



# Article Impact of Forest Fuels on Gas Emissions in Coal Slurry Fuel Combustion

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Received: 15 August 2018; Accepted: 17 September 2018; Published: 19 September 2018



**Abstract:** Anthropogenic emissions from coal combustion pose a serious threat to human wellbeing. One prospective way to solve this problem is by using slurry fuels instead of coal. The problem is especially pressing in China and Russia, so these countries need reliable experimental data on the SO<sub>x</sub> and NO<sub>x</sub> emissions reduction range more than others do. The experiments in this research are based on the components that are typical of Russia. Experimental research was conducted on the way typical forest fuels (ground pine needles, leaves and their mixtures, bark, sawdust, and charcoal) affect the gas emissions from the combustion of slurry fuels based on the wastes. It was established that using forest fuels as additives to coal-water slurries reduces SO<sub>x</sub> and NO<sub>x</sub> emissions by 5–91% as compared to coal or to slurries based on used turbine oil. It was revealed that even small concentrations of such additives (7–15%) could result in a several-fold reduction in SO<sub>x</sub> and NO<sub>x</sub>. The higher the temperature, the more prominent the role of forest biomass. The calculated complex criterion illustrates that forest fuels increase the performance indicator of fuel suspensions by 1.2–10 times.

Keywords: coal; slurry fuel; combustion; forest fuels; biomass; anthropogenic emission concentration

## 1. Introduction

## 1.1. Environmental Issues of Coal-Fired Power Industry

Energy issues are critical in many economic, social, and environmental spheres. It is the efficiency of the energy complex that, to a great extent, governs the economic potential of countries and welfare of people [1,2]. Today, fossil fuels such as oil, coal, gas, oil shale, peat, uranium, etc. are the main energy sources. The present and future of the power industry rely strongly on its resourcing. According to studies [1-3], the share of coal in the global fuel and energy balance makes up 25–35%. Its main consumers are metallurgy and power engineering. 40-45% of the world's electricity is generated using coal [1–3]. One of the main concerns associated with using coal is the harm that its production, processing, and combustion do to the environment. The most important environmental issues (climate change, acid rains and the overall pollution) are directly or indirectly linked to this energy resource [4,5]. Major environmental problems are caused by solid wastes of coal-fired thermal power stations, such as ash and slag. Emissions from coal-fired thermal power stations are largely responsible for benzopyrene, a strong carcinogenic substance causing oncological diseases [5]. These abrasive materials can destroy lung tissue and cause a disease called silicosis. A negative impact of coal-fired power plants on the humankind and environment leads to illnesses, human migration, extinction and migration of animals, and reduction of eco-friendly woodlands [5,6]. This has caused power-generating enterprises in many countries to improve the devices monitoring air pollution [4–6]. Programs to increase energy efficiency and reduce emission with no negative effect on the rapid economic growth come into the picture [7]. In this research field, the authors [8–10] suggest focusing on solving the main fundamental

and practical tasks, primarily with the environment in mind, to determine effective conditions of using high-potential coal-water slurries instead of the traditional energy sources (fuel oil, gas, and coal).

Coal-water slurry (CWS) is used to mean a mixture of a ground coal component with water. Coal sludge, filter cakes, low-grade coal, solid residuals from processing traditional energy resources (coal and oil) as well as resins can serve as a fuel base [8,10]. In the studies [8,10] authors were the first to suggest adding 10–15% of a liquid fuel component to a slurry to provide the necessary level of generating capacity and increase energy efficiency when using coal-water slurry and coal-water slurry containing petrochemicals (CWSP). The ranges of varying relative mass fractions of CWS and CWSP components make up 60–30% for coal dust, 30–50% for a dry filter cake, 0–15% for a combustible liquid, 30–50% for water, and 0.5–1% for plasticizer [10].

The production of composite liquid fuels (CLFs) from wastes is of great social, economic, and international importance [8–10]. First, it will reduce the vast volumes of accumulated wastes. Second, it will extend the resource potential of power-generating facilities. Third, fire and explosion safety gets higher, since water slurries are used instead of easily flammable and fire-hazardous fuels (coal dust, gas, or fuel oil). Fourth, mixing waste with water considerably reduces the environmental load on the surrounding nature. However, the use of liquid flammable wastes and low-reactive components as part of CWSP fuels inevitably leads to the growth of anthropogenic emission concentration. Involving plant additives is deemed to be the main solution to this problem [11–14].

The general trend of recent studies [11–16] on the current topic is to use large volumes of plant additives to produce energy and minimize the negative influence on the environment. Mixing plant waste with coal fuels leads to energy source diversification, as the range of raw materials is vast and growing [12,15,16]. The analysis of the global energy situation reveals the following benefits of co-firing coal fuel with plant biomass to produce energy [11–19]: a low-cost and low-risk renewable energy source is used; otherwise unused waste gets involved in the energy generation; emission concentration decreases; job opportunities in local neighborhoods are created, and external factors connected with fossil fuel combustion are reduced. Generally, most scientific groups exploit a traditional solid coal fuel mixing it with biomass (straw, sawdust, rice hulls and vegetable oil waste). Most of the well-known studies [11–19] investigate the processes of preparation, ignition, combustion, emissions, and ash production at the co-firing of coal and biomass with varying mass fractions of each of the mixture component. There are much fewer studies dealing with the development of CLFs containing various plant additives [19,20]. Until now, no data has been published on the complex analysis results of all main performance indicators of burning slurry fuels containing wood additives.

Over 25% of the world's woodland belongs to Russia, and it is deeply engaged in wood material processing. Two fifth of the country's territory is taken up by forests, 80% of which is coniferous. Russia's forest volume is mainly concentrated in Siberia and the North of the European part of the country [21]. Wood is a renewable resource, but due to large volumes of its production the question of effective and complex use of forest resources is getting increasingly important. The group of forest fuels comprises, besides trees themselves, their plant waste (stumps, branches, twigs, and tops) and woody debris (pine needles, leaves, brushwood, and bark), as well as industrial wastes (offcuts, chips, shavings, sawdust, pallets, etc.) [11,22,23]. The low demand for wood waste emerging from logging and wood processing is explained by insufficient development of recycling enterprises and is detrimental to the economy and the environment.

At present, a big mass of forest fuels in the world is used as fuel in hot-water and steam boilers. These take part in the technological production cycle and satisfy the domestic needs of wood processing enterprises, which reduces their thermal energy expenses [24]. Lumps of wood rather than sawdust, shavings, small pieces, or bark are used as fuel. Besides, a high content of chlorine and alkaline metals in wood waste accounts for high-temperature corrosion of heating surfaces of boiler units. However, the given limitations do not refute the fact that 5–15% addition of wood waste to a fuel can have a great effect in terms of anthropogenic emission minimization [12,13,16].

The analysis shows [21] that many countries (such as China, India, Japan, the USA, Australia, and Russia) using large volumes of coal fuel, have internal resources to forest biomass into the fuel sector [21]. Using plant additives together with coal slurries at thermal power stations or boiler plants can be considered a promising solution to ecological problems connected with anthropogenic emissions and waste recovery (both plant and coal wastes) [11–19].

## 1.2. Forest Fuels

Forest fuels can be regarded as a hydrocarbon fuel with known coefficients of emission, elemental composition, chemical formula, and heat effects. The organic part of vegetation consists primarily of hydrocarbons and a smaller amount of proteins, fats, waxes, and resins which constitute plant cells or fill intercellular space of plant tissue. Cellulose  $(C_6H_{10}O_5)_x$  is the main crystalline component of cell walls. Hemicellulose is a matrix ramified polysaccharide with an amorphous structure. Lignins are complex phenolic polymers filling the spaces between the previous components. The content of cellulose and hemicellulose in the organic part of metaphytes reaches 60%, while that of lignin is 20–30% (depending on the species and age of timber). Plant tissue is saturated with water containing dissolved mineral salts that produce ash during combustion [25,26].

Timber is the most common type of forest biomass [27,28]. In terms of power generation, timber is considered the most appropriate type of plant biomass due to its rather high density, high calorific value, and low content of nitrogen, sulfur, and ash [28,29]. However, the amount of timber is limited and, besides being used in the power industry, it is also the main resource for pulp and paper industry and construction engineering [28]. Thus, waste from timber and construction industries looks most attractive in terms of burning, since a great amount of it has been accumulated and lies idle [30]. The main and most common timber industry waste includes sawdust, shavings, board offcuts, slabs, firewood, and bark [27]. Both needles and leaves also can be considered as fractions of logging residues in forestry (if branches, twigs, tops). They are not usually used as forest fuels directly but can be a portion of chipped logging residues that are used as fuels. This waste is a nuisance to many logging companies, as its recovery entails additional expenses, eventually increasing the product prime cost. Therefore, it is sensible to consider using this waste as an answer to many environmental, economic, and social issues [12,16].

#### 1.3. Aim of the Research

The aim of this research is to determine the influence of forest fuels on the emissions from slurry fuels combustion. The main objective was to evaluate the prospects of using the given additives, as well as to determine their rational concentrations in slurry fuels.

#### 2. Experimental Approach

#### 2.1. Materials

Forest fuel from pine and birch trees from forests in Siberian Federal District (Russia) was used as additives in the present study. The origin of the used needles and sawdust are coniferous trees, mostly pine of the Pinus sylvestris species (Scots pine). The species of birches typical for Siberia is Betula pendula, commonly known as silver birch, which is native to Europe and parts of Asia.

The samples of pine sawdust, needles and birch leaves were taken from a timber processing factory in Tomsk, Russia. In the study, charcoal of grade A (Chernogolovka, Moscow region) was used. For its production, hardwood was used, in particular birch. The oak bark came from debarking operations of Quercus robur logs in the same industrial facility.

All samples of forest biomass were air dried, then milled by Rotary Mill Pulverisette 14 (rotor speed 6000–20,000 rpm). After milling, the samples were sieved. The average particle size was about 100  $\mu$ m. The milled samples, spread in a thin layer, were exposed to air for several days to equilibrate with atmospheric moisture. Additional drying of the samples was not carried out.

In this study, authors used the flotation waste (filter cake) of coking coal as a main fuel component of CWSP. This waste is typical for coal processing plants in many regions; it has a fairly low ash content and better ignition and combustion characteristics in comparison with the flotation waste of some other coal ranks [10]. Waste turbine oil was used as liquid combustible component of CWSP.

Tables 1–3 present the properties of forest biomass used as additives (birch leaves, pine needles, pine sawdust, oak bark, and charcoal). Tables 4 and 5 present the properties of the main CWSP components (filter cake and used turbine oil).

Additive		U	Proximate Analysis					
	C <sup>daf</sup> , %	H <sup>daf</sup> , %	N <sup>daf</sup> , %	O <sup>daf</sup> , %	$S_t{}^d$ , %	$A^d$ , %	$V^{daf}$ , %	Q <sup>a</sup> <sub>s,V</sub> , MJ/kg
Pine needles of Himalayas in India [31]	45.81	5.38	0.98	46.11	0.01	1.5–1.74	-	16.7–18.5
Pine needles (Pinus pinaster) [32]	47.97-48.42	6.84–6.96	0.68–0.75	41.92-42.28	0.83–0.87	1.97	79.4	21.12–22.1
Pine needles (Pinus sylvestris) [33]	48.21	6.57	_	43.72	-	1.5	72.38	19.24
Birch leaves (Betula pendula) [34]	50.1–51.1	5.8-6.4	1.1–1.3	41.6-42.4	0.09–0.11	5.2–5.8		16.05–19.12
Leaves of various trees [35]	41.1–59.6	5.3–9.7	1.03-3.04	27.8–50.6	0.19–0.77	3.8–16	66.8–89.9	14.4-20.7

Table 1. Properties of forest fuels (on the base of data [31–35]).

Table 2. Typical ultimate composition of birch leaves and pine needles (on the base of data [34,36–39]).

Additive	Elements, mg/kg								
	Na	Mg	К	Ca	Mn	Fe	Zn	Р	
Pine needles (Pinus sylvestris) [36–38]	15,388 38,200 –	859 540–760 890–1540	6101 3840–5060 3430–4550	2995 2780–3540 2590–6160	125.3 920–1240 151–370	0.6 _ 40–100	24.5 _ 33.6–73.3	1399 1010–1290 1360–3040	
Birch leaves (Betula pendula) [34,39]	51–75 –	2748–4103 5890	6622–15,232 32,200	7521–24,897 29,000	159–1323 1470	172–243 790	124–185 280	2072–2915 3420	

Table 3. Properties of wood components (based on data from [37,40-56]).

	P	ine Sawdust		Cha	rcoal	Oak	Bark
Samples	Pinus sylvestris	Pinus	Pinus	Charcoal from	Charcoal from	Quercus	Bark of
	from Siberia,	sylvestris	tabulaeformis	Chernogolovka,	Birch, Norway	robur	Various Oak
	Russia	[37,40-44]	[45,46]	Russia	[47]	[48-52]	[53-56]
		C	Chemical analy	sis, %			
С	52.32	50.9-52.8	47.21-49.65	83.11	72.7-91.4	46.08-51.2	40.77-48.9
Н	6.39	5.95-6.2	6.25-8.09	3.46	1.93-4.35	5.5	5.43-6.11
0	40.70	40.5-42.9	41.58-44.40	12.8	7.09-21.61	46.8	39.3-53.54
Ν	0.24	0.1-0.5	0.05-0.1	0.6	0.37-1.13	0.2-1.32	0.2-0.56
S	0.02	0.01-0.09	0.04-0.21	0.03	< 0.02	0.01-0.33	0.1-0.26
			Proximate ana	lysis			
Moisture content, %	7.0	6.4-7.6	7.3-7.84	0.28		-	6.88-12.9
Volatiles, %	83.4	66.9-70.4	73.52-78.95	22.56	6.6-22.3	-	76.3-81.8
Ash content, %	1.6	0.47 - 5.5	0.76 - 1.88	1.49	1.4 - 5.0	0.3	1.64-3.6
Heat of combustion, MJ/kg	18.6	19.3	19.03–19.73	29.60		18.7	17.8–19.3
		Ult	imate analysis	, mg/kg			
Na	-	5-25	379	-	13-43	154	0.06-5.47%
K	-	120-780	435	-	1508-2538	1339-3520	4.32-16.7%
Ca	-	487-1000	1236	-	3332-4865	9750-20,100	16.2-37.3%
Mg	-	80-370	153	-	682-1099	230-340	1.77 - 4.14%
Fe	-	1.9-24	154	-	70-254	28.6-131	0.01-0.63%
Mn	-	25-200	28	-	230-477	280	0.16-3.71%
Cost, \$/kg		0.006		0	.3	0.	006

Coal Rank	Proximate Analysis				Ultimate Analysis				
	<i>W<sup>a</sup></i> , %	$A^d$ , %	V <sup>daf</sup> , %	Q <sup>a</sup> <sub>s,V</sub> , MJ/kg	$C^{daf}, \%$	H <sup>daf</sup> , %	$N^{daf}$ , %	$S_t{}^d$ , %	$O^{daf}, \%$
Filter cake of coking coal (C) (dry)	-	26.46	23.08	24.83	87.20	5.09	2.05	1.022	4.46
Coking coal (C)	2.05	14.65	27.03	29.76	79.79	4.47	1.84	0.87	12.70

Table 4. Properties of Coal and Filter Cake.

Table 5. Properties of liquid component.					
Sample	Density, kg/m <sup>3</sup>	$A^d$ , %	$T_{f'}$ °C	$T_{ign}$ , °C	$Q^a{}_{s,V}$ , MJ/kg
Used turbine oil	868	0.03	175	193	44.99

### 2.2. Experimental Setups

The main elements of the experimental setup included a rotary muffle furnace and a gas analyzer [57]. A muffle furnace can create an air environment with temperatures 700–1000 °C. This temperature range is especially typical of CWS and CWSP combustion in the industrial conditions. Currently, there are several concepts of CWS and CWSP combustion in boilers of different capacity. These include the conventional fluidized bed combustion, vortex combustion of atomized flow, as well as co-firing with other types of fuels, for instance, with coal. Vortex combustion of coal-water fuel is the most widespread one. Combustion of soaring fine aerosol flow makes it possible to prolong the lifetime of particles in a combustion chamber. It also provides rapid mixing of the fuel and oxidizer, which, in turn, ensures more complete burnout of slurry fuel droplets. When it comes to laboratory research, the concept of soaring particles provides a way to gain a deeper insight into the typical mechanisms and stages of CWSP combustion: inert heating of a droplet, evaporation of moisture from its near-surface layer, evaporation of the liquid fuel component in heated air and thermolysis of the organic matter of coal, oxidation of volatiles and vapors of liquid fuel component in heated air, as well as heating and heterogeneous ignition of coke residue. However, using this technology to estimate the anthropogenic impact and measure the concentration of emissions from the combustion of a slurry fuel droplet is very cost-intensive. Vortex and fluidized bed combustion may have different conditions of fuel ignition and combustion, but the portions of fuel being burned are identical, so specific emissions can be considered comparable. To measure the emissions from fluidized bed combustion, it is enough to burn even a small portion of fuel, unlike with vortex combustion.

For fluidized bed combustion, boiler furnaces must also provide quite a long fuel lifetime in the combustion chamber and maintain the required high temperature throughout the said chamber. A thermally insulated rotary muffle furnace in the experimental setup can provide such conditions and make them near-real. The ceramic tube of the muffle furnace protects it without sharply reducing the temperatures in the near-wall area and in the active combustion zone. This is necessary for the stable CWS and CWSP combustion.

For the experiments, the fuel batch was weighed on an analytical balance with 0.01 g increments. The mass of the batch ranged within 0.5–1.5 g in each experiment. The gaseous products released during combustion of fuel in the muffle furnace were recorded and analyzed by the gas analyzer. Its main properties can be seen in Table 6. When averaging, only those results of the experiments were taken into account that did not differ by more than 2.5%.

Process	Measurement Range	Accuracy
O2	0–25 vol%	$\pm 0.2$ vol%
СО	0–10,000 ppm	$\pm 10$ ppm or $\pm 10\%$ of value (0–200 ppm) $\pm 20$ ppm or $\pm 5\%$ of value (201–2000 ppm) $\pm 10\%$ of value (2001–10,000 ppm)
NO <sub>x</sub>	0–4000 ppm	$\pm 5$ ppm (0–99 ppm) $\pm 5\%$ of value (100–1999 ppm) $\pm 10\%$ of value (2000–4000 ppm)
SO <sub>2</sub>	0–5000 ppm	$\pm 10$ ppm (0–99 ppm) $\pm 10\%$ of value (beyond this range)
CO <sub>2</sub> (derived from O <sub>2</sub> measurement)	0-CO <sub>2</sub>	$\pm 0.2$ vol%

Table 6. Gas analyzer sensors.

## 2.3. Research Procedures

The following main components were used: filter cakes, used turbine oil and wood components (needles, leaves, sawdust, charcoal, and bark). Grinding the solid fuel component and plant additives to dust. Rotor Mill Pulverisette 14 was used for grinding. Then, a sample with an average particle size of 80–100  $\mu$ m was collected using plansifter RL-1. Filter cakes from coal washing plants contain coal particles with a size of 60–80  $\mu$ m. Therefore, their grinding is not necessary. Batches of slurry components were prepared using the ViBRA HT 84RCE (increment 10<sup>-5</sup> g). The mass of the batches was calculated from the mass of the resulting composition and corresponding mass fractions of the components: filter cakes 75–100%, used turbine oil 10%, needles 7–15%, leaves 7–15%, mixture of needles and leaves 15%, bark 10%, sawdust 10% and charcoal 10%. The components were mixed in two stages by a homogenizer MPW-324 with a disperser in a metal container, which took 10 minutes.

The procedure of determining the amount of emissions from the fuel combustion comprised the following stages. The fuel sample was placed into a substrate made of stainless steel mesh which was fixed with fasteners at the end of the modular probe of the gas analyzer. The minirobotic arm moved the fuel sample and the gas analyzer probe to the combustion chamber. One experiment lasted 30–60 s, depending on the temperature in the combustion chamber. The flue gases from the combustion of the fuel moved towards the sensor. The sample went to the measuring sensors of the gas analyzer through a gas sampling hose. The EasyEmisson software (version 2.7, Lenzkirch, Germany) performed a continuous monitoring of flue gases. The values of CO,  $CO_2$ ,  $NO_x$ ,  $SO_x$  were recorded.

## 3. Results and Discussion

Figures 1 and 2 present the  $SO_x$ ,  $NO_x$  from the combustion of CWS and CWSP containing forest fuels such as birch leaves, pine needles and their mixtures (with an equal proportion of leaves and needles). Adding forest fuels to CWSP significantly reduces the gaseous emissions of sulfur oxides (Figure 1). The values of  $SO_x$  emissions for such slurries (based on filter cake C) range from 9 to 117 ppm versus 62–360 ppm for coal of the same grade, depending on the combustion chamber temperature (Figure 1).

The decrease in the share of emissions (from 33 to 86%) was due to the chemical composition of the components introduced in the slurry. Alkaline and alkaline-earth metals (Ca, Na, K) present in forest fuel (Table 1) can form substances that remain in the coal ash ( $2CaO + 2SO_2 + O_2 = 2CaSO_4$ ), preventing the formation of SO<sub>x</sub>. The addition of a 15% forest fuel mixture had the most noticeable impact on sulfur oxide release. The SO<sub>x</sub> concentrations in the temperature range under consideration were 17–90 ppm.

According to the data presented in Figure 2, the lowest concentrations of oxides and nitrogen are typical of filter cake C with a 15% addition of forest fuel mixture (88–218 ppm). The latter suggests that a synergistic effect emerges when a mixture of leaves and pine needles is used, especially at high temperatures (900–1000  $^{\circ}$ C). During forest fuel thermolysis, a part of metals (for instance, iron)

remains in solid pyrolysis products. At high temperatures typical of the late pyrolysis, iron reacts with sulfur and nitrogen oxides  $(3CO + Fe_2O_3 = 3CO_2 + 2Fe; 2Fe + 3NO = 3/2N_2 + Fe_2O_3)$ . The synergism between pine needles and leaves reduces the concentration of sulfur oxide (Figure 1) and nitrogen oxide (Figure 2). In addition, there is no need to sort the incoming forest fuel for slurry preparation.



**Figure 1.**  $SO_x$  concentrations at the coal-water slurry (CWS) and coal-water slurry containing petrochemicals (CWSP) (with leaves, needles, or their mixtures) combustion.





The experimental results (Figure 2) have shown that using forest fuels as additives to coal-water slurries also reduces  $NO_x$  emissions by 35–53% and 5–43%, as compared to coal or CWSP based on used

turbine oil without any additives, respectively. First, due to a quick release of volatile particles of forest fuels and their subsequent burning, the amount of  $O_2$  in the combustion chamber decreases. Therefore, the reactions involving fuel nitrogen and oxygen produce a lower amount of NO and NO<sub>2</sub>. Second, a low nitrogen content in plant additives also contributed to lower amounts of NO<sub>x</sub> emissions [58]. Thirdly, metal ions such as Mn, Cu, Fe had a catalytic effect on NO<sub>x</sub> oxides followed by the formation of free nitrogen. The highest concentration of NO<sub>x</sub> comes from filter cake C with 7% of leaves, which is close to the emission values for filter cake C without forest fuels and ranges from 95 to 350 ppm.

The complex analysis was needed to consider the environmental, economic and energy performance aspects. A composite integral index is therefore introduced, which takes into account the above indicators. This coefficient describes the amount of energy per cost of fuel slurry and concentration of the main anthropogenic emissions [33]:

$$D_{cwsp}^{NOx} = Q^{a}_{s,V\_cwsp} / (C_{cwsp} \cdot NO_{x\_cwsp});$$
(1)

$$D_{cwsp}^{SOx} = Q^{a}_{s,V\_cwsp} / (C_{cwsp} \cdot SO_{x\_cwsp});$$
<sup>(2)</sup>

$$D_{cwsp}^{NOx\&SOx} = D_{cwsp}^{NOx} \cdot D_{cwsp}^{SOx};$$
(3)

$$D_{relative} = D_{cwsp} \frac{NOx\&SOx}{D_{coal}} - \frac{NOx\&SOx}{D_{coal}}.$$
(4)

where  $Q^a_{s,V}$  is the heat of combustion of the suspension (coal), MJ/kg; *C* is the cost of the suspension (coal), \$/kg (in the case of a suspension  $Q^a_{s,V}$  and *C* are determined proportional to the concentration of the components); NO<sub>x</sub> concentration of nitrogen oxides, ppm; SO<sub>x</sub> concentration of sulfur oxides, ppm.

The results of calculating the relative performance indicators ( $D_{relative}$ ) considering the main performance aspects of burning CWSP containing forest fuels are shown in Figure 3. Heats of combustion of components are presented in Tables 1, 3 and 4. The cost of forest fuels (needles, leaves and their mixtures) is taken as equal to zero; as with coal processing wastes (filter cakes), transportation expenses making up 0.0058 \$/kg were the only expenses accounted. The costs of slurries were determined in proportion to the components' concentrations assuming zero water cost, since process and waste water may be used for the preparation of CLFs.



**Figure 3.** Relative performance indicators ( $D_{relative}$ ) of burning high-potential CWSP fuels containing leaves, needles, or their mixture vs. coal at varying temperatures in the combustion chamber.

The resulting dependences have shown that adding pine needles, leaves and their mixtures appears attractive in terms of environmental friendliness, energy, and cost efficiency. Plant-based slurries, having the same cost as a filter cake of coking coal, are marked by lower concentrations of the main anthropogenic emissions ( $SO_x$ ,  $NO_x$ ), and in terms of heat of combustion, are highly competitive with coal-water fuels.

In the preparation of slurry fuels before the experiments with burning their batches, it was established that all the wood additives under study can significantly affect the rheology. Being added to CWSP fuels, these components adsorb some of the fuel moisture, thus preventing its lamination. The maximum allowable relative mass fraction for the additives and dopants under study should equal 15%.

The reduction of sulfur dioxide emission in CWSP fuels with wood components (Figures 4 and 5) can be attributed to a low sulfur fraction in the latter, which has direct impact on the overall sulfur content in the slurry. It was established that a fuel based on filter cakes, used turbine oil and 10% of tree bark or 10% charcoal has the lower environmental indicators for sulfur oxides (10–108 ppm). Charcoal can rapidly adsorb many substances, including sulfur, from a fluid or gaseous medium. These substances, sulfur in particular, are present as oxides. Therefore, it is safe to conclude that charcoal adsorbs sulfur and nitrogen from the pyrolysis of coal or liquid fuel component of CWSP.

Although the combustion heat of tree bark is comparable with that of a filter cake, its presence in the slurry can increase the energy performance and improve the ignition and combustion characteristics due to a high content of highly volatile substances in the bark particles. Ignition delay and combustion times decrease. In terms of  $NO_x$  emission (Figure 5), a 10% addition of tree bark did slight compensate for the presence of a liquid fuel component in the slurry, which is largely responsible for the formation of fuel oxides [59].

The 10% of sawdust in the CWSP reduces of NO<sub>x</sub> emission in by more than 1.5 times (209–231 ppm vs. 320–466 ppm for coal) at 900–1000 °C. Sawdust intensifies ignition and increases the yield of carbon monoxide (NO<sub>x</sub> + XCO =  $1/2N_2 + XCO_2$ ).



Figure 4. SO<sub>x</sub> concentrations at the CWS and CWSP (with bark, sawdust, charcoal) combustion.



Figure 5. NO<sub>x</sub> concentrations at the CWS and CWSP (with bark, sawdust, charcoal) combustion.

Adding even 10% of sawdust to CWSP based on flotation waste lowers the ignition temperature (70–80 °C) and increases the combustion rate. The sawdust enhances the effects of fuel droplet micro-explosions [60]. This shortens the ignition delay time and overall reduces the energy consumption at the firing stage. The optimal concentrations of nitrogen oxides are also reached with a 10% concentration of charcoal and do not exceed 190 ppm.

The pyrolysis of wood biomass leaves solid residue, which is similar to charcoal in its properties. As a confirmation, the thermal decomposition of forest fuel as part of CWSP occurs under oxygen deficiency (oxygen cannot reach the surface of wood particles, since the gaseous combustion products of coal and liquid fuel components oust air from the combustion zone). Therefore, it is safe to assume that the thermal decomposition of wood as part of slurry fuels produces charcoal, which can adsorb sulfur and nitrogen compositions.

Figure 6 presents the main performance aspects of burning CWSP fuels with wood additives. The heat of combustion and the cost of components are shown in Tables 3–5. The cost of wood waste (bark and sawdust) is taken as equal to zero; as with coal processing wastes (filter cakes), transportation expenses making up 0.006 \$/kg were the only expenses accounted. The average market cost of charcoal was 0.3 \$/kg.

Charcoal, sawdust, and bark can significantly improve the main performance of burning CWSP. Despite high environmental performance indicators of charcoal as a CWSP additive, its global production is not enough. The use of sawdust and bark as additives to composite coal fuel appears very promising.

The results of numerous studies and the industrial experience of co-firing coal fuels with biomass indicate that this technology is associated with several issues [61–64]. Among them, ash-related problems are the key issues. The chemical composition of lignocellulosic fuels differs significantly from traditional coal. Biomass commonly contains large amounts of water-soluble inorganic salts, which can easily volatilize during combustion and become part of the gas phase [61,62]. This leads to high level of activity for alkali materials in the ash and, consequently, high dirtiness propensity during the co-firing process. The quantity volatilized depends on the property of the fuel, the ambient air, and the combustion technology. SiO<sub>2</sub> and CaO dominate in the biomass ashes, oxides of Mg, Al,

K, Na and P is much lower in the ash. The ash from hard biomass (wood) includes large amount of oxides with low melting points, primarily K and P. In addition, they keep substantially lower levels of heavy metals, then soft biomass (straw) [61]. At high temperatures, metals and their oxides partially evaporate and amounted an active part of the reactions in the gaseous phase. During the gases motion in the boiler's channel, they precipitate on its elements at low temperatures and form small particles on the surface, for example CaO. Then these particles become part of the gases in so-termed "fly ash" (<1  $\mu$ m). Because of a reoxidation and coagulation, particles agglomerate, forming ash size more than 10  $\mu$ m (coarse fly ash). Non-volatile ash compounds melt and coalesce on or in the surface of the particle, contingent on the temperature and chemical compound of the particle and the ambient gases [61,62]. Depending on the particle's density and type, the technology used and the gas speed, these ash fractions could be entrained by the gases, but the majority is deposited. For combustion chamber, heavy ash deposition leads to contamination, corrosion, and defluidization. This can reduce the efficiency of the combustion chamber and damage its equipment, as well as increase maintenance costs [61–64].



**Figure 6.** Relative performance indicators ( $D_{relative}$ ) of burning high-potential CWSP fuels containing bark, sawdust, or charcoal vs. coal at varying temperatures in the combustion chamber.

During combustion of slurry fuel with forest biomass, the chemical composition of which contributes to the corrosive effect on boilers, it is important to realize that ash level is one significant factor in the design stage of the equipment. The combustion process of slurry fuels should be adapted to the requirements for fuels, especially when it comes to industrial waste or forest biomass that are chemically different from traditional fuels to achieve sustainable and stable development of such technologies. There are an amount of decisions that can be taken to avert and decrease corrosion, such as controlling the steam temperature in the boiler design to a level at which the corrosion ratio is agreeable, the choice of more noncorrosive alloy of heat exchangers and other boiler elements and use of additive component that modify the combustion gases chemistry and prevent the ash deposition [61,65].

Dmitrienko et al. [57] used two approaches (one considering solely the environmental performance and the other, the combustion heat, fuel cost and anthropogenic emissions) to show that CWSP and CWS fuels are high-potential solutions to many environmental, economic and energy problems of the modern coal-fired power industry by choosing the necessary components and their concentration. The main conclusion of Dmitrienko et al. [57] is that it is worthwhile to involve numerous coal and oil processing wastes (filter cakes, oils, sludges, etc.) in the fuel cycle. The experimental data presented in this research highlight great prospects of solving tasks set on a brand-new environmental level [57]. In particular, the use of forest fuels makes it possible to reduce anthropogenic emissions to such low levels that it makes sense to simplify flue gas purification cycles at power plants. Thus, the economic benefit from CWS and CWSP technology implementation can be even greater than described by Dmitrienko et al. [57]. Moreover, forest biomass reduces not only the anthropogenic gaseous emissions but also ash residue. This is a very important point for coal enterprises. Using CWS and CWSP fuels results in the lower volume of ash formation as compared to that from coal combustion, as well as longer service life of heat and power equipment with high energy performance indicators [66]. This is explained by less ash sticking to heat exchange surfaces, so the heat absorption remains rather high over a long period of time.

## 4. Conclusions

Based on the anthropogenic emission experimental investigations and results of calculating the integral coefficient of burning CWSP carried out during this paper, the following conclusions were reached:

- (i) The vast majority of the results indicate a significant reduction in the amount of emissions due to the involvement of biomass additives in the power generation process. Thus, the use of forest fuels (leaves, needles, sawdust, and bark) reduces sulfur oxide concentration by 2–5 times, nitrogen oxides by 1.5–2 times (depending on the chosen concentration and temperature conditions of fuel combustion) versus coal or CWSP without additives. Moreover, this type of forest biomass is a cheap and renewable energy source formed in large amounts in forests and in timber processing.
- (ii) The use of wood waste gives an opportunity to recover the accumulated timber industry waste, reduce the environmental load, improve rheological as well as thermal and physical characteristics of the fuel. However, there are other problems worth considering. They include modification or at least reconfiguration of fuel control equipment of boiler units, fuel production and supply systems, slagging, and transportation of the components to the station.
- (iii) The calculated complex indicators  $D_{relative}$  takes into account the energy, economic and environmental aspects of using composite fuel liquids. It illustrates the obvious advantages of CWS and CWSP containing leaves and needles.  $D_{relative}$  for these compositions is 1.2–10 times as high as the same indicator for CWS based on filter cakes and CWSP based on filter cakes and 10% of turbine oil.  $D_{relative}$  for fuel samples with sawdust or bark also demonstrates the benefits of biomass additives and exceeds the values of normal CWSP without dopants by 1.2–2.5 times.
- (iv) The main way to further develop this research is to analyze and specify effective CWS and CWSP fuel compositions from numerous components, additives, and dopants. A compiled database of experimental information with the main energy, economic and environmental performance indicators of burning coal, CWS and CWSP with different dopants (an experimental setup and method from study [67] can be used) will make it possible to develop a predictive model. It can be-based, for example, on statements and numerical solution methods of partial differential equations described in studies [68–70] when studying slurry fuel heating, evaporation, thermal decomposition, combustion processes. This model will enable choosing a relevant component composition to reach high-performance indicators of power equipment.

Author Contributions: P.S. wrote the paper; G.N. performed the experiments.

Funding: This research received no external funding.

Acknowledgments: Research was founded by National Research Tomsk Polytechnic University (project VIU-ISHFVP-184/2018).

**Conflicts of Interest:** The authors declare no conflict of interest.

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