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Emission Mitigation by Aluminum-Silicate-Based Fuel Additivation of Wood Chips with Kaolin and Kaolinite

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Abstract: This study investigates the transferability of aluminum-silicate-based fuel additivation as a primary, fuel-based mitigation measure for inorganic alkali-based particulate matter (PM) emissions during the complete combustion of wood chips. Therefore, wood chips are additivated with 0.5 wt% of three different types of the aluminum-silicate-based additive kaolin, which differ mainly in their particle size distribution, and with one type of kaolinite. The subsequent combustion trials with non-additivated and additivated wood chips are carried out in a small-scale combustion plant. To evaluate the effect of the additivation of the wood chips, the total particulate matter (TPM) emissions, the potassium (K) emissions, the ultra-fine PM emissions and the carbon monoxide (CO) emissions, as well as the chemical composition of the resulting ashes, are analyzed. In order to compare the primary, fuel-side mitigation measure of fuel additivation with the established secondary mitigation measures, an electrostatic precipitator (ESP) is additionally utilized. The respective result shows that the aluminum-silicate-based fuel additivation of the wood chips with kaolin and the use of the ESP lead to comparable reductions in the TPM emissions, as well as the share of the ultra-fine particle fraction in the PM emissions. The addition of the additive kaolin additionally causes the significant mitigation of the K and CO emissions. Overall, the obtained results suggest that the combined utilization of fuel-side aluminum-silicate-based fuel additivation, together with the secondary mitigation measure of the ESP, might be very promising to further reduce PM emissions from combustion devices that operate with wood chips.

Keywords: biomass combustion; particulate matter; particle chemical composition; gaseous compounds; emission reduction; fuel improvement

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1. Introduction

In view of a more environmentally sustainable, secure and increasingly defossilized energy supply, renewable, biogenic solid fuels (e.g., wood) could make an important contribution, especially in the area of domestic heat supply [1–3]. Due to its promising fuel-specific properties, wood could continue to account for a significant share of the heating market and, in the form of wood pellets, wood logs and/or wood chips, could also be used in a wide variety of combustion systems in the future [3–5]. However, the energetic use of wood fuels in such combustion devices—irrespective of both the thermal capacity class considered and the actual combustion technology used—is inevitably associated with the formation and even the release into the atmosphere of PM emissions. These particulates are potentially harmful to human health and the natural environment, and which, in the case of corresponding intensity, have so far had to be reduced to the legally specified limits. So far, this is realized in most cases essentially with the aid of secondary, flue gas-sided mitigation measures [2,6,7]. While larger plants (e.g., biomass-fired CHP plants) frequently address this problem with cost-intensive secondary emission mitigation measures (i.e., ESP, fabric filters, scrubbers and flue gas condensation units), equivalent secondary measures for small-scale combustions plants (i.e., 4 kW to 1000 kW) are currently hardly feasible from an economic point of view [2,5,6,8,9]. Consequently, primary or fuel-side measures for PM emission mitigation have been increasingly investigated, especially for such small-scale combustion plants. As an example, this is true for the optimization of combustion chamber geometry, fuel/combustion air staging, flue gas recirculation and/or the adaptation of the biogenic solid fuel used [2,8,10,11].

A much-considered primary mitigation measure on the fuel side, especially for the reduction in inorganic PM emissions, is the addition of so-called additives to the fuel (i.e., fuel additivation) [12–14]. Additives are usually minerals or other chemical compounds that are able to change/control/influence the ash chemistry, reduce the concentration of problematic emissions (e.g., PM, CO) and/or influence the ash melting behavior during the combustion of biogenic fuels (e.g., straw) [13,14]. Assuming an almost complete combustion of biogenic solid fuels in modern (small-scale) combustion plants, the PM emissions originate mainly from the inorganic components of the solid biomass/the wood fuel [15–18]. Among these inorganic biomass or wood components, the ash- and PM-forming alkali element K is of central importance [17–21]. Depending on the chemical composition of the biomass and the combustion conditions (e.g., temperature), K is mainly released as volatile gaseous compounds (e.g., potassium hydroxide (KOH), potassium chloride (KCl), potassium sulfate (K_2SO_4) and/or potassium carbonate (K_2CO_3)), which, as a result of cooling effects in the stack or the atmosphere, ultimately account for the majority of the inorganic PM emissions in the flue gas [22–25]. To counteract this inorganic PM formation, aluminum-silicate-based additives (e.g., kaolin and kaolinite) in particular have proven to be very effective, since they have the ability to capture K from the solid biofuels in the form of high-temperature stable compounds (e.g., kalsilite ($KAlSiO_4$), leucite ($KAlSi_2O_6$) and/or orthoclase ($KAlSi_3O_8$)) in the resulting ash and, thus, reduce or prevent gaseous K release [13,14,26–28]. The use of kaolin and/or kaolinite as additives has already been extensively investigated in the combustion of (wood) pellets in small-scale combustion plants [13,19,29–33]. The additives are usually introduced during pellet production (e.g., during the pelletizing process), by mixing with already produced pellets (e.g., during fuel conveying) or by adding them directly into the combustion chamber (e.g., via spray systems) [14].

Although there has been an increase in the number of automatically fed combustion plants using wood chips in recent years in Germany, there are only very limited data about the emission reduction (e.g., PM, CO) due to fuel additivation for the combustion of wood chips in small-scale combustion plants, in contrast to wood pellets [1,32,34]. A few studies exist that deal with fuel additivation of wood chips at a power plant scale [13,35,36]. With regard to the valid regulations (1. BImSchV), high environmental requirements in the form of reduced emission limits for PM of 20 mg/Nm^3 and for CO of 400 mg/Nm^3 in the flue gas must also be met by such small-scale combustion plants with automatic fuel supply (i.e., wood chips), which were built after 1 January 2015 [34,37]. Against this background, the aim of the present study is to investigate the transferability of fuel additivation as a primary, fuel-side mitigation measure for inorganic alkali-based PM emissions during the complete combustion of biogenic solid fuels (e.g., pellets) to fuel-type wood chips. For this purpose, combustion trials are carried out in a grateless firing unit with automatic fuel supply and a nominal heat output of 33 kW. The wood chips are additivated with 0.5 wt% of different types of aluminum-silicate-based additive kaolin, which differ mainly in their particle size distribution, and with kaolinite. The evaluation of the additivation within the combustion trials takes into account the TPM emissions, the K emissions, the (ultra-fine) PM emissions and the CO emissions, as well as the chemical composition of the solid combustion residue, namely ash, from the complete combustion of the (additivated) wood chips used. In addition to the primary, fuel-side mitigation measure of fuel additivation, an ESP will also be used for comparison as a common secondary mitigation measure to reduce PM emissions, in order to be able to evaluate the transferability of the fuel additivation in the context of the established mitigation measures. Thus, for the first time, the present research systematically investigates the aluminum-silicate-based fuel additivation of wood chips in a real small-scale combustion plant. The focus here is on the influence of the particle size of the additive used, which has not been considered so far. In addition, this study is the first scientific investigation ever to compare the primary emission mitigation measure of fuel additivation of wood chips using kaolin/kaolinite with the secondary mitigation measure of an ESP. This provides us with the unprecedented opportunity to accurately quantify and characterize emission data in a real small-scale wood chip combustion plant—also taking into account different mitigation measures—in order to better assess their impacts on air quality. Unlike many other studies, the analysis of TPM emissions in the present study, in particular, goes beyond solely gravimetric determination by further characterizing both the chemical composition and the ultra-fine particle fraction of these emissions, which can have a significant impact on the potential toxicity of TPM emissions.

2. Material and Methods

The experimental design of the present study involves the fuel additivation of wood chips (i.e., pine wood) with 0.5 wt% of four aluminum-silicate-based additives (i.e., kaolin and kaolinite) and the subsequent combustion of the resulting additivated wood chips in a small-scale combustion plant (i.e., 33 kW), in particular for the analysis of the occurring emissions. The additive content used (i.e., 0.5 wt%) is based on stoichiometric calculations and our own preliminary investigations [32,38]. For comparison purposes, combustion trials are also carried out with non-additivated wood chips with and without an ESP as a secondary flue gas treatment measure. During all the combustion trials (i.e., without and with additives), the TPM emissions (incl. chemical composition), the K emissions, the (ultra-fine) PM emissions, the CO emissions and the resulting ashes (incl. chemical composition and crystalline phases) are analyzed. The experimental material and the analytical methods are presented below.

2.1. Wood Chips

For the analyses and investigations, untreated pine wood chips with negligible bark content are used. The wood chips are purchased from a local fuel supplier. Table 1 shows the fuel properties and chemical composition of these wood chips [39–41]. With regard to the relevant standards, the wood chips used have a typical chemical composition for untreated solid biofuels made of coniferous wood with insignificant amounts of bark or needles [42–44]. The used wood chips can be assigned to a high-quality class (A1) based on their moisture and ash content [42,43].

Table 1. Fuel properties and chemical composition of the wood chips according to DIN EN ISO 17225-1 (a.r.: wood chips as received, d.b.: dry wood chip basis, *: calculated by mass difference, n.d.: not determined) [39–42].

Parameter	Unit	Wood Chips
Moisture content	$wt\%_{a.r.}$	6.6
Ash content	$wt\%_{d.b.}$	0.3
Carbon (C)	$wt\%_{d.b.}$	49.8
Hydrogen (H)	$wt\%_{d.b.}$	6.4
Oxygen (O) *	$wt\%_{d.b.}$	43.6
Nitrogen (N)	$wt\%_{d.b.}$	<0.1
Sulfur (S)	$wt\%_{d.b.}$	<0.2
Potassium (K)	$mg/kg_{d.b.}$	475
Sodium (Na)	$mg/kg_{d.b.}$	8
Calcium (Ca)	$mg/kg_{d.b.}$	713
Magnesium (Mg)	$mg/kg_{d.b.}$	171
Silicon (Si)	$mg/kg_{d.b.}$	<250
Manganese (Mn)	$mg/kg_{d.b.}$	28
Phosphorus (P)	$mg/kg_{d.b.}$	n.d.
Aluminum (Al)	$mg/kg_{d.b.}$	10
Iron (Fe)	$mg/kg_{d.b.}$	10
Copper (Cu)	$mg/kg_{d.b.}$	3
Zinc (Zn)	$mg/kg_{d.b.}$	7
Lead (Pb)	$mg/kg_{d.b.}$	<1

2.2. Additives

Four different aluminum-silicate-based additives are used (i.e., Kaolin I, Kaolin II, Kaolin III, and Kaolinite) [45–47]. The chemical compositions of these additives are shown in Table 2, while Figure 1 shows the corresponding particle size distributions. The three kaolin types, Kaolin I, Kaolin II, and Kaolin III, have a comparable chemical composition (Table 2) and differ mainly in terms of particle size distribution (Figure 1). Among the additives used, Kaolin I has the largest value with a median for the particle size distribution of about 1.34 mm (Figure 1). For the additives Kaolin II, Kaolin III, and the impurity-free Kaolinite (Table 2), the corresponding figures (i.e., median of the particle size distribution) are lower, with values of about 0.18 mm, 0.09 mm and <0.06 mm (Figure 1), respectively. While for Kaolin I almost 100% of the additive particles have a diameter of $\leq$4.0 mm, the equivalent particle diameter is $\leq$0.5 mm for Kaolin II, $\leq$0.25 mm for Kaolin III and also $\leq$0.25 mm for Kaolinite (Figure 1).

Table 2. Chemical compositions of the aluminum-silicate-based additives Kaolin I, Kaolin II, Kaolin III, and Kaolinite (a.r.: additive as received).

Parameter	Unit	Kaolin I	Kaolin II	Kaolin III	Kaolinite
SiO_2	$wt\%_{a.r.}$	46.9	44.6	50.2	46.5
Al_2O_3	$wt\%_{a.r.}$	37.2	37.5	34.4	39.5
H_2O	$wt\%_{a.r.}$	13.3	14.3	12.0	14.0
Fe_2O_3	$wt\%_{a.r.}$	0.9	2.0	0.5	-
TiO_2	$wt\%_{a.r.}$	0.4	1.1	0.4	-
K_2O	$wt\%_{a.r.}$	1.0	<0.1	2.1	-
Na_2O	$wt\%_{a.r.}$	0.1	0.2	0.2	-
CaO	$wt\%_{a.r.}$	<0.1	<0.1	<0.1	-
MgO	$wt\%_{a.r.}$	<0.1	<0.1	<0.1	-
P_2O_5	$wt\%_{a.r.}$	0.1	0.2	0.2	-

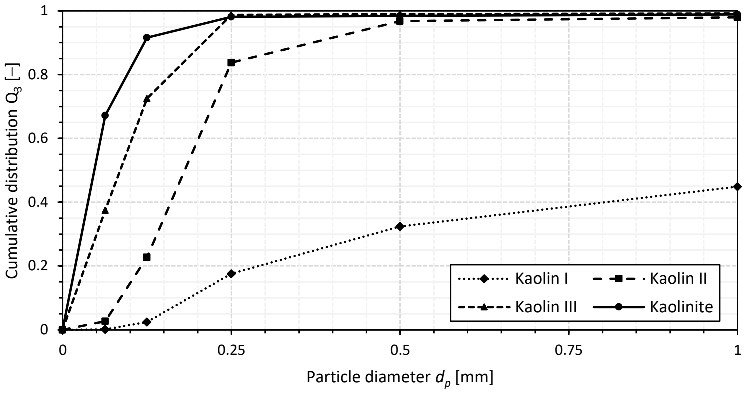

Figure 1. Cumulative particle size distributions of the aluminum-silicate-based additives Kaolin I, Kaolin II, Kaolin III, and Kaolinite (Q_3: cumulative distribution of the quantity type "mass" determined by sieve analysis).

2.3. Combustion Plant

For the combustion trials, a small-scale combustion plant of the RHK-AK boiler series from the company Heizomat—Gerätebau + Energiesysteme GmbH with a nominal heat output of 33 kW is used [48]. The corresponding RHK-AK 30 boiler system is a grateless firing unit with automatic fuel feed (~12 kg/h) and glow-bar ignition. For ash discharging purposes, a deashing chain is implemented. The control of the combustion plant is realized by the Heizocontrol ET200 system. In addition, the combustion unit is equipped with an EF 185 electrostatic precipitator from Heizomat, which can be optionally switched on via the boiler control system. For the analysis of emissions defined above, a measuring section designed in accordance with DIN EN 15259 [49] is connected to this combustion plant. Prior to each combustion trial, the combustion chamber, the automatic fuel supply system and the fuel bunker are cleaned to remove any residues from previous test runs. The emission measurements are carried out for stable operating conditions (i.e., after a constant flue gas temperature has been reached) under full load conditions of the combustion plant.

2.4. Emissions

2.4.1. Total Particulate Matter

The gravimetric determination of TPM emissions is carried out by means of a manual, discontinuous measuring principle based on DIN EN 13284-1 [50] and VDI 2066-1 [51]. A partial volume flow is taken from the flue gas under isokinetic conditions at a representative measuring point in accordance with DIN EN 15259 [49] for a specified period of 5 min each. An out-stack filter unit (Paul Gothe) is used as a sampling device. The TPM contained in the sampled partial volume flow of the flue gas is deposited for each measurement on a weighed-in quartz fiber flat filter, which has previously been heated in a laboratory drying oven (Heraeus LUT 6050) at a temperature of 160 °C for 1 h and then cooled to room temperature for at least 8 h in a desiccator. After sampling, the flat filter loaded with TPM is heated in an identical manner, cooled and weighed again. In addition to the mass increase in the flat filter, the mass deposits in front of the filter in the sampling device are also attributed to the sampled partial volume flow of the flue gas. For each combustion trial (e.g., wood chips without additive), twelve flat filters are used over a total measurement period of about four hours. The TPM emissions are given for dry flue gas under standard conditions (i.e., for a pressure of 101 325 Pa and a temperature of 273.15 K) and an oxygen reference concentration of 13 vol% in the flue gas.

Potassium

To determine the K emissions and to analyze the chemical composition of the TPM emissions, the loaded quartz fiber flat filters (Section 2.4.1) are further analyzed by atomic absorption spectrometry (AAS) and ion chromatography (IC). For the AAS measurements, at least three flat filters are digested according to DIN 22022-1 [52] using aqua regia (i.e., a mixture in a molar ratio of 3 to 1 consisting of hydrochloric acid (32%) and nitric acid (65%) in microwave digestion system (Anton Paar Multiwave GO Plus)). The resulting solutions are then analyzed according to DIN 22022-3 [53] in an air-acetylene or nitrous-acetylene flame of an atomic absorption spectrometer (Analytik Jena contrAA 700) for the concentration of various inorganic elements (e.g., potassium (DIN 38406-13 [54]), sodium (DIN 38406-14 [55]) or calcium and magnesium (DIN EN ISO 7980 [56])). For the IC measurements, demineralized water is added to at least three flat filters and the filtered solutions obtained are analyzed for water-soluble components or dissolved anions (e.g., sulfate and chloride) using an ion chromatograph system (Dionex Sodtron ICS-90), in accordance with DIN EN ISO 10304-1 [57].

Ultrafine Particulate Matter

For the investigation of (ultra-fine) $PM_{(0.1)}$ emissions, a partial volume flow of the flue gas is taken at a representative measuring point in accordance with DIN EN 15259 [49] by means of a fine particle sampler (Dekati FPS-4000) and diluted accordingly. The diluted sample volume flow is then analyzed by a combination of a scanning mobility particle sizer (TSI NanoScan SMPS 3910) and an optical particle sizer (TSI OPS 3330), with respect to the particle size number distribution of the (ultra-fine) $PM_{(0.1)}$ emissions in the size range from 10 nm to 10 µm. A multi-instrument manager (MIM) software is used to standardize and evaluate the data from both measuring instruments (i.e., SMPS and OPS) [58].

2.4.2. Carbon Monoxide

The CO emissions are determined every 10 s by means of a flue gas analyzer (Wöhler A 550) within the measuring section connected to the combustion plant (Section 2.3). The CO emissions are given in relation to dry flue gas under standard conditions (i.e., a pressure of 101 325 Pa and a temperature of 273.15 K) and an oxygen reference concentration of 13 vol% in the flue gas. In addition to CO, the flue gas analyzer used can also detect and record the concentrations of oxygen, carbon dioxide, nitrogen oxides and hydrogen in the flue gas.

2.5. Ashes

The ashes are sampled at five regular intervals during each combustion trial under full load conditions after a constant flue gas temperature has been reached (i.e., stable operating conditions). Following each combustion trail, the five individual ash samples are mixed and homogenized. The chemical composition of the ashes is determined based on a general analysis sample (~100 mg) in accordance with DIN EN ISO 16967 [59] and DIN EN ISO 16968 [60]—analogous to the TPM filters (Section 2.4.1)—using AAS according to DIN 22022-1 [52] and DIN 22022-3 [53] and IC according to DIN EN ISO 10304-1 [57]. The analysis of the crystalline phases of the ashes is also carried out on the basis of general analysis samples (~1 g) by means of X-ray diffraction (XRD), according to DIN EN 13925-1 [61] and DIN EN 13925-2 [62]. An X-ray diffractometer (Siemens D500) is used for this purpose, while the evaluation of the resulting diffractograms and the identification of the crystalline phases is carried out using associated software (Bruker DIFFRAC). All previously mentioned analyses of the ashes were performed in triplicate.

3. Results and Discussion

The results of the conducted combustion trials for the non-additivated (i.e., without and with ESP) and additivated (i.e., 0.5 wt% Kaolin I, Kaolin II, Kaolin III, and Kaolinite) wood chips with respect to the emissions and ashes are presented and discussed below.

3.1. Emissions

3.1.1. Total Particulate Matter

The mean TPM emissions for the combustion of non-additivated (without and with ESP) and additivated (0.5 wt%) pine wood chips using the additives Kaolin I, Kaolin II, Kaolin III and Kaolinite are shown in Figure 2. For the non-additivated wood chips without ESP, the mean TPM emissions are 36 mg/Nm^3 [63,64]. By using the ESP, the mean TPM emissions can be reduced to 23 mg/Nm^3 for the non-additivated wood chips. For the addition of 0.5 wt% Kaolin I, Kaolin II, Kaolin III, and Kaolinite, values of 27 mg/Nm^3, 24 mg/Nm^3, 23 mg/Nm^3, and 47 mg/Nm^3 are obtained for the mean TPM emissions during wood chip combustion, respectively.

The additivation of the wood chips with 0.5 wt% of Kaolin I, Kaolin II, and Kaolin III leads to a verifiable reduction in the mean TPM emissions for all three kaolin types, compared with the non-additivated reference case without ESP (Figure 2). This means that even for an apparently small additive content of 0.5 wt%, adequate adhesion behavior of kaolin to the wood chips can be assumed, resulting in the determined emission mitigations [38]. A comparable mitigation effect of aluminum-silicate-based additives has already been demonstrated in other studies [19,32,33]. Consequently, the present results can be understood as practical evidence, which has not been available previously, that aluminum-silicate-based fuel additivation can in principle be transferred and implemented for real small-scale wood chip combustion. Considering the particle size distributions of the kaolin types (Figure 1), it seems reasonable to hypothesize that a smaller median for the particle size of the additive kaolin has a positive effect on the reduction in the mean TPM emissions during small-scale wood chip combustion. A qualitatively similar behavior has already been demonstrated in the course of several laboratory-scale investigations [23,28,38]. A possible explanation for the increasing reduction in TPM emissions with the decreasing particle size of kaolin could be due to the specific surface area of the additive particles. Smaller kaolin particles (e.g., Kaolin III) have a larger specific surface area, which in turn should favor the heterogeneous gas–solid reaction between the highly volatile K compounds released during wood chip combustion and the kaolin added to the fuel [35]. As a consequence, the better incorporation of K into the resulting ash, and thus a stronger reduction in TPM emissions, can be assumed. This behavior can be confirmed by the results shown in Figure 2 for the practical application.

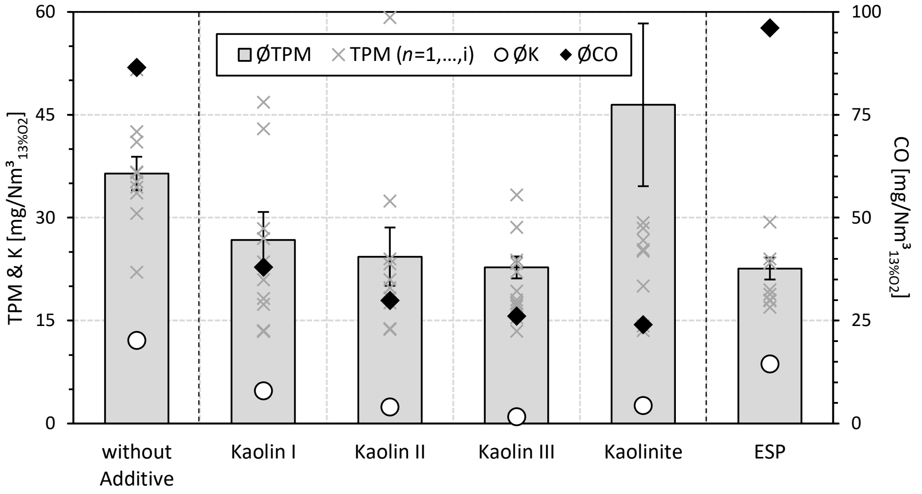

Figure 2. Mean total particulate matter (TPM) (individual measured values ($n \leq 12$) and standard errors), potassium and carbon monoxide emissions for the combustion of non-additivated (without and with electrostatic precipitator (ESP)) and additivated (0.5 wt% Kaolin I, Kaolin II, Kaolin III, and Kaolinite) wood chips (K: potassium, CO: carbon monoxide).

However, it can be observed for Kaolinite in Figure 2 that there can also be a negative influence on the emissions due to a reduction in the additive particle size, since the median of the particle size distribution for Kaolinite (<0.06 mm) is even lower than the comparative value for Kaolin III (0.09 mm) in Figure 1, but the mean TPM emissions for Kaolinite (47 mg/Nm^3) at the same time even exceed the reference value for the non-additivated wood chips without ESP (36 mg/Nm^3). A reason for the observed behavior of TPM emissions could be the entrainment of kaolinite with the flue gas from the combustion chamber of the investigated small-scale combustion plant. This effect has already been described in the literature for very fine kaolin in a CFB boiler [35]. Due to the small particle size of the Kaolinite, there could be sporadic swirling of additive particles during the combustion of the wood chips, which, due to their low weight, could then be entrained with the flue gas and occur as part of the TPM emissions. The larger standard error of the TPM emissions for the wood chips additivated with Kaolinite compared to the other combustion trails favors the hypothesis that additive entrainment, and consequently higher emissions, could occur only in isolated cases. Thus, the use of the additive kaolin, or in this case, in particular the kaolin type Kaolin III, appears to be more appropriate than the impurity-free Kaolinite.

Finally, by adding 0.5 wt% Kaolin III to the wood chips as a primary mitigation measure (i.e., fuel additivation), comparable and almost limit-compliant (i.e., ≤20 mg/Nm^3 according to 1. BImSchV (German Emission Directive)) mean that TPM emissions of about 23 mg/Nm^3 can be achieved, as in the case of using the ESP as a common secondary mitigation measure. This is also interesting beyond the fact that such comparisons of different emission mitigation measures are usually not represented in the literature for the combustion of wood chips in small-scale combustion plants, in that it requires a continuous, power-consuming operation of the secondary mitigation measure for a reliable reduction effect by the ESP. Whereas aluminum-silicate-based additivation could in principle already be realized in the course of fuel production or supply, it must be ensured for the ESP that it is not manually switched off by the plant operator and that, in addition, a power supply is continuously guaranteed [5,9]. Furthermore, the collection efficiency of an ESP, which is usually between 20% and 80%, can be reduced as a result of aging [9].

Potassium

Table 3 shows the chemical composition of the gravimetrically determined TPM emissions for the combustion of non-additivated (without and with ESP) and additivated wood chips using 0.5 wt% of the additives Kaolin I, Kaolin II, Kaolin III, and Kaolinite, respectively [63]. The K emissions (i.e., mean concentration of K in the TPM emissions) are shown in Figure 2. For the non-additivated reference case of the wood chips without ESP, the emissions of the highly volatile, PM-forming alkali element K amount to 12 mg/Nm^3, while a corresponding value of 9 mg/Nm^3 is achieved for the utilization of the ESP. In contrast, the additivation of the wood chips results in K emissions of 5 mg/Nm^3 (Kaolin I), 2 mg/Nm^3 (Kaolin II), 1 mg/Nm^3 (Kaolin III) and 3 mg/Nm^3 (Kaolinite) (Figure 2). A similar reduction in the K emissions as a result of the fuel additivation has already been observed in other studies [19,29,33].

Table 3. Chemical compositions of total particulate matter emissions for the combustion of non-additivated (without and with electrostatic precipitator (ESP)) and additivated (0.5 wt% Kaolin I, Kaolin II, Kaolin III and Kaolinite) wood chips (d.b.: dry TPM basis).

Parameter	Unit	Without Additive	Kaolin I	Kaolin II	Kaolin III	Kaolinite	ESP
Potassium (K)	wt%$_{\text{d.b.}}$	33.3	17.8	9.9	4.3	5.7	38.5
Sodium (Na)	wt%$_{\text{d.b.}}$	0.5	0.7	0.5	0.5	1.2	2.5
Calcium (Ca)	wt%$_{\text{d.b.}}$	4.2	6.9	6.4	6.2	7.2	7.6
Magnesium (Mg)	wt%$_{\text{d.b.}}$	0.3	0.2	<0.1	0.1	<0.1	<0.1
Aluminum (Al)	wt%$_{\text{d.b.}}$	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Iron (Fe)	wt%$_{\text{d.b.}}$	1.8	3.5	3.4	2.9	3.7	3.7
Zinc (Zn)	wt%$_{\text{d.b.}}$	1.0	1.6	1.8	1.5	2.0	1.8
Sulfate (SO_4^{2-})	wt%$_{\text{d.b.}}$	36.9	17.2	9.8	4.0	7.6	35.1
Chloride (Cl^-)	wt%$_{\text{d.b.}}$	5.6	6.1	7.0	4.2	11.0	7.3

The results in Figure 2 show that not only the mean TPM emissions but also the K emissions are increasingly reduced as the mean particle diameter of the kaolin types used decreases (Figure 1). Considering the chemical composition of the TPM emissions (e.g., for non-additivated wood chips without ESP (i.e., high K and sulfate concentrations) in Table 3), this again emphasizes the correlation between the K originating from the fuel or the resulting highly volatile K species (e.g., K_2SO_4 and/or KCl), and the (inorganic) TPM emission formation during the combustion of biomass [13,14,63,65–68]. As the K concentration in the TPM emissions is progressively reduced for a decreasing mean particle size of the three kaolin types in Table 3, the previously stated hypothesis that different reactivities may occur due to the resulting specific surface areas of the additives is solidified. For example, a low K content of 4.3 wt%$_{\text{d.b.}}$ (Kaolin III) in Table 3 suggests that a large part of the K released as highly volatile compounds in the non-additivated reference case (33.3 wt%$_{\text{d.b.}}$) was actually able to react with the additive via the desired heterogeneous gas–solid reaction and is, thus, likely to be present as high-temperature stable compounds in the ash (Table 5) [35]. Therefore, the validity of the theory behind the aluminum-silicate-based fuel additivation can be demonstrated and confirmed for wood chips in a real small-scale combustion plant. Comparable effects, i.e., an increasing reduction in K in the TPM emissions, could so far only be achieved in the literature by increasing the amount of additive used, but not by reducing the additive particle size as in the present study, which in turn offers the possibility of preserving additives [29].

Contrary to the mean TPM emissions, the addition of 0.5 wt% Kaolinite to the wood chips also leads to a considerable reduction in the K emissions (Figure 2). With regard to the chemical composition of the TPM emissions (e.g., low K concentration), it can be hypothesized that the fuel additivation of the wood chips with Kaolinite leads to the desired high-temperature stable incorporation of K into the ash (Table 5) and, thus, to reduced K emissions (i.e., similar to the kaolin types). However, at the same time, the increased TPM emissions (47 mg/Nm^3) and the relatively low proportion of identified inorganic TPM components (<40 wt%$_{\mathrm{d.b.}}$) suggest the increased presence of different (potentially organic) TPM emissions. A comparable behavior has already been observed for the combustion of additivated wood pellets [29].

Finally, Figure 2 shows that the reduction in K emissions for the ESP is significantly lower than for the aluminum-silicate-based fuel additivation (e.g., Kaolin III). Consequently, the reduction in the TPM emissions in the case of the ESP is likely to be due to the separation of organic fractions of the TPM emissions (i.e., a high proportion of identified inorganic TPM components (Table 3)), which makes a combined mitigation concept of aluminum-silicate-based fuel additivation and an ESP appear very worthy of investigation in the future. Aluminum-silicate-based fuel additivation of biogenic solid fuels could already reduce the amount of TPM formed in the combustion process, in particular by reducing the K-related fraction of the TPM emissions, while an ESP installed downstream in the flue gas path could provide an additional reduction in TPM emissions due to size-selective collection efficiency.

Ultrafine Particulate Matter

The particle size number distributions for the PM emissions during the combustion of non-additivated (without and with ESP) and additivated (0.5 wt% Kaolin I, Kaolin II, Kaolin III, and Kaolinite) wood chips are shown in Figure 3. For the reference case without additives and without ESP, the mode (i.e., modal value) of the particle size number distribution is 56 nm [69,70], while a corresponding value of 34 nm is obtained when the additive Kaolin I is used. A similar shift in the particle size number distribution towards smaller particle diameters (i.e., median) due to the fuel additivation has already been observed previously [13,29]. Using the ESP increases the mode, i.e., the modal value, of the particle size number distribution to a value of 70 nm. For the three additives Kaolin II, Kaolin III, and Kaolinite, in contrast to the non-additivated reference case without ESP (i.e., unimodal [63,64,70]), bimodal particle size number distributions can be obtained as shown in Figure 3. The modes or modal values of the corresponding distributions are 29 nm and 87 nm (Kaolin II), 25 nm and 94 nm (Kaolin III), as well as 27 nm and 103 nm (Kaolinite). In view of the chemical composition of the TPM emissions (Table 3) and the reduced K emissions (Figure 2) due to the use of the four aluminum-silicate-based additives, it can be assumed that the shift of the cumulative particle size number distributions into the range of lower particle diameters compared with the non-additivated reference case without ESP (Figures 3 and 4) may be due to the increased presence of organic particles with diameters $\leq$50 nm [13,29,71,72]. Consequently, the reduction effect of the additives, especially with regard to the reduced inorganic K emissions (Figure 2), could result in a reduction in K-containing PM$_{0.1}$ particles with a particle diameter between 50 nm and 100 nm. In contrast, the use of the ESP leads to an increased reduction in PM particles with a diameter <50 nm as well as >100 nm. Thus, the different effects on the particle size number distributions for the PM emissions due to fuel additivation and the utilization of an ESP also seem to make the combination of the two mitigation measures (i.e., primary aluminum-silicate-based fuel additivation and secondary electrostatic particle separation) appear highly promising, as their mechanisms of action appear to be focused on different size fractions of the PM emissions, which could harness synergetic effects.

To increase the comparability of the results, the cumulative particle size number distributions are additionally shown in Figure 4. The cumulative distribution for the reference case (i.e., without additive and without ESP) shows a median of 54 nm (i.e., slightly below the mode, i.e., the modal value, of 56 nm in Figure 3). For the addition of 0.5 wt% of the aluminum-silicate-based additives Kaolin I, Kaolin II, Kaolin III, and Kaolinite, the corresponding median values of 38 nm, 41 nm, 48 nm and 37 nm are obtained. The median for the cumulative distribution using the ESP is 67 nm. Moreover, Figure 4 shows that for the non-additivated wood chips without ESP, about 90% of the PM emissions can be assigned to the ultra-fine particle fraction PM$_{0.1}$ (i.e., these particles have a particle diameter of ≤100 nm). For the additivated wood chips, the corresponding shares of the $PM_{0.1}$ fraction in the PM emissions are 91% (Kaolin I), 84% (Kaolin II), 79% (Kaolin III), and 81% (Kaolinite), respectively. Here, it is also reasonable to assume that the demonstrable reduction in K emissions (Figure 2 and Table 3) in the context of the aluminum-silicate-based additivation of the wood chips with coarser kaolin (i.e., Kaolin I) has a disproportionate effect on inorganic PM particles with a diameter of ~100 nm, while, as a result of smaller particle sizes of the additive, K-related PM particles with a diameter of <50 nm are also increasingly reduced, which in turn results in a reduction in the ultra-fine particle fraction in the PM emissions. For the non-additivated wood chips using the ESP, 77% of the PM emissions can be assigned to the $PM_{0.1}$ fraction. Thus, the secondary emission mitigation measure actually results in the smallest share of the ultra-fine particle fraction in the PM emissions, i.e., the PM emissions for the ESP proportionately consist of more coarser particles than in the case of the aluminum-silicate-based fuel additivation. It is worth noting in that the toxicological potential of PM emissions, in addition to chemical composition, tends to be ranked higher for smaller particles than for coarser emissions. Ultimately, an air quality-enhancing effect can be established by the present study for both mitigation measures considered.

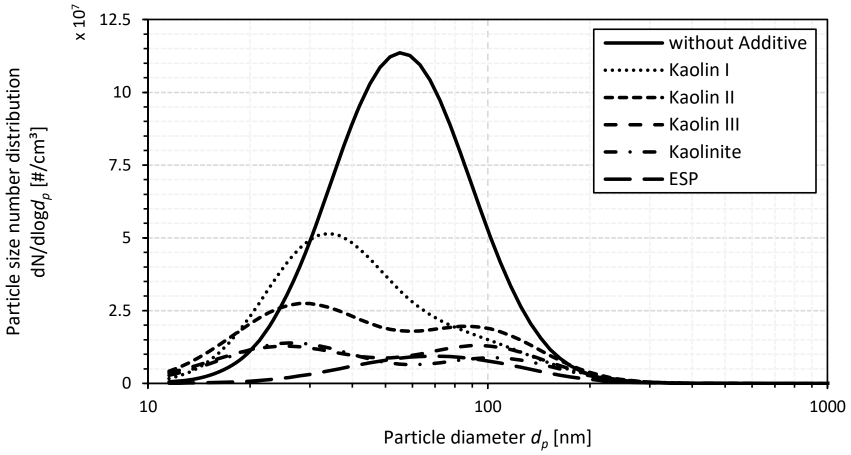

Figure 3. Particle size number distributions of the particulate matter (PM) emissions for the combustion of non-additivated (without and with electrostatic precipitator (ESP)) and additivated (0.5 wt% Kaolin I, Kaolin II, Kaolin III, and Kaolinite) wood chips.

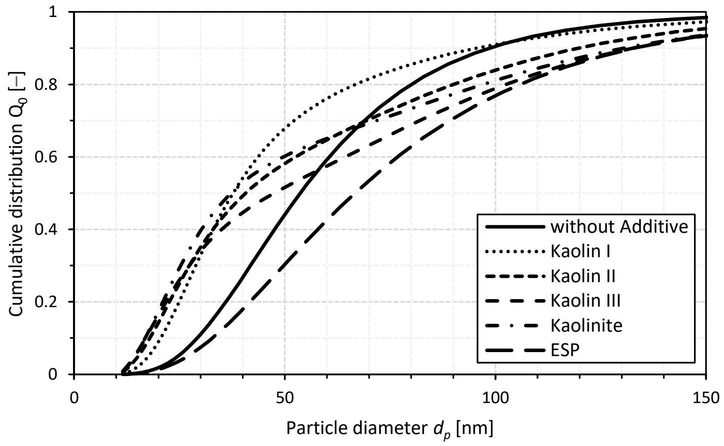

Figure 4. Cumulative particle size number distributions of the particulate matter emissions (PM) for the combustion of non-additivated (without and with electrostatic precipitator (ESP)) and additivated (0.5 wt% Kaolin I, Kaolin II, Kaolin III, and Kaolinite) wood chips (Q_0: cumulative distribution of the quantity type "number" determined by mobility and optical analysis).

3.1.2. Carbon Monoxide

Figure 2 shows the mean CO emissions for the combustion of non-additivated (without and with ESP) and additivated wood chips using 0.5 wt% of the aluminum-silicate-based additives Kaolin I, Kaolin II, Kaolin III and Kaolinite, respectively. In the reference case without additive and without ESP, the mean CO emissions for the wood chips amount to 87 mg/Nm^3. For the additional use of the ESP, the CO emissions show a corresponding value of 96 mg/Nm^3. The mean CO emissions for the ESP should not be understood as an increase in emissions compared to the non-additivated reference case, since both values are based on a certain standard deviation; therefore, they are at a comparable level for small-scale combustion, i.e., no significant change in CO emissions due to the secondary mitigation measure. Instead, the two mean values for non-additivated wood chip combustion (without and wit ESP) should be interpreted as evidence of the good replicability of the emission data in the context of the study carried out, which in some cases is only given to a very limited extent in the literature. The aluminum-silicate-based fuel additivation of the wood chips results in mean CO emissions of 38 mg/Nm^3 (Kaolin I), 30 mg/Nm^3 (Kaolin II), 26 mg/Nm^3 (Kaolin III) and 24 mg/Nm^3 (Kaolinite). A comparable mitigation in CO emissions has already been demonstrated in other work, although the underlying mechanism of action has not yet been understood, but may possibly be associated with the catalytic activity of kaolin/kaolinite [19,32].

Hence, the mean CO emissions for the three kaolin types show identical behavior to the corresponding mean TPM and K emissions in Figure 2; i.e., as the particle size of the kaolin decreases (Figure 1), the mean CO emissions are increasingly reduced and simultaneously reach values that are significantly below the value for the non-additivated reference case without ESP. In contrast to the TPM and K emissions, this correlation between the mean additive particle size and the resulting CO emissions identified for the kaolin types can also be transferred to the additivation of the wood chips with 0.5 wt% kaolinite (Figure 2). While a small particle size of an additive to be used does not necessarily appear to be beneficial with regard to the TPM emissions, this hypothesis, thus, does not appear to be valid with regard to the CO emissions.

Finally, it can be stated that both the aluminum-silicate-based fuel additivation (e.g., 0.5 wt% Kaolin III) and the utilization of an ESP can reduce the TPM emissions during the combustion of wood chips, but the associated CO emissions can only be reduced at the same time by using aluminum-silicate-based additives. Thus, in contrast to the ESP (i.e., secondary mitigation measure), the primary aluminum-silicate-based fuel additivation can lead to a simultaneous reduction of two air pollutants limited according to the 1. BImSchV (German Emission Directive) (i.e., CO $\leq$ 400 mg/Nm^3 and TPM $\leq$ 20 mg/Nm^3).

3.2. Ashes

The chemical composition of the ashes for the combustion of non-additivated (without and with ESP) and additivated (0.5 wt% Kaolin I, Kaolin II, Kaolin III, and Kaolinite) wood chips are shown in Table 4, while Table 5 shows the identified crystalline phases in the corresponding ashes. The results in Table 4 show that the fuel additivation changes the composition of the resulting ashes compared to the two non-additivated cases [19,29]. While the relative proportion of aluminum amounts to ~7 wt% for the non-additivated reference case without ESP and to ~4 wt% for the utilization of the ESP, the corresponding proportions in the ashes significantly increase to ~12 wt% (Kaolin I), ~15 wt% (Kaolin II), ~14 wt% (Kaolin III), and ~13 wt% (Kaolinite) for the additivated wood chips. This increase in the relative proportion of aluminum in the ashes is a common indication in the literature for successful additivation, which can be attributed to the chemical composition of the additives (Table 2) added to the wood, while at the same time increasing the absolute amount of ash produced (e.g., due to the presence of more non-volatile, ash-forming elements, such as aluminum or silicon originating from the additives, as well as due to the additional ash incorporation of highly volatile elements such as K) [29,32]. In particular, due to the increased ash generation as a result of the addition of the additives, the relative proportion of the non-volatile calcium in the ashes also decreases compared to the non-additivated cases (Table 4), which in the literature is often referred to as the ash dilution effect [13].

Table 4. Chemical compositions of the ashes for the combustion of non-additivated (without and with electrostatic precipitator (ESP)) and additivated (0.5 wt% Kaolin I, Kaolin II, Kaolin III, and Kaolinite) wood chips (d.b.: dry ash basis).

Parameter	Unit	Without Additive	Kaolin I	Kaolin II	Kaolin III	Kaolinite	ESP
Potassium (K)	$wt\%_{d.b.}$	7.7	7.9	6.9	6.9	6.7	13.3
Sodium (Na)	$wt\%_{d.b.}$	0.4	0.1	0.2	0.1	0.1	0.1
Calcium (Ca)	$wt\%_{d.b.}$	18.3	11.0	10.3	9.1	9.2	23.6
Magnesium (Mg)	$wt\%_{d.b.}$	3.6	2.7	2.6	2.2	2.0	5.7
Aluminum (Al)	$wt\%_{d.b.}$	7.4	11.9	15.0	14.3	13.4	4.3
Iron (Fe)	$wt\%_{d.b.}$	2.0	1.1	1.5	1.2	0.8	0.9
Zinc (Zn)	$wt\%_{d.b.}$	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sulfate (SO_4^{2-})	$wt\%_{d.b.}$	1.6	1.1	1.5	1.2	1.2	1.4
Chloride (Cl^-)	$wt\%_{d.b.}$	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 5. Crystalline phases of the ashes for the combustion of non-additivated (without and with electrostatic precipitator (ESP) and additivated (0.5 wt% Kaolin I, Kaolin II, Kaolin III, and Kaolinite) wood chips.

Parameter	Without Additive	Kaolin I	Kaolin II	Kaolin III	Kaolinite	ESP
K_2SO_4	x					x
K_2CO_3	x					x
$K_2Ca(CO_3)_2$						x
$KAlSiO_4$			x	x	x	
$KAlSi_3O_8$					x	
Al_2O_3		x				
SiO_2		x		x		
$CaCO_3$	x	x	x	x	x	x
MgO		x		x	x	x

In contrast to calcium, the highly volatile K does not show a distinct reduction in the relative proportion in the ashes due to the aluminum-silicate-based fuel additivation of the wood chips (i.e., ~8 wt% (Kaolin I), ~7 wt% (Kaolin II), ~7 wt% (Kaolin III), and ~7 wt% (Kaolinite)) compared to the non-additivated reference without ESP (~8 wt%), whereby the absolute amount of ash is also increased accordingly by the addition of the additives [29]. Consequently, it can be assumed that the ashes of the additivated wood chips contain a higher absolute amount of K than for the non-additivated cases. This effect can be attributed to the incorporation of K in the ashes by the aluminum-silicate-based additives (Table 5), which provides qualitative evidence of the effectiveness of the fuel additivation as a primary mitigation measure.

Additionally, the results in Table 5 show that both for the non-additivated reference case without ESP and for the non-additivated wood chips using the ESP, the crystalline compounds K_2SO_4 and K_2CO_3 can be identified in the associated ashes [73]. Both compounds have moderate melting temperatures and, when exposed to thermal treatment during combustion, can lead to a gaseous release of K with subsequent inorganic TPM formation [23,24]. The same applies to the crystalline K compound $K_2Ca(CO_3)_2$, which is detectable in the ash in the non-additivated case without ESP. As crystalline compounds of the non-volatile alkaline earth elements (i.e., calcium and magnesium) contained in the wood chips (Table 1), calcium carbonate ($CaCO_3$) can mainly be identified in the ashes of the non-additivated wood chips (i.e., without and with ESP), and, in the case of the use of the ESP, magnesium oxide (MgO) [33,73]. Accordingly, it can be assumed that the relatively high cumulative share of alkaline earth elements in the chemical composition of the ashes (Table 4) is at least partly due to the presence of these compounds.

Considering the results of the crystalline phase analysis in Table 5, this hypothesis can also be applied to the ashes for the aluminum-silicate-based additivation of the wood chips with Kaolin I, Kaolin II, Kaolin III, and Kaolinite, respectively. While no crystalline compounds of the highly volatile alkali element K can be identified in the ash for the addition of 0.5 wt% Kaolin I to the wood chips, the high-temperature stable potassium-aluminum silicates kalsilite ($KAlSiO_4$) and orthoclase ($KAlSi_3O_8$) can be detected in the corresponding ashes of the wood chips additivated with 0.5 wt% Kaolin II, Kaolin III, and Kaolinite (Table 5) [71]. The presence of these compounds can be interpreted as qualitative evidence for the reaction between the aluminum-silicate-based additives and the K originating from the wood chips (Table 1) [14,23,24]. The occurrence of kalsilite ($KAlSiO_4$) and orthoclase ($KAlSi_3O_8$) in the ashes correlates with the reduced K and partly TPM (Figure 2), as well as (ultra-fine) PM emissions (Figures 3 and 4) during the combustion of additivated wood chips compared to the non-additivated reference case without ESP.

4. Conclusions

The aim of this study was to investigate the transferability of fuel additivation as a primary, fuel-side mitigation measure for inorganic alkali-based PM emissions during the complete combustion of biogenic solid fuels (e.g., pellets) to fuel-type wood chips. Therefore, wood chips were additivated with 0.5 wt% of three different types of the additive kaolin, which mainly differing in their particle size distribution (i.e., Kaolin I > Kaolin II > Kaolin III), and with one type of kaolinite for reference purposes. Combustion trials with non-additivated and additivated wood chips were carried out in a small-scale combustion plant (33 kW). To evaluate the fuel additivation of the wood chips, the TPM emissions, the K emissions, the (ultrafine) $PM_{(0.1)}$ emissions and the CO emissions, as well as the chemical composition of the resulting ashes from the combustion trials, were analyzed. In order to compare the primary, fuel-side mitigation measure of fuel additivation with the established secondary mitigation measures, an ESP was additionally used during selected combustion trials for non-additivated wood chips. The main findings of the present study are summarized as follows:

- As a result of a reduction in the mean particle size of the aluminum-silicate-based additive kaolin, in addition to the increasing mitigation of TPM emissions, a progressive decrease in the K emissions, as well as in the CO emissions, occurs during the fuel additivation of wood chips compared to the non-additivated reference case without ESP. Thus, the lowest absolute TPM emissions (23 mg/Nm^3), K emissions (1 mg/Nm^3) and CO emissions (26 mg/Nm^3) are obtained for the aluminum-silicate-based fuel additivation of the wood chips, with the kaolin demonstrating the smallest mean particle size (i.e., Kaolin III). Consequently, the aluminum-silicate-based fuel additivation can be regarded as transferable and implementable for real small-scale wood chip combustion.
- Although the mean particle size of the impurity-free aluminum-silicate-based additive Kaolinite is smaller than for Kaolin III, the overall emission mitigation (i.e., TPM emissions (47 mg/Nm^3), K emissions (3 mg/Nm^3) and CO emissions (24 mg/Nm^3)) for the fuel additivation of the wood chips with Kaolinite is worse than with Kaolin III. Hence, kaolin is to be given preference over kaolinite in the aluminum-silicate-based fuel additivation of wood chips.
- Comparing the primary, fuel-side mitigation measure of aluminum-silicate-based fuel additivation (e.g., Kaolin III) and the secondary mitigation measure of ESP, both measures result in comparable reductions in absolute TPM emissions (23 mg/Nm^3) regarding the non-additivated reference case without ESP (36 mg/Nm^3). However, K emissions (9 mg/Nm^3) and CO emissions (96 mg/Nm^3) are higher for the ESP than for the use of 0.5 wt% Kaolin III. Consequently, fuel additivation of wood chips with kaolin offers the additional benefit of simultaneously reducing other air pollutants (e.g., CO) compared

to the ESP, although the different chemical compositions of the TPM emissions make the combined utilization of the two mitigation measures very promising.

- While the use of an ESP as a secondary emission mitigation measure tends to shift the particle size number distribution of the PM emissions to larger particle diameters during small-scale wood chip combustion, more small particles are emitted for fuel additivation using kaolin or kaolinite, respectively. Nevertheless, comparable reductions in the share of $PM_{0.1}$ emissions in PM emissions can be achieved for both the aluminum-silicate-based fuel additivation using Kaolin III and the utilization of the ESP. Again, a combined use of the two mitigation measures appears to provide added value over considering them alone.
- Finally, the ashes for the aluminum-silicate-based fuel additivation of the wood chips show that, in contrast to the non-additivated wood chips (i.e., without and with ESP), there is evidence of high-temperature stable ash incorporation of the ash- and PM-forming alkali element K through the addition of kaolin, or kaolinite, which in turn reduces the (inorganic) TPM emissions. Thus, aluminum-silicate-based fuel additivation of wood chips releases fewer TPM emissions overall, which could subsequently be potentially further reduced by the utilization of an ESP.

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