

Article

Foliage and Grass as Fuel Pellets—Small Scale Combustion of Washed and Mechanically Leached Biomass

Jan Hari Arti Khalsa ^{1,*}, Frank Döhling ¹ and Florian Berger ²

¹ Deutsches Biomasseforschungszentrum gemeinnützige GmbH (DBFZ)/German Biomass Research Center, Leipzig 04347, Germany; frank.doehling@freenet.de

² florafuel AG, München 81829, Germany; florian.berger@florafuel.de

* Correspondence: jan.khalsa@dbfz.de; Tel.: +49-341-2434-369

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Abstract: The high contents of disadvantageous elements contained in non-woody biomass are known to cause problems during small and large scale combustion, typically resulting in a higher risk of slagging, corrosion, and increased emissions. Mechanically leaching the respective elements from the biomass through a sequence of process steps has proven to be a promising solution. The florafuel process used here is comprised of size reduction followed by washing and subsequent mechanical dewatering of the biomass. Densification of the upgraded biomass into standardized pellets (Ø 6mm) enables an application in existing small-scale boilers. The presented combustion trials investigated the performance of pellets made from leached grass, foliage and a mixture of both in two small-scale boilers (<100 kWth) with slightly different technology (moving grate *versus* water-cooled burner tube) during a 4-h measurement period. Emissions were in accordance with German emissions standards except for NO_x (threshold is 0.50 g/m³) in the case of pure grass pellets (0.51 g/m³) and particulate matter (PM) in all but one case (foliage, 13–16 mg/m³). An electrostatic precipitator (ESP) unit installed with one of the boilers successfully reduced PM emission of both the grass and mixture fuel below the threshold of 20 mg/m³ (all emission values refer to 13 vol.% O₂, at standard temperature and pressure (STP)). Bottom ash composition and grate temperature profiles were analyzed and discussed for one of the boilers.

Keywords: solid biofuel; residue biomass; combustion; mechanical leaching; emission reduction

1. Introduction

According to the National Renewable Energy Action Plans of the European Union member states bioenergy is the largest contributor to the renewable energy targets for 2020 with 54.5% and energy from solid biomass will contribute 36% [1]. Hence, a strong increase in biomass utilization has been observed in the last two decades in many European countries. As modern society, beyond 2020, will be driven by a low-carbon economy, or rather by a bio-economy based on the principle of cascading, more and more biomass will be utilized for non-energy purposes. This requires the efficient recovery of residue biomass, for e.g., heat production, as high-value biomass will be mainly used for material purposes.

With a growing share of wind and solar power in the energy mix, bioenergy becomes a vital renewable energy source for compensating the fluctuating availability of wind and solar power dependent on weather conditions. A smart utilization of bioenergy will be integrated with the other renewable energies and bio-based products, acknowledging that wind, solar, and bioenergy need to be complementary in order to achieve a 100% renewable heat and power production by the end of the century [2].

The provision of a large variety of non-woody-residue biomass for small-scale heat and power production will be made possible through adequate fuel-enhancement technologies in order to diminish disadvantageous fuel characteristics when combustion or gasification is the conversion of choice.

Two of the most frequently available residue biomass types in urban areas across central Europe are both grass clippings and foliage. For Germany the biomass potential of grass clippings from road-side verges alone was estimated to be as much as one million tonnes (fresh matter (FM)) in 2009 and their conversion to bioenergy has been suggested [3]. Public parks, lawns, cemeteries, and road-side verges are commonly planted with grass and other non-woody species, while deciduous trees may be present in all of those areas, too. Currently, the periodically incurring amounts of foliage and grass-clippings are gathered during park maintenance activities, *etc.* Often, parts of the biomass are stored for composting while, due to missing alternative utilization strategies, excess biomass has to be burned in waste combustion plants. In the case of composting, added value can be generated; however, no greenhouse-gas savings are to be expected [4], which will be the case for combustion or gasification applications when fossil fuels are substituted.

Compared to wood as a raw material for fuel pellets, the main insufficiency of grass and foliage are their chemical and physical-mechanical characteristics [5,6]. Especially the high ash content (up to 45% dry matter (DM) in foliage, due to soil-uptake during collection [7]) and with it the non-organic matter are a challenge during combustion. The high concentrations of potassium (K), chlorine (Cl), nitrogen (N), sulfur (S), and the sum of elements highly involved in particulate matter (PM) formation (K, Na, Zn, Pb) are of great concern since they are known to be the main agents of high gaseous (HCl, SO₂, NO_x) and PM emissions [8]. These elements and their interactions during combustion can be summarized by fuel indexes [9] to help foresee possible emission, corrosion, and slagging related issues that might reduce the performance of combustion plants. Furthermore, the low bulk density of loose grass and foliage, as well as their moisture content, is disadvantageous for transport and storage.

It is evident that residue biomass needs to be upgraded before application in combustion systems, especially small scale boilers, as has been suggested by several studies over the past 20 years [10–13]. In many of those studies the term “leaching” [10,12,13] was used to describe the underlying principle of fuel enhancement while the actual technology was referred to as a combination of hydrothermal conditioning [11] and mechanical dewatering [11,13]. In all cases the intention is to address the aforementioned problems of high non-organic matter content in residue biomass by washing and leaching those constituents. While earlier studies on straw and grass, and recent ones on foliage, have been on small amounts of material prepared in lab-scale setups, data from trials with grass in at least two different prototype plants with a capacity (input) of 300 kg FM (30% DM content) per day [14] and 3000 kg FM/h (20% DM content) [15] is available. The latter one is the prototype plant built according to the florafuel process which was introduced by the florafuel AG, Germany [15]. In this particular concept the enhancement process includes up to ten different process steps (a detailed description can be found in 2.2 and Figure 1) of which the washing and cutting of wet biomass and the mechanical dewatering are most crucial.

It is suggested that the press water extracted from the raw material during the process (containing particulate organic material and solved alkali and earth alkali salts) can be utilized for anaerobic digestion to produce biogas [15,16] and the digestate may still be valuable as fertilizer [17]. The solid fraction (press cake) will be used as fuel for combustion and investigations on the press cake of grass and foliage after application of the florafuel-process have shown reductions in Cl concentration by 90% and 77% DM, respectively [15]. K concentrations in grass were reduced by 83% and N by 50% DM. Similar results were obtained across a whole range of grassland biomass types processed with the prototype presented by Hensgen *et al.* [14].

In the literature the results of leaching and the respective change in fuel characteristics are well discussed amongst the studies published, in some cases going as far as estimating ash melting behavior (for foliage [6] and grass [11]) and potential performance during combustion (e.g., regarding emissions) by means of guiding values [14,18]. However, no studies have been published which show actual

combustion performance of leached, hydrothermally-conditioned, and/or mechanically-dewatered fuels. This seems to be a major research gap which the authors of this paper would like to address.

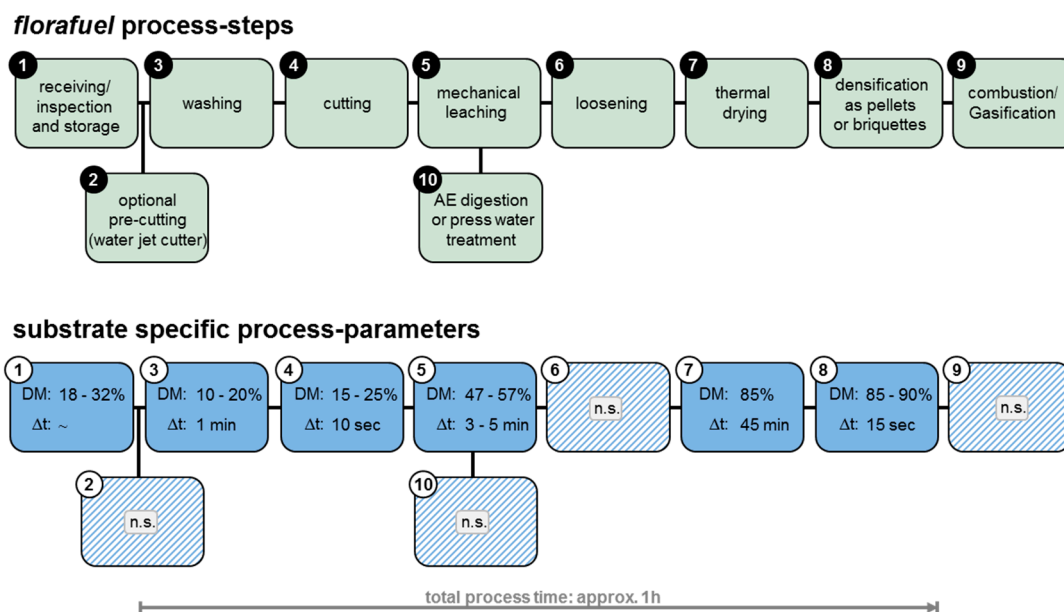


Figure 1. The florafuel process-steps are shown, as well as the dry matter (DM) content of a typical substrate (e.g., grass or foliage) at the relevant steps. Furthermore, the duration of time the substrate will be retained in each step is indicated (unless it could not be specified, n.s.) as well as the overall process duration.

For standardized emission measurements and an investigation of fuel performance during combustion small-scale boilers are most suitable and they might also be the application of choice for a future market for leached biomass pellets. The performance of several types of small-scale boilers with pellets from agricultural residues have been studied previously [19–21]. For that purpose the densification of upgraded raw material into either pellets or briquettes is desirable depending on the requirements of the boiler type. Other than that, densification is a common measure to improve handling, transport, and storage of the fuel. Extensive research has been conducted in recent years to fully understand and optimize the processes that occur during densification of biomass [22]. While the global wood pellet production has grown from 4 million tons to 24 million tons in the last ten years [23] pellet production from non-woody residue biomass is mainly limited to raw materials, such as straw or miscanthus. Grass pellet production is currently more a matter of animal fodder than a means for fuel production. Yet, recent studies are specifically dealing with pelletization of alternative biomass, such as grassland biomass for energy purposes [24,25].

In Germany, the strict emission thresholds that exist for non-woody biomass when burnt in small-scale appliances and the respective lack of experience and trust in a rather new product, such as leached biomass fuels, might partly be the reason why they are currently not commercially available.

The goal of this study was to investigate the performance of solid biofuel pellets made from leached, non-woody raw material in available small-scale boilers by comparing the emissions with the given German legislation for boilers with a nominal thermal heat output of <100 kW (1. BImSchV [26]), which currently has the strictest PM thresholds within Europe and North America [27]. Furthermore, the fuel and bottom ash characteristics of grass, foliage, and mixed (50% grass, 50% foliage) pellets were compared and discussed using fuel indexes, for example. Providing data from small-scale combustion trials with these novel fuels will help bridge the gap between the theoretical understanding of their fuel characteristics and the actual performance during combustion.

2. Materials and Methods

2.1. Raw Material and Fuel Types

Both raw materials (grass and foliage) were collected as part of urban park maintenance and management of public areas in Southern Germany (in and around the city of Munich) in late summer (grass) and autumn (foliage) of 2014. The two raw material batches were washed and mechanically leached with the florafuel process (see Section 2.2) and subsamples of the treated materials were mixed with a 1:1 ratio to create a third fuel. All of the batches were pelletized (see Section 2.2) to yield pure grass pellets (Grass 100%), pure foliage pellets (Foliage 100%) and mixture pellets (Mix 50/50). Fuel analyses (see Section 2.3) were done on all three fuels while, for grass and foliage, the non-treated raw material was also analyzed in order to calculate the change in elemental composition (raw material data can be found in Table S1).

2.2. Mineral Leaching (florafuel Process) and Densification of the Biomass

The florafuel process (patent EP2274406—Method and apparatus for producing fuel from moist biomass) is described in Figure 1 including the change of DM content with each process step and the respective duration. The florafuel plant prototype has a production capacity of approximately 600 kg FM output material (with $\leq 15\%$ water content) per hour.

A subsequent compaction step of the mechanically- and thermally-dried biomass enables utilization in automatically-fed small scale boilers or gasification appliances. In the presented study a pellet diameter of 6 mm, using a ring-die press (Münch RMP250, 15 kW, mass flow 40–110 kg/h, detailed description and depiction can be found in Kirsten *et al.* [24]), was chosen, as it is a typical fuel shape for such appliances. The pelletizing followed the process schema shown in Kirsten *et al.* [24] with milling, conditioning, pelletizing, and subsequent cooling, and an example for energy consumption during hay pelletizing at this scale of operation can be found in Pilz *et al.* [25].

2.3. Raw Material, Fuel, and Ash Characteristics

The raw materials and fuels (florafuel-treated materials) were analysed according to the analytical methods proposed in the international standard DIN EN ISO 17225-1 [28]. From each raw material and fuel a sample of 500 g was taken to conduct the following chemical analysis at the laboratory of the German Biomass Research Center (DBFZ): determination of calorific value, ash content (550 °C), moisture content (oven dry method), content of volatile matter, total content of C, H, and N, total content of S and Cl, and major and minor elements (respective methods are indicated in Table 1). As a point of reference for the upgraded fuels, mean values of four wood pellet samples (all in accordance with ENplus/DINplus quality standards), which were analyzed according to the same methodology, were calculated. The focus of the results presented was on chemical parameters important for the characterization of solid biomass fuels by fuel indexes (as presented by Sommersacher *et al.* [9]), physical-mechanical quality parameters of pellets and the ash melting behavior (according to DIN CEN/TS 15370-1 [29]). The bulk density and durability were analyzed at the DBFZ which required approximately 7 kg of each fuel while the ash melting behavior was analyzed by an external laboratory (500 g samples of each fuel). The four defined ash melting temperatures which were analyzed are shrinkage starting temperature (SST), deformation temperature (DT), hemisphere temperature (HT), and the flow temperature (FT). Furthermore, bottom ash was sampled and major elements were analyzed according to DIN EN ISO 16967 at the DBFZ to then estimate and discuss the concentration of the ten most relevant oxides (SiO_2 , CaO , K_2O , P_2O_5 , Al_2O_3 , MgO , Fe_2O_3 , SO_3 , Na_2O , and TiO_2) as normalized to 100%.

2.4. Combustion Technology and Emission Measurements

The combustion experiments were performed in two different commercially-available boiler types with a nominal thermal power (kW_{th}) of 25 kW_{th} and 49 kW_{th}.

The 25 kWth boiler was a GUNTAMATIC Powercorn 30 (Guntamatic Heiztechnik GmbH, Peuerbach, Austria) which was specifically designed for grain and wood pellets (where it can reach 30 kWth at full load) with a moving grate and two separate air supplies. The primary air is inserted via the grate system and the secondary air is supplied in the secondary combustion zone. The moving grate is designed to deal with relatively high ash content in the combustion chamber and higher amounts of slagging as can be expected from the solid fuels used. Two temperature sensors (Super-OMEGACLADTM-XL, type K, Ø = 3mm, temperature range 0–1250 °C; OMEGA Engineering GmbH, Deckenpfronn, Germany) were installed in the moving grate, one at the top of the grate (T₁) and one after the first moving elements of the grate (T₂). The distance between the tips of the two sensors is approximately 9 cm.

Table 1. Chemical composition of the three fuels and physical-mechanical characteristics of the respective pellets. Also indicated (where applicable) is the relative change (Δ_{leached}) of each parameter achieved by the florafuel process (as compared to the raw material) as well as the average values of four wood pellet samples. LHV: lower heating value; FM: fresh matter.

Fuel Composition		Method	Grass (100%)		Foliage (100%)		Mixture (50/50)	Wood
Parameter	Unit	(DIN EN ISO)	Leached	Δ_{leached} (in %)	Leached	Δ_{leached} (in %)	Leached	Mean values (n = 4)
LHV	DM MJ/kg	18125	18.4	+10	18.9	+7	18.2	18.8
Ash	% DM	18122	8.1	−58	10.5	−40	11.0	0.32
Water	% FM	18134-1	14.6	-	16.2	-	13.9	6.2
Volatiles	% DM	18123	75.1	+19	72.1	+8	71.8	84.9
C	% DM	16948	48.0	+7	51.3	+7	49.1	51.4
H	% DM	16948	5.8	+6	6.0	+19	5.3	6.3
N	% DM	16948	1.4	−29	0.8	−7	1.3	0.2
S	% DM	16994	0.10	−55	0.06	−42	0.13	0.007
Cl	% DM	16994	0.02	−94	0.01	−94	0.02	0.004
Al	g/kg DM	16967	0.70	−82	0.50	−76	1.32	0.05
Pb	g/kg DM	16968	0.004	−43	-	-	-	0.001
Ca	g/kg DM	16967	15.1	−42	31.6	−16	26.4	1.0
Fe	g/kg DM	16967	1.1	−70	1.2	−41	1.9	0.08
K	g/kg DM	16967	3.26	−84	1.47	−77	2.48	0.5
Mg	g/kg DM	16967	2.59	−62	1.70	−57	3.03	0.2
Na	g/kg DM	16967	0.45	−4	-	-	0.23	0.01
P	g/kg DM	16967	2.03	−68	0.60	−73	1.50	0.09
Si	g/kg DM	16967	3.33	−89	11.7	−55	14.6	0.64
Ti	g/kg DM	16967	0.05	−75	0.04	−76	0.09	0.003
Zn	g/kg DM	16968	0.09	+30	0.05	+53	0.11	0.01
Pellet characteristics		-	Grass	-	Foliage	-	Mixture	-
Bulk density	kg/m ³	17828	600	-	659	-	628	-
Mechanical durability	%	17831-1	98.7	-	97.7	-	98.7	-

The 49 kWth boiler, ÖKOTHERM Compact C0 (A.P. Bioenergietechnik GmbH, Hirschau, Germany), is equipped with a water-cooled burner tube which was especially designed for alternative fuels, such as miscanthus, grains, and similar products (e.g., olive kernels, cocoa pellets), and is also suitable for wood fuels (chips and pellets). In addition the 49 kWth boiler was equipped with a commercially available electrostatic precipitator (ESP)-unit (AL-Top 500-200, Schröder Abgastechnologie, Kamen, Germany) which uses electrostatic charging of the particles to precipitate them on a special bedding. The filter unit is designed for wood and agricultural fuels and can be used on boilers of up to 100 kWth thermal output with an expected PM reduction of 80%–90%. All combustion experiments were conducted so that emissions could be monitored for a duration of 4-h at full load (starting at stable combustion, at least 30 min after the point of ignition). The boiler settings only varied slightly for the different fuels (Table S2). The flue gas components CO, NO, NO₂, SO₂, HCl, and total hydrocarbon (THC) were

measured continuously with a Fourier-transformed infrared (FTIR) spectroscope (Gaset CX 4000, Gaset Technologies Oy, Helsinki, Finland). O₂ concentrations were measured with PMA 100-L analyzer (M and C TechGroup Germany GmbH, Ratingen, Germany). The presented NO_x concentrations were calculated as the sum of NO and NO₂ concentration. The sampling line and probe were kept constant at 180 °C. Dioxin and furan polychlorinated dioxin/furan (PCDD/F) concentrations in the exhaust gas according to DIN EN 1948-1 [30] are cost and labor intensive and can only be measured in separate combustion trials. Hence, PCDD/F was only measured for one fuel (the one for which highest PCDD/F emissions were to be expected) and with one boiler.

All values, including the ones cited from the literature, are given either in g/m³ or mg/m³ and refer to 13 vol.% O₂ at standard temperature and pressure (STP). The raw data recorded during each trial was aggregated in 15 min mean values (Tables S3 and S4), which were then summarized and presented in the respective figure in Section 3.2.

The PM emissions were measured by isokinetic sampling according to VDI 2066 [31] at 160 °C. An automatic isokinetic control unit (ITES, Paul Gothe GmbH, Bochum, Germany) was used according to the out stack method. For the sampling a plane filter (Munktell MK360, retention > 99.998%, Ø = 45 mm; Munktell & Filtrak GmbH, Bärenstein, Germany) was used to collect the particles after prior drying of the filter (180 °C, for > 1-h). After the measurement the filter was again dried (160 °C, for > 1-h) and subsequently cooled and conditioned in a weighing chamber for 8-h. During each trial three samplings for 30 min each were conducted and the PM values presented here are the mean values of those three consecutive measurements. In case of the combustion experiments conducted with the 49 kWth boiler plus ESP the PM emissions were measured (with three samples each) both before and after the precipitator.

3. Results and Discussion

3.1. Fuel Characteristics

Several studies on the elemental composition and fuel characteristics of untreated grass from landscape management and urban foliage have been published in the past years. Khalsa *et al.* [32] found grass from extensive management to have an ash content ranging between 5.3% and 22% DM, depending on plant species composition and harvest date, with an average of 9.4% DM. Piepenschneider *et al.* [6] observed the mean ash content in untreated urban leaf litter to be at 13.8% DM, while the range was between 6.7% and 19.4% DM, depending on tree species and soil contamination.

The florafuel-treated grass and foliage had ash contents of 10.1 and 8.5% DM, respectively, which was a reduction due to the washing and leaching by 58% DM for grass and 40% DM for foliage (Table 1). Yet, in both cases, the ash content is considerably higher than in woody biomass (mean of 0.32% DM for the reference pellets) which is largely due to the remaining amounts of Ca, Si, K, and Mg, even though they were reduced by the mechanical leaching process by 42%, 89%, 84%, and 62% DM, respectively. The ash content and the elemental composition of the 50/50 mixture of the two leached materials did not result in mean values of the respective parameter in all cases. The ash content of the mixture, 11% DM, was higher than both the ash content of the pure grass and pure foliage material. The same was true for the Mg (3.03% DM) and Si (14.6% DM) concentration in the mixture. This is probably linked to inhomogeneity in the bulk during sampling of the leached grass, leached foliage, and the mixture, even though the grass and foliage samples were taken after Step 7 (Figure 1) when a high degree of homogenization should have been achieved. The mixture was sampled after Step 8 in order to minimize the inhomogeneity that may have occurred during manual mixing of its two components.

The observed increase in Zn content after application cannot be attributed to the leaching but is rather a result of contamination by a zinc-coated component of the florafuel-plant. The respective component was replaced with a stainless steel part in later trials and thereafter reduction in Zn as part of the leaching could be observed as it was also shown by other studies e.g., Piepenschneider *et al.* [6].

In order to get a first reading of the solid fuel quality in regards to emission, slagging and corrosion based on the chemical analysis, three fuel indexes were calculated and the N content in the fuel was categorized for the original raw materials as well as the leached biomass. The sum of K, Na, Zn, and Pb yields a good indication of the amount of PM (especially fines with particles smaller than 1 μm) that will occur during combustion and a value >10 g/kg DM is to be expected for grass pellets [9]. This is in line with the findings of this study (Figure 2a) where untreated grass had a value of 21.3 g/kg DM, while the pellets made from leached grass, with a value of 3.8 g/kg DM, were in the same range as bark or waste wood (between 1 g/kg and 10 g/kg DM, according to Sommersacher *et al.* [9]). The reason for this improvement was mainly the reduction in K by 84% DM. In actual PM emission values observed by Sommersacher *et al.* [9] this might indicate a reduction from 300 mg/m³ to well below 100 mg/m³ in the exhaust gas. For foliage, the value dropped from 6.8 g/kg to 1.5 g/kg DM when applying the florafuel procedure, which is almost as low as the mean value of 0.5 g/kg DM between the four ENplus-quality wood pellet samples. Again, the reduction in K by 77% DM was the main driver for this improvement. With 2.8 g/kg DM the mixture was right between the leached grass and the foliage.

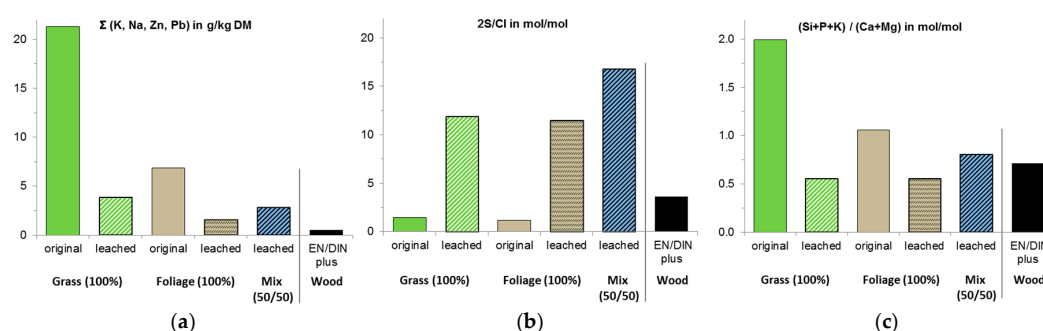


Figure 2. Most relevant fuel indexes were calculated for the three fuels and compared to mean values of four selected wood pellet samples. Values of the untreated material (original) and the upgraded material by means of applying the florafuel-process (leached) are shown. The index shown in: (a) is relevant to predict PM emissions; (b) is to foresee the high temperature corrosion risk; and (c) is to assess the risk of ash-melting problems during combustion. In (c) the value for wood pellets refers to the molar ratio of Si/(Ca + Mg).

According to the classification suggested by Sommersacher *et al.* [9] of fuels being low-N fuels, medium-N fuels, or high N-fuels when they contain less than 0.4% DM, between 0.4% and 1% DM or 1%–10% DM of N, the leached foliage fuel would be a medium-N fuel (0.8%) while both grass and mixture would be a high-N fuel (1.4 and 1.3, respectively). Thus, for all three fuels, NO_x emissions above 200 mg/m³ will have to be expected.

The risk of high-temperature corrosion can be assessed by the molar ratio 2S/Cl whereby its value should be at least 4 for a minor risk of corrosion or better >8 in order to rule out any corrosion risk [9]. All three leached fuels (grass, foliage, mixture) showed values far above the recommended value of 8 (11.9, 11.5, 16.9, respectively), while their original values were below 2 and, therefore, in the high-risk category (see Figure 2b). The reason for this improvement is the much stronger reduction of Cl as compared to S with 94% DM *versus* 55% DM for grass, and 94% DM *versus* 42% DM for foliage (Table 1).

Furthermore, the slagging risk was assessed by the molar ratio (Si+P+K)/(Ca+Mg) which is recommended for P-rich fuels, such as grass, while for wood, for example, Si/(Ca+Mg) is more applicable [9]. Increased ash melting tendencies are to be expected for values above 1. Figure 2c shows how the slagging risk is reduced substantially for grass from 2.0 to 0.6 and 1.1 to 0.6 for foliage, indicating that foliage fuel without treatment can almost be categorized as a low slagging risk fuel. The value of the mixture was, as for the 2S/Cl index, not the mean between the two constituents. This might be, again, a reflection of inhomogeneity in the bulk even after thorough mixing. The value for the wood pellets was with 0.7, in between that of the mixture (0.8) and the leached grass and foliage fuel (both 0.6).

Having discussed the theoretical problems that could occur when using the leached fuels the next section will show the results obtained during combustion trials in regular boiler systems designed for pellet fuels from residue/agricultural biomass.

3.2. Combustion

3.2.1. Legislative Background

The combustion experiments were mainly conducted to assess whether existing small-scale boiler technology can be used for the combustion of upgraded grass and foliage pellets when the respective German immission legislation is applied. For small-scale boilers with nominal heat output between 4 kWth and 100 kWth the First Ordinance on the Implementation of the Federal Immission Control Act (1. BImSchV) is the guiding legislation in Germany, differentiating between 13 different fuel types [26]. Woody biomass is divided into several categories, all indicated by consecutive numbers (e.g., #5a would be pellets and briquettes while #4 is log wood), depending on the origin or use of the woody material. Straw-like biomass and grains are classified in the legislation under category #8, while all other non-woody biomasses would be referred to as #13 fuels. For all three fuel types investigated here the same emission standards apply (Table 2), while grass would most likely be considered a #8 fuel, foliage a #13 fuel, and the mixture of both also a #13 fuel. The thresholds were recently updated and boilers installed from 1 January 2015 onward will have to comply with the most recent values while boiler installed between 22 March 2010 and 31 December 2014 have to comply with the thresholds effective during that period.

Table 2. Emission thresholds during operation of a small-scale boilers $4 \leq$ and < 100 kWth according to the German legislation. The thresholds apply to boilers fueled with straw-like biomass, grains (both indicated in the legislation as #8 fuels) and other non-woody biomasses (#13 fuels). The thresholds applicable for type testing conditions are also displayed. The thresholds from 2010 and the recently updated ones (effective from 1 January 2015) are shown. No thresholds apply for SO₂, HCl, and total hydrocarbon (THC). PCDD/F: polychlorinated dioxin/furan; PM: particulate matter.

Parameter	Unit	1. BImSchV (#8 and #13 Fuels)			
		2010		2015	
		Operation	Type Testing	Operation	Type Testing
CO	g/m ³	1.0	0.25	0.4	0.25
NO _x	g/m ³	-	0.6	-	0.5
PM	g/m ³	0.1	-	0.02	-
PCDD/F	ng/m ³	-	0.1	-	0.1

In order for a boiler manufacturer to be able to sell a product in accordance with the given standard, a so called type-testing would have to be undertaken before the product can be offered on the German market. For type-testing the emission standards are slightly different than what the chimney sweep will have to check during regular operation. Hence, both thresholds are being discussed in the following section.

3.2.2. Boiler (25 kWth) with Moving Grate

During the first set of combustions trials with the 25 kWth boiler the trends indicated by the fuel indexes regarding PM emissions and NO_x could be confirmed (Figure 3). PM emissions of the leached material were well below 100 mg/m³ with a mean of 43, 50, and 38 mg/m³ for grass, mixture, and foliage, respectively. The required concentration of 20 mg/m³ and below, however, could not be complied with, making a flue gas cleaning step for PM reduction inevitable. The mean NO_x value during grass pellets combustion of 0.59 g/m³ was above the threshold of 0.50 g/m³, which is only applicable during type-testing. The mean NO_x emissions of the mixture were at 0.51 g/m³

and would, therefore, as for grass pellets, require an adjustment of combustion process in order to reduce NO_x values (through e.g., lowering primary λ and making sure that the temperature in the primary combustion chamber is in an ideal temperature range [8]) unless a mixture with predominately foliage would be chosen as foliage was well below the threshold with 0.46 g/m^3 . In any case, Carvalho *et al.* [21] discussed the adjustment of the excess air ratio by plotting the NO_x emissions when burning pellets made from different agricultural biomass in a 15 kWth boiler against λ . They achieved a reduction of NO_x emissions of up to 22% by lowering λ toward 1.5 away from the optimum for the lowest CO emissions of $\lambda = 2.0$. The CO threshold did not pose a problem for any of the three fuels burnt in this trial. Yet, adjusting the excess air ratio in the primary combustion chamber in order to achieve lower NO_x emissions may, in turn, increase CO emission. In the study by Carvalho *et al.* [21] CO emissions increased drastically when λ was lowered to be between 1.7 and 1.9 for hay pellets, while NO_x emission were lowest at $\lambda = 1.7$.

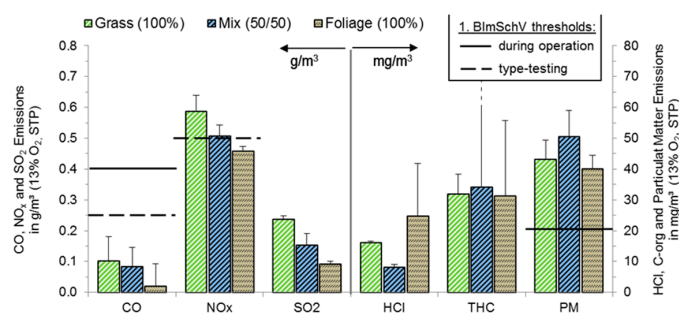


Figure 3. Mean and maximum emission values of CO, NO_x , SO_2 (all in g/m^3), and HCl, THC, PM (all in mg/m^3) recorded over a 4-h period during combustion trials in a pellet boiler (25 kWth) designed for alternative fuels (THC_{max} of the mixture was 135 mg/m^3). Trials were conducted with pellets made from mechanically-leached biomass.

PCDD/F concentration was measured for the grass pellets in this boiler and the observed value was 0.05 ng/m^3 , which is well below the threshold required for type-testing. No further PCDD/F measurements were done as the highest concentrations could be expected from the fuel with the highest Cl concentration which in this case was grass.

Regarding the slagging behavior in the 25 kWth boiler, the sporadically-occurring fused pellet structures when using foliage or grass pellets broke up during movement of the step grate and caused no lasting problems during the 4-h operation period (a view of the combustion chamber of the same boiler when using leached foliage pellets can be seen in Khalsa *et al.* [33]). This was to be expected given the positive indication of the fuel index forecasting the slagging behavior in Figure 2c (ash melting behavior and bottom ash composition is discussed in detail in 3.3). Additionally, Carvalho *et al.* [34] found a 15 kWth boiler with moving grate to be most efficient in ash removal when comparing four boilers in the range of 10–25 kWth when burning agricultural residues. However, a 4-h combustion trial may not be representative for regular operation during the heating period in the winter season, for example, when constant operation at full load for several days may be necessary. Yet, a 4-h test period is enough to encounter major issues or, as in this case, highlight a positive trend.

3.2.3. Boiler (49 kWth) with Water-Cooled Burner Tube and Electrostatic Precipitator

The second set of combustion trials was to assess performance of the fuel in a slightly different boiler type and especially to test the potential of integrating a flue gas cleaning step (for PM). The noticeable difference between the results obtained from combustion in this boiler (49 kWth) and the results obtained in the 25 kWth boiler is, that PM emissions for foliage pellets were even without an additional flue gas cleaning step below the required threshold of 1. BImSchV (Figure 4) with values ranging between 13 mg/m^3 and 16 mg/m^3 . As the ash composition should have been the

same during the combustion trials with the two different boiler types, the difference in PM emissions might be partly due to the differences in temperature the fuels were exposed to in the combustion chamber. Knudsen *et al.* [35] found the K release, which is closely linked to the PM formation, to be temperature-dependent when no differences in ash composition can be observed, leading to higher K release with higher temperatures.

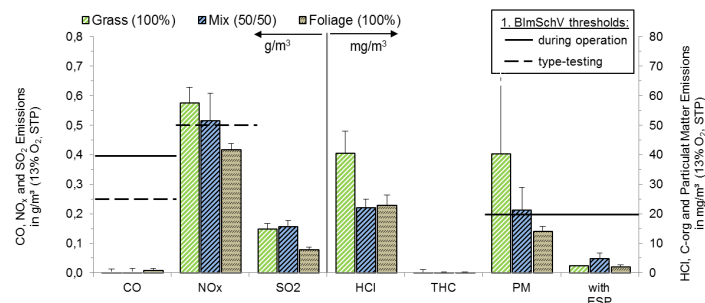


Figure 4. Mean and maximum emission values of CO, NO_x, SO₂ (all in g/m³), and HCl, THC, PM (PM, all in mg/m³) recorded over a 4-h period during combustion trials in a pellet boiler (49 kWth) designed for alternative fuels (PM_{max} of grass was 71 mg/m³). Trials were conducted with pellets made from mechanically-leached biomass. The PM values were recorded before and after the electrostatic precipitator (ESP) unit.

If the low PM emission observed here in the 49 kWth boiler can be confirmed in further tests with a whole range of foliage assortments and mixtures, as they would naturally occur on municipal waste grounds when gathered from across an urban area, pellets from leached foliage material would have the potential to be a valid alternative to other standard fuel pellets in the small-scale market. Döhling *et al.* [7] observed a promising trend when subjecting three batches of foliage with a wide range of ash concentration (26.7%, 20.7%, 48.5% DM) to the florafuel process and, thereby, homogenizing their ash concentration to a small range of 9%–10% DM.

Especially for grass, including an ESP unit would be inevitable as the range of PM emissions were between 24 mg/m³ and 71 mg/m³ with a mean of 40 mg/m³ before the precipitator and were constant around 3 mg/m³ after the unit (see exemplary images of filter samples taken before and after the ESP in Figure S1). The mean PM emissions during combustion of the mixture were close to the threshold with 21 mg/m³ while the actual range was between 17 mg/m³ and 29 mg/m³ when no filter was applied. With filter unit the mixture had PM-emissions ranging between 4 mg/m³ and 7 mg/m³ and a mean of 5 mg/m³. A slightly more foliage dominated mixture might be a feasible way to stay below the threshold and avoid high costs for an ESP unit. As discussed in the previous section (Section 3.2.2.) NO_x emissions will have to be adjusted through tuning of the combustion parameters in order to comply with the thresholds required for type testing, at least when grass is considered as a fuel (mean NO_x value of 0.57 g/m³). The mixture as it was, had a mean NO_x value of 0.51 g/m³ which could fall below the required 0.50 g/m³ if more foliage was given to the mixture.

Regarding ash melting in the 49 kWth boiler, no complications with build-up of bottom ash and high amounts of slagging could be observed during the 4-h combustion trials. This might only partly be due to fuel characteristics, but rather due to the water-cooled burner tube in which the combustion takes place (hence, bottom ash and ash melting for the 49 kWth boiler was not further discussed). Paulrud and Nilsson [36] reported a positive experience with ash removal when burning reed-canary grass (as briquettes) with up to 10% DM ash in a boiler from the same manufacturer with slightly higher output (180 kWth). They found that adjusting the ash pusher might be necessary for high-ash fuels. In any case, long-term tests should be conducted to monitor operation under real-life conditions.

Overall, the combustion of all three fuel types in the 49 kWth boiler appeared complete as can be seen by the low CO and THC emissions. In the 25 kWth boiler, the higher CO and THC emissions indicate a remaining carbon fraction which did not get converted to energy and an improvement toward a complete combustion is desirable.

3.3. Bottom Ash and Ash Melting

3.3.1. Grate Temperature Profile

The grate temperature profiles recorded during the three combustion trials with the 25 kWth boiler give insight into the build-up of the fire bed and the performance of the moving grate depending on the fuel as well as the actual temperature the fuel and ashes were exposed to (Figure 5a–c). While the foliage pellets show a scenario where the fire bed remains focused in one part of the grate (near T_1), resulting in a constant combustion temperature and an efficient removal of the ash by the moving grate (toward T_2 and, ultimately, to the ash tray), the observations made for grass and the mixture were different.

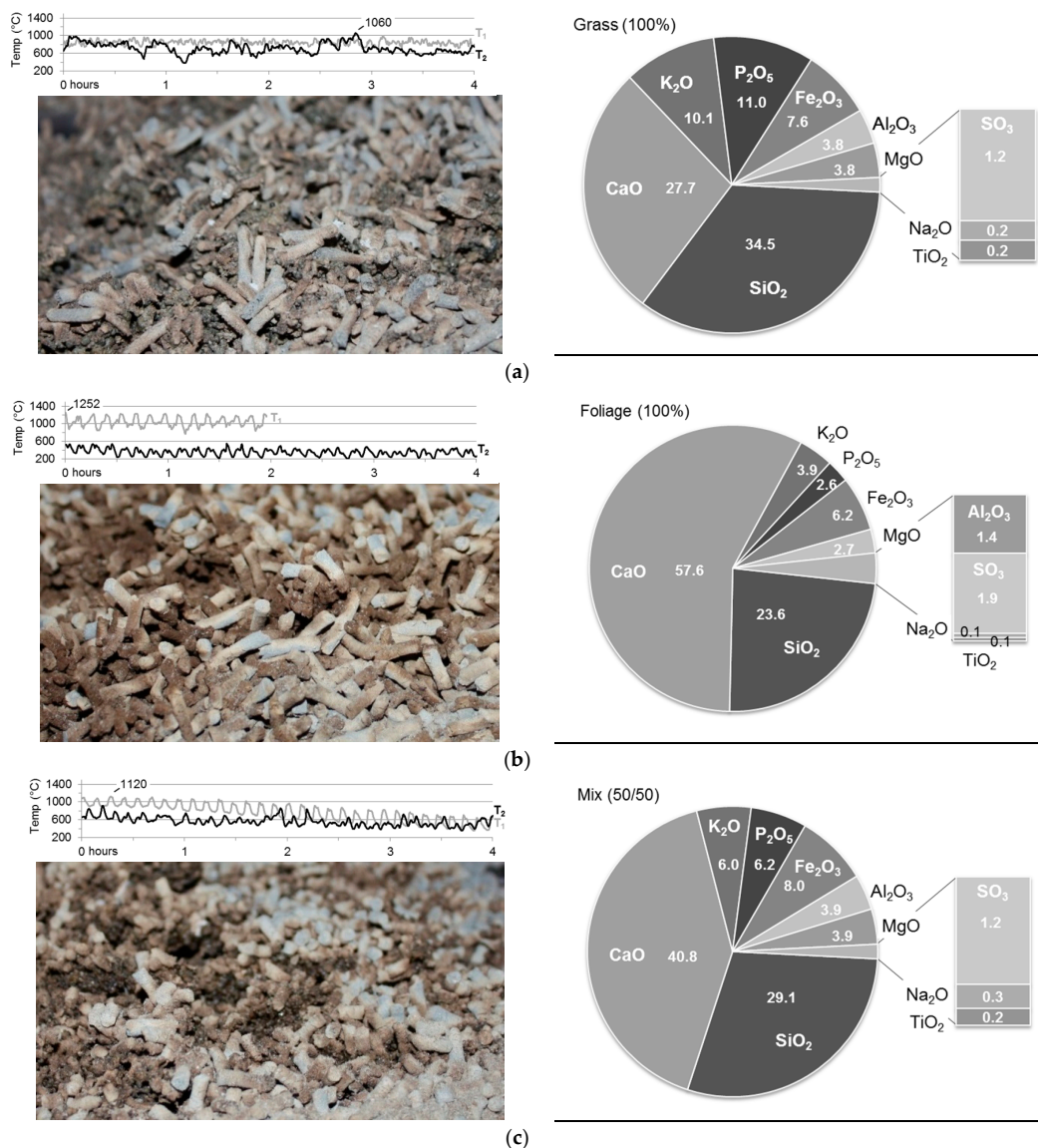


Figure 5. Chemical composition and visual characteristics of the bottom ash generated by the combustion trials in the 25 kWth pellet boiler. Pie charts show ash composition of the ten major oxides normalized to 100% for (a) grass, (b) foliage, and (c) mixture of both. The temperature profiles were recorded at two different spots of the moving grate (T_1 , beginning of the grate; T_2 , further toward the ash tray), numbers indicate the highest temperature the fuels/ashes were exposed to. The pictures of the respective bottom ash were taken in the boiler after complete burnout.

Focusing on the first hour of temperature recording the grass pellets had similar mean grate temperatures at T_1 and T_2 of 850 °C while combustion of foliage pellets and the mixture resulted in a mean T_1 of 1050 °C and 965 °C, respectively. The temperature profiles for foliage and the mixture showed the characteristic oscillation caused by moving grate resulting in a steep temperature drop from T_1 and T_2 at least in the first hour of recording with ΔT_1-T_2 of 665 K and 315 K, respectively. For both the maximum temperature on the grate was observed within the first half hour of recording with 1252 °C (foliage) and 1150 °C (mixture). For grass, the maximum temperature occurred between the second and third hour of measurement at 1060 °C.

In the second hour, however, a noticeable decline in mean temperature of T_1 occurred for the mixture resulting in a ΔT_1-T_2 of 250 K and, in the last two hours, ΔT_1-T_2 was down to 105 K. This may be an indication of the temperature sensor T_1 being slowly covered up by an increasing layer of ash during the trial with the mixture pellets. The temperature sensor T_1 showed a malfunction after two hours during the foliage trial, yet a stable continuation of the profile of the first two hours can be expected. Skotland [37] recorded temperature zones in a water cooled moving grate boiler (1 MW_{th}) and found similar peak temperatures pellets with increased ash content. The total length of the grate investigated by him from fuel inlet to ash tray was 2.7 m on which eight thermoelements (T_1 - T_8) were placed in 20 cm distance from each other. That allowed that identification of the special distribution of the hottest zones which occurred, depending on the fuel, either at T_4 or T_5 , with peak temperatures of 1062 °C for pure wood pellets and 1128 °C for wood pellets with 8% sewage sludge. However, grate temperature recordings in appliances like the 25 kW_{th} boiler used here are scarce in the literature.

3.3.2. Ash Melting Characteristics

According to the results of the ash melting analysis (under oxidizing conditions) both grass and mixture appear to have the same SST (1150 °C and 1160 °C, respectively) and are about 200 K higher than for foliage which had a SST of 950 °C (Table 3). This was unexpected as the slagging index had stated equally low risks for both grass and foliage. When looking at DT, however, foliage has the highest value of all three fuels with >270 K difference to the mixture and >320 K difference to the grass. When visually assessing the bottom ash after the combustion trials the ash of foliage pellets could be categorized as low-slagging while grass was categorized as high-slagging with large parts of the bottom ash still being in the shape of pellets (Figure 5a–c). Bottom ash still being the shape of pellets was also observed by Paulrud *et al.* [19] after burning reed-canary-grass pellets with ash content >7%.

Table 3. Ash melting temperatures according to DIN CEN/TS 15370-1 [29]. The four characteristic temperatures which were evaluated are shrinkage starting temperature (SST), deformation temperature (DT), hemisphere temperature (HT), and flow temperature (FT). According to the standard the characteristic temperature are evaluated in an oxidizing and inert atmosphere.

Pellets	Ash Melting Behavior			
	SST (°C)	DT (°C)	HT (°C)	FT (°C)
Oxidizing				
Grass (100%)	1150	1180	1210	1220
Foliage (100%)	950	>1500	>1500	>1500
Mix (50/50)	1160	1230	1280	1290
Inert				
Grass (100%)	760	1160	1200	1230
Foliage (100%)	770	>1500	>1500	>1500
Mix (50/50)	950	1270	1290	1300

The maximum values observed on the grate of the 25 kW_{th} boiler indicate that SST for foliage would have been surpassed by 300 K while DT was never reached with a minimum of 250 K difference. Hence, only shrinkage and no deformation of the ash should have been observed for foliage.

However, Paulrud *et al.* [19] observed lower melting temperature than what was predicted by a similar standardized ash melting test (ASTM D1857-87 [38]). This could explain why slagging was observed for all three fuels even though their respective DT was not reached according to the temperature sensors. On the one hand, this shows the limitation of standardized methods for analyzing ash melting behavior when applied to real-life conditions and, especially, to non-woody fuels. On the other hand, as discussed in Section 3.3.1, T_1 and T_2 may have not recorded the actual maximum temperature in the fire bed (at least for grass and mixture). Supporting the first issue, Piepenschnieder *et al.* [6] had problems recording DT and HT correctly when analyzing leached leaf litter for their ash melting behavior according to DIN 51730 [39]. However, their SST (ash softening temperature) was higher across five leaf litter types with a mean of 1230 °C which is a more realistic value than the observed 950 °C for the foliage fuel. On the other hand they observed an average FT (ash flowing temperature) of 1300 °C with only some maximum values reaching almost 1500 °C as observed for the foliage fuel in this study. Böhle *et al.* [11], using the same leaching technology as Piepenschnieder *et al.* [6], studied the ash melting behavior of leached grass from different origin and species composition. They observed mean values across 18 samples of 1050, 1150, 1230, and 1280 °C for SST, DT, HT, and FT, respectively. The values observed for the grass fuel in this study fit right into the range observed by Böhle *et al.* [11] with SST being slightly higher (100 K) and FT slightly lower (60 K) than their mean values.

In addition to the ash melting behavior relevant for combustion (oxidizing atmosphere) the fuels analyzed here were also investigated for gasification conditions (inert atmosphere). The results may give a first indication on how to operate a gasifier if it was to be feed with these fuels. Huffman *et al.* [40], when studying ash melting behavior of different coal ashes, found that their melting was accelerated under reducing conditions and the percentage of molten ash increased predominantly between 900 °C and 1100 °C. This is in line with the lower temperature obtained for SST_{in} (obtained in an inert atmosphere) for all three fuels. Lloyd *et al.* [41] observed a difference in ash melting temperatures of coal ashes obtained under oxidizing and reducing temperatures to vary between −9 K and +236 K ($T_{ox}-T_{in}$), while the difference observed here for leached grass was +290 K for SST ($SST_{ox}-SST_{in}$).

3.3.3. Bottom Ash Composition

When looking at the composition of the bottom ash (10 major oxides) generated by the three combustion trial in the 25 kWth boiler the differences between the foliage and grass become obvious once again (Figure 5a–c). While the foliage ash is composed of almost 58% CaO, 24% SiO₂, and only 4% K₂O, grass has as much as 10% of K₂O, only 28% of CaO and 35% SiO₂. When looking for similar compositions in the extensive list collected by Vassilev *et al.* [42] the foliage bottom ash comes closest to high temperature ash of wood and woody biomass with a CaO value, much like pine bark (56.8%), a SiO₂ value like balsam bark (26.1%), and a K₂O value like pine chips. Grass bottom ash, when looking at the same list, could be compared to adler-fir sawdust in terms of SiO₂ and CaO concentration (37.5% and 26.4%, respectively) while the K₂O is more that of forest residue (10.2%). However, the values recorded for high temperature ash often refer to temperatures in the range of 500–600 °C and are not directly comparable with the bottom ashes of this study which originated at temperatures well above 1000 °C.

4. Conclusions

Leaching, through conditioning and mechanical dewatering, in general, and the florafuel process, in particular, is a suitable approach to create a competitive solid fuel from grass and foliage. Significant improvements of fuel characteristics resulted from reduction of critical elements and reduced ash. Pellets from leached foliage material have the potential to be a valid alternative to wood pellets in the small-scale market and, when combusted, their emissions may comply with German standards even without a costly upgrade of installing flue gas cleaning technology. For the utilization of grass pellets

ESP technology, which is available on the market, will have to be used. Two different small-scale boilers could be successfully operated with the presented fuels and additional fine tuning of the operational parameters, as well as the fuel blend, could further improve the positive results. Future research and development efforts should focus on monitoring of long-term operation as well as quality management and market integration of the fuels.

Supplementary Materials: The following are available online at www.mdpi.com/1996-1073/9/5/361/s1.

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

Abbreviations

DM	dry matter
DT	deformation temperature
ESP	electrostatic precipitator
FM	fresh matter
FT	flow temperature
FTIR	Fourier transformed infrared
HT	hemisphere temperature
LHV	lower heating value
PCDD/F	polychlorinated dioxin/furan
PM	particulate matter
SST	shrinkage starting temperature
STP	standard temperature and pressure
THC	total hydrocarbon
BImSchV	First Ordinance on the Implementation of the Federal Immission Control Act

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