T-grade coal and wood with a change in the proportion of the latter in the mixture from 10% to 50%: (a) lean coal 100%; (b) lean coal 90%/wood waste 10%; (c) lean coal 75%/wood waste 25%; (d) lean coal 50%/wood waste 50%.

The results of determining the sulfur oxides concentration in the pyrolysis products of T-grade coal, wood, and the mixed fuels based on them, shown in Figure 6, allow us to conclude that proportion of sulfur oxides formed during pyrolysis is steadily decreasing with an increase in the proportion of the wood component up to 50% in the fuel mixture. A decrease in the peak concentration of sulfur oxides in fuels based on T-grade coal was

90.2% in relation to the concentration of these gases during pyrolysis of homogeneous lean coal. The scale of the maximum concentration reduction in sulfur oxides is comparable to that obtained by pyrolysis of mixed fuels based on metalignitous coal and wood. The results obtained suggest that wood biomass intensifies the processes of reducing the concentration of sulfur oxides in mixed fuels based on these two different, but at the same time quite typical, energy coals, as a result of the calcium and aluminum salts forming in the ash of such fuels [54].



Figure 7. Cont.



Figure 7. Changes in the concentration of nitrogen oxides in the gaseous products of the thermal decomposition of mixed fuels based on T-grade coal and wood with a change in the proportion of the latter in the mixture from 10% to 50%: (a) lean coal 100%; (b) lean coal 90%/wood waste 10%; (c) lean coal 75%/wood waste 25%; (d) lean coal 50%/wood waste 50%.

The analysis results of the nitrogen oxides formation during pyrolysis of T-grade coal, wood, and the mixtures based on them in an inert medium are shown in Figure 7.

According to the results of the experimental studies (Figure 7), it was found that the greatest decrease in the peak concentration of nitrogen oxides in mixed fuels based on T-grade coal and wood occurs with an increase in the share of the latter by 25% and is 57.7%

relative to homogeneous T-grade coal. There is a decrease in the concentration of nitrogen oxides by 49.0% with the share of wood in the mixture up to 50%. The results obtained allow us to conclude that wood biomass has a significantly greater effect on reducing the yield of nitrogen oxides during thermal decomposition of mixtures based on lean coal compared to mixed fuels based on metalignitous coal.



Figure 8. Cont.



Figure 8. Changes in the concentration of carbon dioxide in the gaseous products of the thermal decomposition of mixed fuels based on T-grade coal and wood with a change in the proportion of the latter in the mixture from 10% to 50%: (a) lean coal 100%; (b) lean coal 90%/wood waste 10%; (c) lean coal 75%/wood waste 25%; (d) lean coal 50%/wood waste 50%.

Figure 8 shows the analysis results of carbon dioxide formation during pyrolysis of T-grade coal, wood, and the mixtures based on them with an increase in the proportion of the wood component in the mixture from 10% to 50%.

Figure 8 shows that an increase in the wood component proportion in the mixture with T-grade coal to 50% leads to a decrease in the maximum concentration of carbon dioxide

by 53.4%, and the most significant decrease in the proportion of this gas occurs during the pyrolysis of a mixture of coal and wood in the ratio of components (coal/wood) 75%/25% (decrease of 65.5% relative to the results obtained by pyrolysis of homogeneous lean coal). It is worth noting that the characteristics of the carbon dioxide formation process in mixed fuels based on T-grade coal with wood significantly differs from the characteristics of the processes occurring during the pyrolysis of mixed fuels prepared on the basis of D-grade coal. This difference is manifested in a significant decrease in the concentration of carbon dioxide in the pyrolysis products of mixed fuels based on T-grade coal and the wood component relative to the initial coal. The reason for this may be that lean coal contains more bound carbon (84.30%) than metalignitous coal (74.20%).



Figure 9. Cont.



Figure 9. Changes in the concentration of carbon oxide in the gaseous products of the thermal decomposition of mixed fuels based on T-grade coal and wood with a change in the proportion of the latter in the mixture from 10% to 50%: (**a**) lean coal 100%; (**b**) lean coal 90%/wood waste 10%; (**c**) lean coal 75%/wood waste 25%; (**d**) lean coal 50%/wood waste 50%.

Figure 9 shows the analysis results of carbon oxide formation during pyrolysis of T grade coal, wood, and the mixtures based on them with an increase in the proportion of the wood component in the mixture from 10% to 50%.

Analysis of Figure 9 showed an increase in the carbon monoxide concentration. The increase in the maximum peak concentration was 51%, which is only 10% less compared to the calculated area under the same curve.

The results of calculating the areas under the gas curves for lean coal are presented in Table 3.

Element -	The Composition of the Mixture						
	100% Coal	90% Coal/10% Wood	75% Coal/25% Wood	50% Coal/50% Wood			
SO ₂ ,%	Delta	-22.46	-67.52	-80.24			
Meaning	258.61	200.52	84.00	51.11			
NO _x ,%	Delta	-56.33	-44.43	-5.81			
Meaning	382.65	167.10	212.65	360.41			
CO ₂ ,%	Delta	-72.00	-40.29	-23.73			
Meaning	259,895.84	72,760.39	155,183.33	198,214.65			
CO,%	Delta,	+13.10	+48.37	+61.76			
Meaning	33,047.00	38,026.00	64,013.00	86,429.00			

Table 3. Results of calculating the areas under the gas curves for lean coal.

Analysis of the areas under the gas curves for T-grade coal made it possible to reliably state a significant 80.24% decrease in sulfur oxides in the thermal decomposition products of mixed fuels with an increase in the biomass fraction in the mixture. The difference between the maximum concentration of sulfur oxides and the area under the curve was no more than 10.02%.

The results of the experiments allow us to conclude that addition of wood to coals of different grades (for example, D, T) does not lead to an identical process of formation of sulfur, nitrogen, and carbon oxides. An increase in the concentration of pine sawdust in the mixed fuel up to 50% leads to a significant increase in the yield of carbon oxides for D-grade coal. The concentration of CO_2 in the pyrolysis products of a mixture of T-grade coal with wood is significantly reduced in comparison with homogeneous T-grade coal. A smaller discrepancy in the concentrations of nitrogen oxides was found after experiments with mixtures of wood with D- and T-grade coal. A stable and significant decrease in concentrations was found only for sulfur oxides in pyrolysis products of mixtures of D- and T-grade coals with wood. According to the results of similar experiments [51], a hypothesis was formulated that products of thermal decomposition interact during the joint combustion of mixtures of crushed wood with dispersed coals, which results in formation of calcium and aluminum sulfates in the ash of the studied fuel mixtures. Introduction of wood (in the form of pine sawdust) in a mixture with T-grade coal leads [55] to an increase in the concentration of sulfur, calcium, and aluminum in the ash residue of the mixture compared to the ash of homogeneous coal. However, analysis of the total elemental composition shows that the formation intensity of such salts can differ quite significantly for different coals (depending on the mineral composition of the fuel).

Analysis of the total elemental composition of the ash of T- and D-grade coals and wood obtained at a medium temperature of 1073 K was performed to substantiate the hypothesis formulated in [50]. The analysis was performed using iCAP Duo, Thermo Scientific instrument, Santa Clara, United States. This optical emission spectrometer with inductively coupled plasma allows for qualitative, semi-quantitative, and quantitative elemental analysis. The results of the study are shown in Figure 10.

Analysis of Figure 10 allows us to conclude that wood ash contains significantly more calcium in comparison with homogeneous coals. However, the presence of calcium in wood can enhance the synergistic effect of calcium sulfates formation in the ash of mixed fuels. The content of aluminum in T grade coal was 23%, and in the D grade coal—27%. The high concentration of this metal in comparison with other elements contained in the ash of the initial components suggests that it has a significant effect on reducing the yield of sulfur oxides; for example, in the gaseous products of the thermal decomposition of mixtures of the studied coals and wood.

X-ray phase analysis of the ash of the main components (D- and T-grade coal and wood (pine sawdust)) and mixed fuels prepared on their basis was performed in order to substantiate the formulated hypothesis. The concentration of calcium and aluminum sulfates in the ash was determined using an XRD-7000S X-ray diffractometer, Santa Barbara, USA. Experimental studies for each fuel mixture were conducted at least five times under identical conditions. The results of the experiments showed good repeatability. Systematic errors in determining the component concentrations were less than 2%, and random

errors were less than 3.5%. The results of determining the content of calcium and aluminum sulfates in the ash of the coal, wood, and mixtures based on them are shown in Figures 11 and 12, respectively.



Figure 10. Ultimate elemental composition of the ash of the studied wood waste, lean coal, and metalignitous coal.



Figure 11. Changes in the content of calcium and aluminum sulfates in the ash of fuel mixtures based on metalignitous coal and wood with an increase in the proportion of wood in the initial mixture during pyrolysis in an inert medium at T = 873 K.



Figure 12. Changes in the content of calcium and aluminum sulfates in the ash of fuel mixtures based on lean coal and wood with an increase in the proportion of wood in the initial mixture during pyrolysis in an inert medium at T = 873 K.

Analysis of the content of calcium and aluminum sulphates (Figures 11 and 12) in the ash of mixed fuels based on D- and T-grade coal and wood allows to conclude that an increase in the share of the wood component in a mixture with D grade coal to 50% leads to a significant increase in calcium (45.1%) and aluminum (by 43.2%) sulphates in the mixture ash. An increase in the concentration of these salts in the ash of mixed fuels based on T-grade coal is 35.1% and 38.6%, respectively. According to the results of the experiments, it can be concluded that the content of the elemental composition of ash in a mixed fuel based on two types of coal, lean coal and metalignitous coal, and wood in the form of pine sawdust, cannot be calculated proportionally to the content of the wood in the mixed fuel. The ash composition can only be determined experimentally using special equipment.

At the same time, it should be emphasized that effect of wood biomass on the yield of nitrogen and carbon oxides during pyrolysis of D and T grades of coal is significantly different. There are no experimental data so far on the content of nitrogen and carbon compounds in the ash of mixtures of D- and T-grade coals after pyrolysis. Therefore, there is no sufficient basis for describing the mechanisms of decreasing (or increasing) the concentrations of nitrogen oxides and carbon in the gaseous products of the pyrolysis of a mixture of coal and wood.

Accordingly, the efficiency of a mixture combustion of any coal with biomass is still difficult to predict theoretically. Special studies are required for reliable estimates of the yield of anthropogenic oxides in such variants of fuel mixtures using, for example, the methodology described in this article.

4. Conclusions

Based on the experimental studies carried out, a fundamental conclusion can be drawn: the composition of the coals has a significant effect on the yield of anthropogenic oxides after pyrolysis of coal mixtures with woody biomass.

Analysis of the content of calcium and aluminum sulfates in the ash of mixed fuels based on D- and T-grade coals and wood allows us to conclude that an increase in the proportion of the wood component in a mixture with coal of grade D to 50% leads to a significant increase in the content of calcium sulfates (45.1%) and aluminum (43.2%) in the ash of the mixture. The increase in the content of these salts in the ash of mixed fuels based on T-grade coal is 35.1% and 38.6%, respectively.

The results of experimental studies make it possible to substantiate the possibility of using a wood component as an additive that helps to reduce anthropogenic gas emissions (sulfur oxides from 10% to 96%, nitrogen oxides from 6% to 56%) when co-fired with traditional coals in power boiler furnaces. However, it was found that the composition of the resulting gaseous products (during the thermal decomposition of various mixtures of the two studied grades of coal with wood) depends on the reactivity of the initial coal, which must be taken into account when preparing mixed fuels.

In future works, the authors plan, on the basis of their own accumulated experimental base, to reasonably prove the physicochemical processes of binding anthropogenic-induced gases during the co-combustion of various types of coal with wood processing waste.

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