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Combustion behaviour and slagging tendencies of pure, blended and kaolin additivated biomass pellets from fen paludicultures in two small-scale boilers < 30 kW

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ABSTRACT

Pure, blended and additivated biomass pellets from four fen paludicultures were produced at TFZ and combusted in two small-scale biomass boilers (15 kW, 30 kW). Feedstocks derived from straw of *Typha* ssp., *Phragmites australis*, *Phalaris arundinacea* and *Carex* ssp. that were harvested during winter 2018, 2019 (used for pelletization) and 2020. Additivation of fuels with kaolin before pelletization or blending of fuels with EN*plus* wood pellets (A1 quality) after pelletization were applied. Straw and pellets were analyzed for physical and chemical fuel properties according to international standards for solid biofuels. Physical properties of pellets met the requirements of ISO 17225–6. Chemical properties of *Typha* indicated high TPM emissions due to high contents of K and Na in fuels while severe slagging was predicted for the other species by a high molar (Si + K + Al)/(Ca + Mg + P) ratio. During combustion in both boilers, CO and total particulate matter (TPM) emissions were high for *Typha* but slightly reduced by additivation with 2.3% kaolin. Blending of fuels significantly reduced NO_X, SO_X and HCl emissions due to lower N, S and Cl concentrations. Slagging was high for pure and additivated pellets of *Phragmites*, *Phalaris* and *Carex* with >50% of total ash consisting of particles >2 mm. No steady-state boiler operation could be achieved with either pure or additivated fuels. In conclusion, paludiculture pellets are challenging fuels for small-scale combustion plants. Their use cannot be recommended for the tested boilers. Technical solutions may be easier applied in medium sized combustions plants above 100 kW.

1. Introduction

With the revision of their Climate Change Act from the year 2021, the German Federal Government redefined their national climate protection goals regarding the reduction of greenhouse gas (GHG) emissions with a new target set to reach climate neutrality by 2045. Following this law, a reduction of annual GHG emissions of 40 Mio. tons of CO_2 equivalent is required for the sector "land-use, land-use change and forestry" (LULUCF).

Most types of existing peatlands are currently protected by the EU according to the European Directive 92/43/EEC on habitats, flora, and fauna. This directive prohibits the deterioration of these species-rich areas. In Germany, existing peatlands are further protected by the Federal Nature Conservation Act. However, according to recent data of the Federal Environment Agency of Germany from 2019, approx. 92% of peatlands in Germany are currently drained and intensively used while the remaining areas are endangered due to climate change, low water levels or high nutrient inputs [1]. Drained peatlands are responsible for up to 54 Mio. tons of CO_2 equivalent annually due to enhanced mineralization of the aerobic peat layer. Approx. 83% of these areas are used for agricultural purposes such as farming or grasslands. Rewetting and restoration of peatlands is usually recommended as a suitable measure to mitigate GHG emissions [2–6]. As most of these areas are owned by farmers, knowledge transfer on sustainable management strategies for their utilization after rewetting, e. g. by farming fen paludiculture species as agricultural crops [7], but also information on national or European funding for the rewetting process of drained peatlands are required as they were developed in the National Peatland Protection Strategy of Germany [1]. In Germany, the national strategy follows the principles of "protection, renaturation and sustainable utilization". At the same time, innovations and dedicated research on fen paludicultures

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Abbreviations

A =	ash content, i. e. the mass fraction of ash in % (d)
ar =	as received
BD =	bulk density in kg m^{-3}
d =	on dry basis
DIN =	German Institute for Standardization
D =	diameter of pellets in mm
DT =	deformation temperature in °C
DU =	mechanical durability in %
ISO =	International Organisation for Standardization
L =	length of pellets in mm
M =	moisture content, i. e. the mass fraction of H_2O in fuels related to fuels sample's original dry weight in %
Q =	net calorific value in MJ kg^{-1} (d)
TFZ =	Technology and Support Centre in the Centre of Excellence for Renewable Resources
TIC =	total inorganic carbon in % (d) of ash samples that derive from combustion at 550 °C
TPM =	total particulate matter emissions
VDI =	Association of German Engineers

strongly increased during the last couple of years as highlighted by a recent review of Ziegler et al. [8].

The term "paludicultures" refers to the productive use of wet peatlands using species such as cattails (*Typha* ssp.), common reed (*Phragmites australis*) or *Sphagnum* moss. The main goal of implementing paludicultures as an agricultural practice is to give farmers interesting and sustainable cultivation methods for their rewetted peatlands but also to preserve the existing peat layer and, in many cases, to enable new peat formation. Utilization of the harvested materials includes traditional methods such as reed farming for thatched roofs but also innovative approaches including both material and energetic use of the biomass [4,8].

The research project "MOOR*use*" aims at developing and implementing innovative and sustainable utilization strategies for fen peatlands in Southern Germany. The project focus lies on the recovery of ecological functions (biodiversity, water balance regulation, etc.), the prevention of further mineralization of the existing peat (neutral greenhouse gas balance), on economic aspects, and on the integration of paludiculture biomass into regional value chains. Within the project, three test areas with different paludiculture species were established on rewetted peatlands. The harvested material was analyzed regarding its suitability e. g. as a substrate for biogas [9], as raw materials for insulation and building material, as a peat substitute for horticulture [10,11], biogenic polymers or for animal feed. One additional utilization strategy was the use of the harvested paludiculture straw for heat production in decentralized, small-sized boilers.

Paludiculture species such as *Typha* ssp., *Phragmites australis*, *Phalaris arundinacea* or *Carex* ssp. belong to the "herbaceous" biomasses according to ISO 17225–1 [12]. As such, they have numerous physical and chemical fuel properties that are disadvantageous when agricultural fuels are burned in small to medium-sized biomass furnaces (≤100 kW to 1 MW) [13–29]. These include a reduced net calorific value (Q), an increased ash content (A) and increased concentrations of chemical elements that are deemed critical for combustion such as nitrogen (N), potassium (K), chlorine (Cl), or sulfur (S). High N in fuels can lead to increased NO_X emissions [13,30,31]. High amounts of aerosol forming elements such as K and Na may increase total particulate matter (TPM) emissions by forming mineral aerosols [13,32–34]. High shares of Cl may lead to high temperature corrosion [13,35]. Consequently, paludiculture biomass might be challenging for failure-free and low emission combustion compared to conventional fuels such as wood pellets.

Information on fuel quality and combustion behaviour of paludiculture fuels as well as on recommendations regarding processing of these feedstocks, e. g. in the form of pellets, are scarce and only few studies investigated paludiculture species as solid biofuels before [27–29,36,37]. Due to the expected challenges during combustion of agricultural fuels, certain fuel upgrading steps might be recommendable. In addition to conventional processing steps such as drying and compaction of the biomass, e. g. by pelletization or as bales, chemical fuel quality might be optimized by adding certain mineral additives to the fuel mix or by blending of the agricultural biomass with other, more suitable fuels such as wood.

Additivation of agricultural fuels or woody biomass is often performed using e. g. aluminum based additives such as the clay mineral kaolin to reduce particle emissions during combustion [14,38–47]. According to the literature [13,30,32–34,48], the main aerosol forming elements are the alkali elements K and Na, the trace elements zinc (Zn) and lead (Pb) as well as S and Cl. For solid biofuels, the most relevant element for aerosol formation is K followed by Na. K is mainly released to the gas phase as KOH and KCl, but also to small amounts as K_2SO_4 and K_2CO_3. Kaolin consists mainly of the mineral kaolinite ($Al_2(Si_2O_5)(OH)_4$). According to the following equations, alkali compounds such as K can react to high-melting crystalline products such as kalsilite ($KAlSiO_4$) as well as to leucite ($KAlSi_2O_6$) if kaolinite is present.

$$2\,KOH + Al_2Si_2O_5(OH)_4 \rightarrow 2\,KAlSiO_4 + 3\,H_2O$$

$$2\,KCl + Al_2Si_2O_5(OH)_4 \rightarrow 2\,KAlSiO_4 + 2\,HCl + 2\,H_2O$$

$$K_2SO_4 + Al_2Si_2O_5(OH)_4 \rightarrow 2\,KAlSiO_4 + SO_3 + 2\,H_2O$$

$$2\,KOH + Al_2Si_2O_5(OH)_4 + 2\,SiO_2 \rightarrow 2\,KAlSi_2O_6 + 3\,H_2O$$

$$K_2SO_4 + Al_2Si_2O_5(OH)_4 + 2\,SiO_2 \rightarrow 2\,KAlSi_2O_6 + SO_3 + 2\,H_2O$$

$$2\,KCl + Al_2Si_2O_5(OH)_4 + 2\,SiO_2 \rightarrow 2\,KAlSi_2O_6 + 2\,HCl + H_2O$$

Recent studies suggest that the mineral fraction of TPM emissions might be strongly reduced if a suitable amount of kaolin is added to the fuels [14,21,38–41,46,49]. The necessary amount can be calculated, e. g. by applying the guidelines of the ERA-NET project "BioFlex!" [33] using the concentrations of K and Na in fuels (see section 2.2). Other mineral additives might help to mitigate problems related with slag formation such as $CaCO_3$, CaO, MgO or calcite [35,40].

Blending of agricultural biomass with woody biomass to optimize chemical composition of the feedstocks was also investigated previously in several recent studies [21,40–43,50,51]. For instance, Mack et al. [21] investigated blending of wheat straw with wood before pelletization resulting in lower emissions (NO_X, TPM) but also in less slagging related problems during combustion (at increased blending levels with >75% wood). Similar, Zeng et al. [50,51] reported benefits during combustion of herbaceous biomass in terms of slagging risk or emission behaviour when a high blending level (>50–70% of woody biomass) was applied. Dragutinovic et al. [40,41] focused on both additivation and blending of wheat straw, corn stover or corn cobs with wood pellets highlighting benefits in terms of emissions and slag formation. Overall, these studies indicated that problems related to challenging chemical composition of agricultural fuels might be mitigated by mixing the biomass with wood fuels but that a high share of woody biomass might be required.

Aim of the present study was to investigate the fuel quality and the combustion behaviour of straw and pellets from four fen paludiculture species. Fuel upgrading (additivation with kaolin, blending with wood pellets) was applied to improve the chemical fuel properties of the biofuels. The work included:

- the investigation of physical and chemical fuel properties of the unpelletized straw fuels,
- the pelletization of the materials including the application of fuel upgrading techniques such as additivation of fuels with kaolin before pelletization or blending of fuels with EN*plus* wood pellets (A1 quality) after pelletization,
- the investigation of physical and chemical fuel properties of the produced pellet fuels,
- combustion of the fuels in up to two small-scale boilers (15 kW, 30 kW) including determination of the gaseous and TPM emissions and
- evaluation of the slagging tendency of the fuels by applying ash melting analysis, the PASSA method ("Pellet Ash and Slag Sieving Assessment") and by means of a gravimetric analysis of the particle size distribution of the real boiler ashes that derived from the combustion trials.

On basis of these results, general recommendations were drawn on the suitability of paludiculture biomass as a biofuel for small-scale applications.

2. Materials & methods

2.1. Feedstocks

Four biomass fuels from the MOOR*use* test area "Freisinger Moos" (48°22′43.6″N, 11°41′00.4″E), i. e. *Typha* ssp., *Phragmites australis*, *Phalaris arundinacea* and *Carex* ssp., were harvested in February 2018, 2019 and 2020. After each harvest, the biomass was transferred into containers (approx. 6 m^3, each) in which ambient air ventilation rapidly reduced the moisture content of the fresh material. After two weeks of drying, the biomass was chopped and stored for several weeks in a roofed open storage building. After storage, chopped straw fuels were delivered to TFZ and analyzed for their physical and chemical fuel properties (see section 2.3). Pellets produced from straw fuels of the 2019 harvest were used for combustion trials in up to two small-scale biomass boilers (see section 2.4).

2.2. Pellet production and kaolin additivation

Pelletization was performed at TFZ. In a first step, straw fuels were milled in an Amandus Kahl 33–390 pellet mill using a die designed especially for comminution of biomass. Portions of each fuel were additivated using kaolin at levels that were calculated according to the guidelines from the ERA-NET project "BioFlex!" [33]. This calculation is mainly based on the mass fraction of K and Na in fuels.

Following the equations presented in section 1, the fixation of 2 mol K requires 1 mol of $Al_2Si_2O_5(OH)_4$. From this, the amount of kaolinite required for the stoichiometric fixation of K can be calculated using the molar weights of the elements and the K content of the biomass (see section 3.1). The same applies for the stochiometric fixation of Na. Thereby, the kaolinite content of the kaolin (here: 78%) must be considered, as well. To ensure that enough kaolin is incorporated into the pellets, the calculated additivation level was raised by 10%. The chemical composition of the additive is given in Table 1. Stochiometric calculations resulted in an additivation level of 2.3% kaolin for *Typha* ssp., 0.6% for *Phragmites australis*, 1.2% for *Phalaris arundinacea* and 1.5% for *Carex* ssp. on dry basis, respectively (see section 3.1).

Table 1
Chemical composition of the kaolin (d = dry basis).

Chemical compound	Mass fraction in % (d)
SiO_2	43.00
Al_2O_3	31.50
Fe_2O_3	2.20
CaO	0.20
MgO	0.30
K_2O	1.50
Na_2O	<0.10
P_2O_5	0.10

Mixing of the milled straw with the additive and adjustment of the fuel moisture content for pelletization was done manually in an industrial mixer (Stockmann Landtechnik GmbH, type 500 ESK). Afterwards, pelletization was performed in the same Amandus Kahl pellet mill already used for comminution but by applying dies designed for pelletization.

Two standard wood pellet batches (EN*plus* quality A1) from the German pellet market and wheat straw pellets from the ERA-NET project "BioFlex!" [21] were used as reference fuels. Wood pellets were also mixed with pure *Phalaris arundinacea* pellets after pelletization to produce pellet blendings with a mixing ratio of 30:70 and 10:90 (*Phalaris arundinacea* to wood). Overall, a total of 13 pellet fuels and two comminuted straw fuels (*Phalaris arundinacea* with and without kaolin) were used for combustion trials in two different boilers during this study (Table 2).

2.3. Fuel property analysis

Pellets and unpelletized straw were analyzed for their physical and chemical fuel properties according to international standards for solid biofuels (Table 3). These include the analysis of the moisture content and ash content (i. e. the mass fractions of H_2O and ash in fuels, respectively), net calorific value, bulk density, mechanical durability, pellet length, pellet diameter, mass fraction of fine particles in pellets, mass fraction of carbonates in ash samples that derived from combustion at 550 °C, concentration of chemical elements, and ash melting temperatures. Fuel quality was classified according to the specifications of ISO 17225–6 for non-woody pellets.

2.4. Test stand and combustion trials

Two boilers were used for the combustion trials. Boiler 1 was a moving grate boiler with a lateral fuel insertion (Fig. 1, left). The boiler is suitable for wood chips (7–30 kW), wood pellets (7–30 kW), grain (7–25 kW) and miscanthus (7–25 kW) according to the user manual. The primary air enters the combustion chamber from below through the grate. The combustion gases leave the primary section of the combustion chamber via a vortex nozzle. Here, secondary air is added to ensure that

Table 2
Fuels used for combustion trials in two boilers during this study as indicated by "X"

Fuel	Variant	Produced at TFZ	Boiler 1, 30 kW		Boiler 2, 15 kW
			Pellets	Straw	Pellets
Wood (1)	EN*plus* A1	-	X	-	-
Wood (2)	EN*plus* A1	-	-	-	X
Wheat straw	ERA-NET-BioFlex! [22]	X	X	-	-
Typha ssp.	pure	X	X	-	X
	with 2.3% kaolin	X	X	-	X
Phragmites australis	pure	X	X	-	-
	with 0.6% kaolin	X	X	-	-
Phalaris arundinacea	pure	X	X	X	X
	with 1.2% kaolin	X	X	X	X
	with 70% Wood (2)	X	-	-	X
	with 90% Wood (2)	X	-	-	X
Carex ssp.	pure	X	X	-	-
	with 1.5% kaolin	X	X	-	-

Table 3
Sampling, sample preparation, analysis methods and equipment used for fuel properties of solid biofuels (ar = as received, d = dry basis).

Process step/fuel parameter	Unit	Equipment	ISO standard
Sampling	-	TFZ-sample divider (self-constructed); zone sampler Spiralus (Bürkle GmbH)	ISO 18135
Sample preparation	-	Cutting mill Fritsch Pulverisette 19 (Fritsch GmbH), <250 μm	ISO 14780
Mass fraction of H_2O, i. e. "moisture content" (*M*)	%, ar	Drying cabinet FED720-02-42004 (Binder GmbH)	ISO 18134–1 ISO 18134-3
Mass fraction of ash, i. e. "ash content" (*A*)	%, d	Muffle furnace LT15 (Nabertherm GmbH)	ISO 18122
Net calorific value (*Q*)	MJ kg^{-1}, d	Calorimeter IKA C 2000 basic (IKA-Werke GmbH & Co. KG)	ISO 18125
Bulk density (*BD*)	kg m^{-3}, ar	Standardized 5 l bucket; platform scale MT KA32s with ICS429 (Mettler-Toledo GmbH)	ISO 17828
Pellet lenth (*L*) and diameter (*D*)	mm, ar	Caliper CD-15DC (Mitutoyo Corporation)	ISO 17829
Durability (*DU*)	%, ar	Standardized durability tester (self-constructed); screen (Ø = 400 mm with 3.15 mm round holes); precision scale CPA8201 (Sartorius AG)	ISO 17831-1
Mass fraction of particles <3.15 mm, i. e. "fine content" (*F*)	%, ar	Screen (Ø = 400 mm with 3.15 mm round holes); precision scale CPA8201 (Sartorius AG)	ISO 18846
Mass fraction of total inorganic carbon (TIC) in ash samples (550 °C)	% CO_2, d	TIC/TOC-analyser LECO RC612 (LECO Instrumente GmbH)	own method [52]
Mass fraction of C, H, N	%, d	Analysis performed in external laboratory	ISO 16948
Mass fraction of S, Cl	%, d	Analysis performed in external laboratory	ISO 16994
Concentration of Al, Ca, Fe, Mg, P, K, Si, Na und Ti	mg kg^{-1}, d	Analysis performed in external laboratory	ISO 16967
Concentration of As, Cd, Cr, Cu, Ni, Pb, Zn	mg kg^{-1}, d	Analysis performed in external laboratory	ISO 16968
Ash melting temperatures	°C	Analysis performed in external laboratory	ISO 21404

the combustion gases are burned as completely as possible. The hot exhaust gas passes from the combustion chamber into a tube bundle heat exchanger equipped with turbulators. A lambda probe is installed in the exhaust gas outlet of the boiler to measure the residual oxygen content in the flue gas. The ash is removed via the moving grate to a screw conveyor which transports the ashes into the ash box. A square storage tank with a slanted floor and a screw conveyor was used for fuel feeding for pellet fuels. A larger, round storage tank was used for comminuted straw fuels. To determine the fuel consumption during combustion, the storage tank was placed on a platform scale (Mettler-Toledo GmbH, MT KD600) with a resolution of 0.005 kg.

Boiler 2 was a 15 kW pellet boiler that is designed only for high quality wood pellets fulfilling the EN*plus* A1 label. The boiler has an integrated storage tank for approx. 30 kg of pellets (Fig. 1, right) and is equipped with a tilting grate. The fuel passes from the storage tank via a dosing screw to a rotary valve and is then conveyed laterally into the combustion chamber via a stoker screw. Combustion takes place in an uncooled combustion chamber before the exhaust gases passes through the heat exchanger equipped with turbulators. A lambda probe in connection with the speed-controlled induced draft fan ensure high combustion efficiency. During combustion, automatic grate cleaning takes place by rotating the tilting grate against a comb. Two conveyor screws are used to transport ashes into the ash box. To determine fuel consumption in boiler 2, the boiler was placed on the same platform scale that was already used for the storage tank of boiler 1.

When restarting, the pellets are ignited with a ceramic glow element. Burning takes place in an uncooled, hot combustion chamber made of stainless steel before the heating gases in the heat exchanger transfer the heat to the heating water. A lambda probe should ensure high efficiency in connection with the speed-controlled induced draft fan. During fire breaks, automatic cleaning takes place by rotating the grate against a comb. By moving the turbulators, all heat exchanger passes are cleaned automatically every day. Under the grate and the heat exchanger, two ash screws convey the ash into a removable ash box.

Fig. 1 shows schematic drawings of each test stand and the arrangement of the measurement devices. The heat consumption was permanently regulated to nominal load following EN 303–5. The gaseous components CO, CO_2, and O_2 were determined using a single component analyser (ABB Automation GmbH ABB AO2020), NO_X by a chemiluminescence detector (Eco Physics GmbH CLD 822 Mhr Analysator), and for water vapour content, SO_X, HCl and CH_4 a FTIR analyser (Ansyco GmbH FTIR DX4000 N) was used. The recording interval for the continuous measurement was set to 10 s. The total particulate matter (TPM) was isokinetically sampled following VDI 2066 part 1 applying a filtration temperature during sampling of 160 °C and the filter pre- and post-treatment temperature of 180 °C and 160 °C, respectively. Deposition in the sampling line was considered through rinsing with acetone at the end of the measurement day. The boilers were operated at nominal load operation using a constant flue gas draught of either -15 ± 2 Pa (boiler 1) or -12 ± 2 Pa (boiler 2), respectively, as suggested by the boiler manufacturers. The diameter of the flue gas duct and the connection pipe was 150 mm (boiler 1) or 110 mm (boiler 2). The flue gas velocity was continuously measured using a vane anemometer (Höntzsch GmbH, ZS25/25-ZG4) in the narrowed measurement section having a diameter of 100 mm for boiler 1 and 80 mm for boiler 2.

Each boiler was connected to a self-constructed heat output measuring system that met the requirements of EN 303–5. Thereby, the heat emitted by the boiler can be determined directly via the water flow (Endress + Hauser Promag 53) and the temperature spread between flow and return (PT100 Thermokon).

For the experiments with comminuted straw of *Phalaris arundinacea* (only boiler 1), kaolin was added during fuel feeding directly using a separate dosing screw that mixes the additive into the screw conveyor between storage tank and boiler [53]. To ensure that the required amount of additive is achieved, throughput rates of the two conveyor screws were determined individually before the experiment. The dosing screw was placed on a platform scale so that the exact amount of additive mixed into the fuel can be calculated.

For each combustion trial, the respective boiler was pre-heated to nominal load for approx. 1–2 h followed by a continuous nominal load operation of approx. 6 h. Emission measurements ($n = 5$) were distributed evenly throughout the nominal load operation of the trial. With exception of the blending ratio 90:10 (wood to *Phalaris arundinacea*), sever slag formation in boiler 2 required to manually start the automatic grate cleaning cycle of the boiler after each TPM measurement (see section 3.3). In case of the blending ratio 70:30 (wood to *Phalaris arundinacea*), only one cleaning cycle was necessary during the respective trial. The following measurement was started directly when the boiler once again reached nominal load.

2.5. Slagging behaviour

After each combustion trial, the boiler cooled down to room temperature and the total amount of ash and slag was collected. Slagging behaviour was evaluated according to a granulometric ash evaluation procedure. First, a 2D-sieving was performed for 1 min at 200 rounds per minute using a sieve with either 3.15 mm or 8 mm round holes (Ø 400 mm). If the amount of ash was too high, then the ash was sieved in

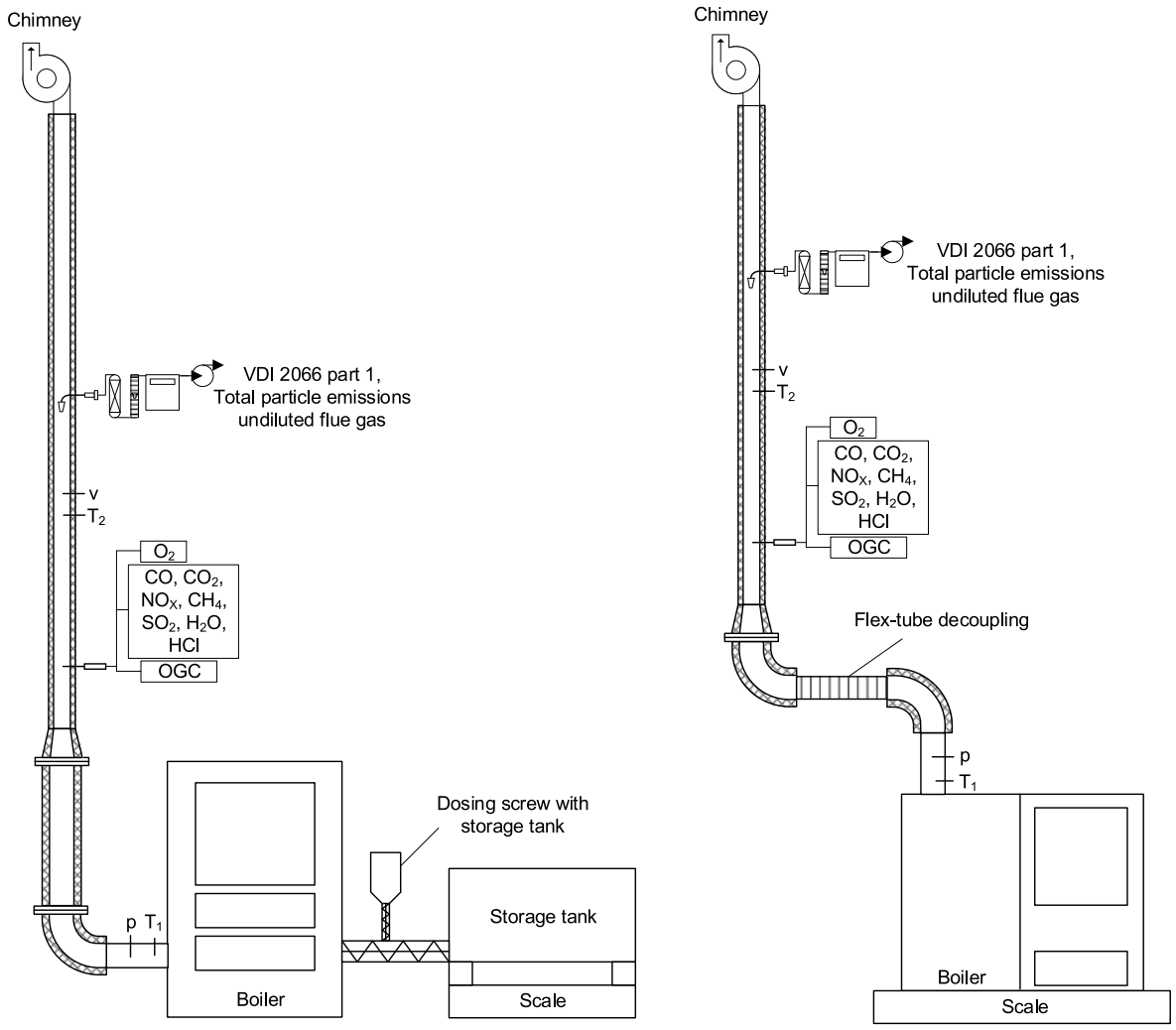


Fig. 1. Schematic drawing of the test stand with boiler 1 (30 kW, left) and with boiler 2 (15 kW, right) (T = Temperature, p = pressure, v = air velocity).

separate runs. The large particle fraction (i. e. > 3.15 mm or >8 mm) was weighted, and the mass was recorded. Afterwards, all ash particles within the smaller ash fraction were sieved using a 3D-sieving machine while applying an amplitude of 0.5 for 5 min. The metal wire cloth sieves had opening widths of 0.5, 1.0 and 2.0 mm (Ø 200 mm). Again, if the amount of ash was too high, several runs were performed. The so called "slag index" was calculated by relating the mass of particles >2 mm to the whole ash. In addition, for the trials with boiler 2, the two largest slag particles per ash sample were selected manually and their length, width and height were measured individually using a caliper (CD-15DC, Mitutoyo Corporation).

In addition to the granulometric assessment of the real boiler ashes, each paludiculture pellet fuel was tested following the PASSA method that was developed in the EU project "AshMelT" [54]. Here, the PASSA method was adapted slightly in that approx. 200 g of pellets per fuel were transferred into crucibles and thermally treated in a muffle furnace (LT15, Nabertherm GmbH) for 4 h at 250 °C followed by 30 min at 1000 °C (L40/11 BO, Nabertherm GmbH). Heating was adjusted to 10 K min^{-1}. After cooling down, ashes were analyzed using the same 3D-sieving as described for boiler ashes above. The mass of molten ash particles that were fused to the crucibles was added to the mass of the ash particle fraction >2 mm. Like boiler ashes, slag indices were calculated for the PASSA method, as well.

2.6. Statistical analysis

ANOVA with Tukey post-hoc tests were performed to identify significant differences ($p \leq 0.05$) among mean values e. g. of selected physical fuel properties but also regarding differences in emission behaviour of the paludiculture fuels during combustion in both boilers. Homogeneity of variance was tested using Brown Forsythe test. All statistical analyses were performed using Origin Lab 2019.

3. Results & discussion

3.1. Fuel properties of straw fuels and stochiometric kaolin demand

Moisture content (*M*) of straw fuels after harvest in February 2018, 2019 and 2020 varied from 19.9 to 48.2% with high standard variations of up to 19.1% (Table 4). Such strong variation in *M* was expected as the fuels derived from a test field that applies a variable water gradient in the peat from dry to wet growing conditions. In addition, a previous study by Wichtmann et al. [28] suggested that *M* of paludiculture straw that is harvested during winter also depends on climate conditions such as rainfall and might therefore range from <15% to 60%. As the fuels all derived from the same test area, this effect might explain differences between harvesting years but probably not regarding differing trends among species within the same year of harvest. Still, depending on the circumstances given by the test area (e. g. differing water level) but probably also depending on variable climate conditions, *M* of

Table 4
Fuel properties of paludiculture straw harvested in winter 2018, 2019 and 2020 (mean values ± standard deviation; M_H = moisture content of straw directly after harvest in February; M = moisture content of straw sample delivered to TFZ; A = ash content; BD = bulk density; Q = net calorific value; ar = as received; d = dry basis; n = 2 to 10 depending on analysis method; chemical fuel quality determined as n = 1 using homogeneously mixed samples of n = 3).

Parameter	Unit	*Typha* ssp.			*Phragmites australis*			*Phalaris arundinacea*			*Carex* ssp.		
		2018	2019	2020	2018	2019	2020	2018	2019	2020	2018	2019	2020
M_H	%, ar	27.9 ± 10.5	48.2 ± 14.1	49.5 ± 10.1	24.6 ± 6.2	19.9 ± 3.0	18.5 ± 3.5	35.5 ± 13.1	33.9 ± 19.1	39.5 ± 15.3	39.8 ± 4.0	33.2 ± 9.2	45.8 ± 12.7
M	%, ar	10.3 ± 0.3	9.1 ± 0.3	7.5 ± 0.1	8.8 ± 0.0	9.3 ± 0.2	6.7 ± 0.1	10.1 ± 0.4	9.8 ± 0.2	7.3 ± 0.1	10.3 ± 0.1	11.0 ± 0.7	8.1 ± 0.1
A	%, d	5.2 ± 0.0	6.0 ± 0.1	5.2 ± 0.0	4.7 ± 0.0	4.8 ± 0.1	5.5 ± 0.1	3.9 ± 0.1	9.9 ± 0.5	4.5 ± 0.1	5.0 ± 0.1	5.1 ± 0.0	6.3 ± 0.0
BD	kg m^{-3}, ar	35.2 ± 0.3	23.1 ± 1.5	58.7 ± 2.3	95.3 ± 1.1	48.5 ± 1.9	81.2 ± 4.4	66.2 ± 1.5	42.7 ± 1.2	59.0 ± 1.8	78.0 ± 2.9	36.5 ± 0.3	59.6 ± 3.2
Q	MJ kg^{-1}, d	17.61 ± 0.01	17.62 ± 0.02	17.53 ± 0.01	17.89 ± 0.02	17.88 ± 0.02	17.45 ± 0.02	17.83 ± 0.00	16.88 ± 0.04	17.84 ± 0.03	17.67 ± 0.00	17.09 ± 0.00	17.62 ± 0.03
C	%, d	47.0	48.4	47.5	47.3	48.4	46.8	46.7	46.2	47.5	46.8	48.8	47.4
H	%, d	5.9	5.9	5.9	5.9	5.9	5.8	5.9	5.7	5.8	5.8	5.8	5.8
N	%, d	0.95	0.99	0.89	0.82	0.59	0.63	0.88	1.24	1.16	1.12	1.17	1.15
S	%, d	0.061	0.092	0.093	0.063	0.071	0.079	0.105	0.117	0.117	0.120	0.116	0.134
Cl	%, d	0.163	0.202	0.176	0.065	0.071	0.166	0.090	0.068	0.046	0.279	0.185	0.190
Al	mg kg^{-1}, d	165	262	445	71	171	62	129	1290	1070	54	172	501
Ca	mg kg^{-1}, d	14,500	13,300	12,300	2050	1800	1640	2590	5270	2860	4330	4660	5410
K	mg kg^{-1}, d	1730	1420	3620	1620	740	2130	1080	1910	1760	3370	2460	4010
Mg	mg kg^{-1}, d	1980	1740	1310	457	637	734	775	611	932	3300	2530	2350
Na	mg kg^{-1}, d	2350	1750	1490	119	277	623	199	369	150	589	401	336
P	mg kg^{-1}, d	1400	1180	1120	276	276	456	874	925	837	1760	1270	1300
Si	mg kg^{-1}, d	836	681	4100	14,700	11,800	20,000	11,200	19,600	12,800	9840	9070	46,500

paludiculture straw was very heterogeneous and usually too high for direct combustion in a small-scale boiler. Thus, for using paludiculture biomass as a biofuel, some method for moisture content determination [55,56] and active drying of the biomass before combustion are recommended, even if fuels are harvested during winter.

Before transport to TFZ, all fuels were dried actively and stored in an open storage building for several weeks (see section 2.1) leading to sufficient pre-drying of the biomass. After drying and storage, the unpelletized straw of the four fen cultures had a moisture content of 7.3–11.0% (Table 4). No further active or passive drying was required before pelletization or combustion. At low $M < 20\%$, degradation of the biomass by bacteria and fungi during storage is strongly inhibited allowing for even longer storage periods of the dried material [13].

Bulk density (BD) of the straw fuels ranged between 23.1 and 95.3 kg m^{-3} (ar = as received) and was therefore in a typical range for paludiculture straw, e. g. for giant reed (<40–120 kg m^{-3}, ar) [36]. BD of fuels from 2018 and 2020 was always higher compared to the respective material in 2019 (Table 4), probably due to different harvesting techniques and cut lengths that were applied for chopping and retrieval of the biomass. Overall, BD was considered too low for direct use in small-scale boilers <100 kW due to a low energy density (in MJ m^{-3}, data not shown), and fuels would require some method of compaction such as pelletization or the use as bales [13,26,29,36]. Thereby, the use of the latter was already successfully demonstrated for paludiculture biomass in a communal heat plant (800 kW) in Northern Germany [29]. For small-scale application, pelletization might be the method of choice [36] to produce fuels that might be easily transported from bunker to boiler and that allow for rather uniform combustion conditions on the grate [13].

In eleven of twelve cases, ash content (A) for the pure paludiculture fuels ranged from 3.9% (d = dry basis) to 6.3% (d, see Table 4), exhibiting a typical range for paludiculture biomass [27–29,36,37] or of agricultural straw and grass fuels, in general [12,13,17]. Most straw fuels in this study complied with the ash requirements for fuel class A according to ISO 17225–6 (i. e. ≤ 6.0%, d). The highest ash content was measured for *Phalaris arundinacea* straw from the harvest of 2019 (9.9%, d) indicating some contamination of the biomass with either fibrous peat during harvesting or with soil material during storage (see also chemical composition, below) [57–59]. At the same time, net calorific value (Q) of *Phalaris arundinacea* from 2019 was decreased to 16.88 MJ kg^{-1} (d), also suggesting a high share of inorganic material in the biomass, while Q of all other fuel samples was within a typical range for paludiculture species from 17.61 to 17.90 MJ kg (d) [28,36]. An analysis of a fibrous peat sample collected from the *Phalaris arundinacea* plots of the MOOR*use* test field "Freisinger Moos" resulted in an ash content of 53.4% (d) and a net calorific value of 8.69 MJ kg^{-1} (d), respectively. Therefore, A of the peat sample was higher and Q was lower compared to values for pure peat as reported in Refs. [20,57,60–64] and might also hint at contamination by other sources such as an addition of mineral soil [58,59]. Considering A and Q of the *Phalaris arundinacea* straw samples from 2018 and 2020 and the peat sample as a reference, these values indicate a theoretical contamination of the 2019 *Phalaris arundinacea* straw with peat and/or soil material of approx. 10.5–11.4%.

The chemical composition of the straw fuels is given in Table 4. As expected for paludiculture species [27–29,36,37] and for agricultural biomass in general [12,17,22–25], the here investigated straw fuels were enriched in N, S, Cl, and in ash forming elements such as Ca, K, Mg or Si compared to conventional high quality wood pellets with an EN*plus* A1 label. These values indicate increased gaseous emissions (NO_X, SO_X, HCl), total particulate matter (TPM) emissions and slag formation during the combustion (see also section 3.2 on fuel quality of pellets for reference fuels). Like A and Q, results on chemical fuel properties of *Phalaris arundinacea* from the 2019 harvest also indicate some contamination of the sample with either soil material and/or fibrous peat as Si content increased from 11,200 mg kg^{-1} (d) in 2018 and 12,800 mg kg^{-1} (d) in 2020 to 19,600 mg kg^{-1} (d) in 2019. Although grass species often have high Si content ranging from 3000 to 12,000 mg kg^{-1} (d) [12,13], *Phalaris arundinacea* of 2019 exceeded this range by the factor 1.6. At the

same time, Al content of the same *Phalaris arundinacea* sample was increased by the factor 10 from 2018 to 2019. Si and Al are usually enriched in soils and can be used as an indicator for contamination of solid biofuels with inorganic materials [58,59]. At the same time, both Si and Al can be enriched in fibrous peat [64]. This was also true for the peat sample from the *Phalaris arundinacea* plots with approx. 7800 mg kg^{-1} (d) of Al and 127,000 mg kg^{-1} (d) of Si, respectively. Consequently, results on chemical composition of the 2019 *Phalaris arundinacea* sample also strongly indicate that the material was indeed contaminated during processing with either fibrous peat and/or soil material. Similar to *Phalaris arundinacea* of 2019, increased ash and Si contents were found in *Phragmites australis* and *Carex* ssp. samples from 2020 also indicate contamination within these samples.

Straw fuels from the 2019 harvest were pelletized at TFZ. For each paludiculture species, both pure and additivated fuels were produced. Additivation levels were calculated following the guidelines of the ERA-NET project "BioFlex!" [33] using K and Na contents of the 2019 straw samples (Table 5). This led to additivation levels of 0.6–2.3%. Theoretically using the chemical composition of straw samples harvested in 2018 and 2020 as a reference, the calculation would have resulted in slightly higher kaolin requirements for most species (e. g. 2.2–3.0% kaolin for *Typha* ssp.), indicating that additivation levels might be underestimated during this study.

3.2. Fuel properties of pellets

All fuels were pelletized at TFZ to a pellet diameter of 6 mm, either as pure fuels or as fuels that were additivated with kaolin. Table 6 summarizes the results on physical fuel properties of the paludiculture pellets and the selected reference fuels. Mean *M* of pellets was 5.5–11.8% and complied with fuel class A of ISO 17225–6 (≤12.0%). Mean *BD* of pure and additivated pellets was 747–796 kg m^{-3} and therefore significantly ($p \leq 0.05$) increased towards the reference fuels (wood and wheat straw pellets) and to values as reported by Dahms et al. [36]. Consequently, blending of *Phalaris arundinacea* pellets with wood pellets led to a reduction of *BD* to values of approx. 700 kg m^{-3}. These results led to the assumption that the here performed pelletization step might be optimized in terms of energy input during the production process as the very high values for *BD* indicate an unnecessary strong densification of the fuels compared to standard wood pellets. At the same time, mechanical durability (*DU*) of paludiculture pellets was high with values ranging from 98.6% to 99.3%. In contrast to Mack et al. [21], no trend in *BD* could be detected depending on the additive, probably due to the rather low additivation levels of <2.3%.

Ash content of pure and additivated paludiculture pellets ranged from 4.8 to 7.1% (d) (Table 6). Thereby, four pellet fuels met the ash requirements of fuel class A according to ISO17225-6 (≤6.0%, d), while the other fuels met the requirements of fuel class B (≤10%, d). In three out of four cases, additivation with kaolin (ash content = 89.7%, d) significantly increased *A* in fuels ($p \leq 0.05$). Interestingly, this was not the case for *Typha* ssp., i. e. the fuel with the highest additivation level, with pure and additivated pellets both having an *A* of 6.8% (d). Thereby, ash samples of pure *Typha* ssp. (deriving from combustion at 550 °C in a muffle furnace) had much higher shares of total inorganic carbon (*TIC*) compared to the other paludiculture pellets. This results in a calculated *A* for *Typha* ssp. of 5.4% (d) excluding the share of carbonates. During this study, much lower *TIC* contents were measured in additivated *Typha* pellets resulting in a calculated *A* of 6.0% (d). Thus, the missing increase in *A* measured for pure and additivated *Typha* ssp. might be explained by differences in *TIC*. No pronounced influence of *TIC* on *A* could be observed for the other fuels due to either low *A* (i. e. for the reference wood pellets) or low *TIC* (for the other paludiculture fuels).

As expected, blending of *Phalaris arundinacea* pellets with wood resulted in a strong reduction of *A* to values from 2.5 down to 1.0% (d) while *Q* increased due to the overall large differences in *A* and *Q* of both feedstocks. Interestingly, for pure *Phalaris arundinacea*, results on *A* of pellets (5.0%, d) were much closer to values of straw fuels from 2018 (3.4%, d) and 2020 (4.5%, d) (see Table 4) and to results from literature [28,36] compared to *A* of the respective straw fuel from 2019 (9.9%, d). The same applies for *Q*. Consequently, results of the 2019 straw sample of *Phalaris arundinacea* must be considered non-representative for the whole batch and the above discussed contamination of the sample with peat should not be expected to affect the whole delivery. Moreover, due to intense mixing of the milled fuels in the mixer before pelletization (see section 2.2), heterogeneity of pellet fuels was expected to be low.

Chemical fuel properties of additivated or blended pellets were calculated from the chemical composition of the reference (straw) fuels and the additive (Table 7). This procedure is commonly used when additivation or experimental contamination of pellet fuels are performed [21,58]. For pure *Phalaris arundinacea*, chemical fuel concentrations were measured once again from the produced pure pellets directly, as results on *A* and *Q* of the straw and pellet fuels indicated non-representative contamination of the analyzed straw sample (see above).

Compared to the certified wood pellets (EN*plus* A1 quality), pure paludiculture fuels had higher shares of all chemical elements that are considered critical for combustion (N, Cl, S, K, Si) [13,23,48]. Apart from K and Cl, this was also true when pure paludiculture fuels were compared to pellets from wheat straw that were produced in the ERA-NET project "BioFlex!" [21]. As K is highly relevant for aerosol formation, higher TPM emissions can be expected during the combustion of wheat straw pellets compared to pellets from paludicultures.

After additivation, Al and Si increased in all fuels due to the high share of these elements in the kaolin (Table 7). Other elements that are also present in the additive such as Ca, Mg, Na or K, and that had a similar concentration in both the pure fuels and in the kaolin, led only to minor changes in the element composition of the additivated fuels. Elements that were not detected in the additive such as N, Cl and S did not change much in the additivated fuels as the additivation level was rather low (<2.3%), leading to almost no dilution effect in the biomass.

Fuel indices that are commonly used to predict combustion behaviour, i. e. to predict NO_X emissions (N content), TPM emissions (sum of K, Na, Pb, Zn, S and Cl), slag formation (molar (Si + P + K)/(Ca + Mg + Al) ratio) or the fixation of K into the ash (molar Si/K ratio, molar Cl/Si ratio), were calculated from chemical fuel properties (Table 8) [30,32,48,65–67].

The sum of aerosol forming elements (K, Na, Pb, Zn, Cl, S) is often used as an indicator for TPM emissions [13,30,34,48,65]. According to the index, highest TPM emissions are expected for *Typha* ssp. due to both high levels of K and Na in fuels. For all other paludiculture fuels, the sum of aerosol forming elements was lower compared to *Typha* ssp. but still much higher compared to EN*plus* A1 wood pellets. Consequently, blending of *Phalaris arundinacea* with wood strongly decreased the index and thus, blending should lead to a clear reduction of TPM emissions as it was already seen in previous studies [21,51].

Additivation with kaolin strongly increased Si in pellets. As predicted by an increased molar Si/K ratio (at values above 2.5) [48] and by a

Table 5
Stochiometric kaolin demand calculated from straw fuels of 2019 (d = dry basis) including an addition of 10% to the calculated value.

Fuel	K	K	Na	Na	Stochiometric kaolin demand +10%
	mg kg^{-1} (d)	mol kg^{-1} (d)	mg kg^{-1} (d)	mol kg^{-1} (d)	% (d)
Typha ssp.	1420	0.04	2350	0.08	2.28
Phragmites australis	740	0.02	119	0.01	0.57
Phalaris arundinacea	1910	0.05	199	0.02	1.20
Carex ssp.	2460	0.06	589	0.02	1.49

Table 6
Physical fuel properties of the pellet fuels (mean ± standard deviation; *M* = moisture content; *A* = ash content; *BD* = bulk density; *Q* = net calorific value; *DU* = durability; *L* = mean length; L_{Max} = maximal length; *D* = diameter; ar = as received; d = dry basis; n. D = not determined; *n* = 2 to >150 depending on analysis method).

Pellet fuel	*M*	*A*	*A* excluding carbonates	*BD*	*Q*	*DU*	*L*	L_{max}	*D*
	%, ar	%, d	%, d	kg m^{-3}, ar	MJ kg^{-1}, d	%, ar	mm, ar	mm, ar	mm, ar
Wood (1)	7.9 ± 0.0	0.3 ± 0.0	0.3	684 ± 5	18.89 ± 0.04	99.3 ± 0.0	12.3 ± 5.8	32.2	6.1 ± 0.1
Wood (2)	7.7 ± 0.1	0.4 ± 0.0	0.2	703 ± 2	18.99 ± 0.01	99.2 ± 0.0	15.3 ± 4.9	25.6	6.0 ± 0.1
Wheat straw	8.8 ± 0.0	4.3 ± 0.0	4.0	625 ± 2	17.52 ± 0.01	96.4 ± 0.2	13.0 ± 5.2	23.2	6.2 ± 0.1
Typha ssp.	7.8 ± 0.1	6.8 ± 0.1	5,4	781 ± 2	17.62 ± 0.02	99.0 ± 0.0	15.3 ± 6.4	27.1	6.0 ± 0.0
Typha. + 2.3% kaolin	5.9 ± 0.3	6.8 ± 0.0	6,0	787 ± 2	17.25 ± 0.01	98.8 ± 0.1	11.3 ± 6.2	25.3	6.0 ± 0.0
Phragmites australis	5.5 ± 0.1	4.8 ± 0.0	4,7	796 ± 4	17.92 ± 0.00	98.7 ± 0.1	14.4 ± 5.5	26.8	6.0 ± 0.0
Phragmites + 0.6% kaolin	5.4 ± 0.2	5.2 ± 0.0	5,2	790 ± 2	17.76 ± 0.01	99.3 ± 0.0	18.2 ± 6.2	27.0	6.0 ± 0.1
Phalaris arundinacea	11.8 ± 0.3	5.0 ± 1.4	4,9	787 ± 2	18.22 ± 0.00	99.0 ± 0.0	20.1 ± 4.9	27.5	6.1 ± 0.1
Phalaris + 1.2% kaolin	7.7 ± 0.1	7.1 ± 0.1	6,9	747 ± 1	17.47 ± 0.01	98.9 ± 0.0	16.6 ± 5.8	26.4	6.0 ± 0.0
Phalaris + 70% Wood (2)	7.6 ± 0.1	2.5 ± 0.0	2,4	690 ± 0	18.41 ± 0.01	n. d.	n. d.	n. d.	n. d.
Phalaris + 90% Wood (2)	8.1 ± 0.4	1.0 ± 0.0	0,9	700 ± 1	18.63 ± 0.06	n. d.	n. d.	n. d.	n. d.
Carex ssp.	6.0 ± 0.4	5.6 ± 0.0	5,4	780 ± 4	17.67 ± 0.01	98.6 ± 0.1	15.2 ± 6.6	27.8	5.9 ± 0.1
Carex + 1.5% kaolin	8.3 ± 0.5	7.1 ± 0.1	6,9	772 ± 2	17.98 ± 0.02	99.0 ± 0.1	18.9 ± 6.3	27.6	6.0 ± 0.0

Table 7
Minor and trace elements of the pellets (d = dry basis). Concentration of the additivated or blended fuels were calculated from the analyses of the pure straw samples (^{S}), pure pellet samples (^{P}) and the additive applying the respective mixing ratios.

Pellet fuel	N	S	Cl	Al	Ca	K	Mg	Na	P	Si
	%, d	%, d	%, d	mg kg^{-1}, d	mg kg^{-1}, d	mg kg^{-1}, d	mg kg^{-1}, d	mg kg^{-1}, d	mg kg^{-1}, d	mg kg^{-1}, d
Wood (1)^{P}	<0.10	0.005	0.006	25	811	414	131	15	55	166
Wood (2)^{P}	0.07	0.007	<0.005	<10	677	402	129	<10	46	245
Wheat straw^{P}	0.44	0.072	0.209	145	2860	8450	767	42	638	9460
Typha ssp.^{S}	0.99	0.092	0.202	262	13,300	1420	1740	1750	1180	681
Typha + 2.3% kaolin	0.97	0.090	0.197	4062	13,020	1661	1748	1733	1153	5246
Phragmites australis^{S}	0.59	0.071	0.071	171	1800	740	637	277	276	11,800
Phragmites + 0.6% kaolin	0.58	0.069	0.069	1128	1795	805	645	281	270	12,885
Phalaris arundinacea^{P}	1.27	0.139	0.094	568	4230	2150	1140	292	1160	8460
Phalaris + 1.2% kaolin	1.24	0.136	0.092	2568	4191	2268	1152	301	1134	10,773
Phalaris + 70% Wood (2)	0.43	0.047	0.032	177	1743	926	432	95	380	2710
Phalaris + 90% Wood (2)	0.19	0.020	0.014	66	1032	577	230	38	157	1067
Carex ssp.^{S}	1.17	0.116	0.185	172	4660	2460	2530	401	1270	9070
Carex + 1.5% kaolin	1.14	0.113	0.181	2654	4606	2602	2524	410	1241	11,925

Table 8
Fuel indices to predict combustion behaviour of paludiculture pellets, calculated using minor and trace elements (d = dry basis, ^{S} = measured from straw sample, ^{P} = measured from pellet sample).

Pellet fuel	K + Na + Pb + Zn + S + Cl	Molar (Si + P + K)/(Ca + Mg + Al)	Molar Cl/Si	Molar Si/K	Molar 2S/Cl
	mg kg^{-1}, d	mol mol^{-1}	mol mol^{-1}	mol mol^{-1}	mol mol^{-1}
Wood (1)^{P}	554	0.69	0.03	0.56	1.79
Wood (2)^{P}	545	0.91	0.02	0.85	3.10
Wheat straw^{P}	11,306	5.29	0.02	1.56	0.76
Typha ssp.^{S}	6138	0.24	0.24	0.67	1.01
Typha + 2.3% kaolin	6294	0.49	0.03	4.39	1.01
Phragmites australis^{S}	2470	5.78	0.00	22.19	2.21
Phragmites + 0.6% kaolin	2506	4.31	0.00	22.28	2.21
Phalaris arundinacea^{P}	4822	2.27	0.01	5.48	3.27
Phalaris + 1.2% kaolin	4895	1.93	0.01	6.61	3.27
Phalaris + 70% Wood (2)	1828	1.95	0.01	4.07	3.25
Phalaris + 90% Wood (2)	973	1.53	0.01	2.57	3.21
Carex ssp.^{S}	5902	1.88	0.02	5.13	1.39
Carex + 1.5% kaolin	5984	1.67	0.01	6.38	1.39

reduced molar Cl/Si ratio (at values below 0.1) [68], higher shares of K might be fixed into the ash due to additivation by forming potassium aluminum silicates [21,33]. According to both indices, this effect should be more pronounced for *Typha* ssp. compared to the other species as both the molar Si/K ratio and the molar Cl/Si ratio already predicted good K fixation for the pure pellets of *Phragmites australis*, *Phalaris arundinacea* and *Carex* ssp.

A high molar (Si + P + K)/(Ca + Mg + Al) ratio is often used to predict slag formation during combustion [21,30,48,58,66] although a high share of alternative indices were proposed depending on the chemical composition of the investigated biofuels [66,67]. Results indicate that the lowest slag formation can be expected during combustion of *Typha* ssp. due to the low amount of Si and the high amount of Ca in the fuels, while for *Phragmites australis*, results were close to that of wheat straw. During the ERA-NET project "BioFlex!", combustion of pure wheat straw pellets resulted in the shutdown of boiler 1 due to severe slag formation [21]. Thus, according to the index, high slagging risks can also be expected during combustion of pure *Phragmites australis* pellets when they are applied to the same boiler. Blending of *Phalaris arundinacea* with wood decreased the index indicating an improved combustion behaviour in terms of slag formation.

3.3. Combustion trials

During this study, lowest gaseous and total particulate matter emissions were usually measured during the combustion of wood pellets in both boilers. Relevant differences in combustion behaviour were detected depending on the different paludiculture species but also on the

tested variants (additivation, blending, comminuted straw vs. pellets). Since combustion trials with the second reference fuel, i. e. pure wheat straw pellets, resulted in a shutdown of boiler 1 due to sever slag formation as seen in the ERA-NET project "BioFlex!" [21], no results on emissions can be presented for this fuel. The following section summarizes the results on CO, OGC, NO_X, SO_X, HCl and TPM emissions but also on the heat output achieved during combustion. All emission values are calculated to dry flue gas at 0 °C, 1013 hPa and 13% O_2.

Mean CO emissions during combustion ranged from 14 to 292 mg m^{-3} for boiler 1 and from 7 to 68 mg m^{-3} for boiler 2, respectively (Fig. 2). Thereby, mean CO values remained below the emission threshold for wood or straw fired boilers according to the first ordinance of the German emission control act (i. e. 400 mg m^{-3} at 13% O_2 for wood boilers <1 MW and straw boilers <100 kW, 1. BImSchV, stage 2).

Increased CO emissions are an indicator for incomplete combustion of the fuel [13,17,69]. For boiler 1, highest CO emissions were detected for *Typha* ssp. followed by *Phalaris arundinacea* while CO emissions of both *Phragmites australis* and *Carex* ssp. resembled that of the reference fuel, i. e. of EN*plus* A1 wood pellets (1). Thereby, CO was significantly higher in boiler 1 for pure *Typha* ssp. compared to all other fuels ($p \leq 0.05$).

In boiler 1, additivation of pellets with kaolin led to a significant decrease of CO emissions for *Typha* ssp. ($p \leq 0.05$) and by trend for *Phalaris arundinacea* (both pellets and straw). The same applies for *Typha* ssp. in boiler 2 but not on a significant level (Fig. 2). A positive effect of kaolin on CO emissions was reported in previous studies [21,45]. So far, no distinct cause for this effect could be identified. One possible explanation might be a positive change in the ventilation of the fuel bed due to an improved ash melting behaviour of the fuels. Another explanation might be a more porous structure of the already charred pellets during charcoal burnout caused by kaolin, which might enhance the penetration of oxygen into the charcoal leading to an overall better burnout of the gaseous components. Bozaghian et al. [35] proposed that high CO emissions might also be due to a still to be identified effect of high shares of gaseous alkali compounds in the flue gas that might affect the oxidation of CO to CO_2. Consequently, kaolin would not only lead to a reduction of TPM (see below) but also of CO by decreasing alkali compounds in the flue gas.

Interestingly, CO emissions strongly increased during the study of Bozaghian et al. [35] when $CaCO_3$ was used as an additive for straw. Similar, very high CO emissions were measured during combustion of Ca-rich grass pellets by Mack et al. [21]. During the here presented trials, CO was highest for *Typha* ssp., i. e. for the paludiculture species with the highest values for both *TIC* and Ca indicating high shares of Ca-carbonates in the fuel. Thus, differences in chemical composition of agricultural fuels seem to not only affect NO_X, SO_X, HCl or TPM emissions (see below) but also CO emissions. Overall, further studies are required to explain these effects in more detail.

Blending of *Phalaris arundinacea* with wood pellets resulted in a clear but not significant decrease of CO emissions in boiler 2 to values even lower as of pure wood pellets. Still, results indicate that blending of agricultural fuels with wood might be a suitable method to decrease CO emissions in small-scale boilers.

Interestingly, combustion of comminuted *Phalaris arundinacea* straw instead of pellets in boiler 1 resulted in lower CO emissions. As this did not alter chemical composition of fuels, differences were most likely due to changes in fuel particle size distributions resulting in e. g. differences in the fuel bed structure.

One fuel parameter often affecting CO emission during solid biofuel combustion is *M* in fuels [13,70]. Thereby, high *M* might lead to cooling of the combustion chamber resulting in incomplete combustion. During this study, no trend was detected between *M* and CO emission ($R^2 = 0.02$ for boiler 1 and 0.10 for boiler 2, only pellet fuels). This was expected due to the overall low range in *M* among pellets (see section 3.2).

Results on organic gaseous carbon (OGC) emissions followed the same trend as for CO emissions (Fig. 3). As expected for automatically fed boilers, OGC emissions were on a rather low level during this study, in general. Thereby, emissions were significantly increased for pure *Typha* ssp. compared to all other fuels in boiler 1 and for all pure and additivated paludiculture fuels compared to wood pellets in boiler 2 ($p \leq 0.05$).

Like CO, high OGC emissions result from incomplete combustion of

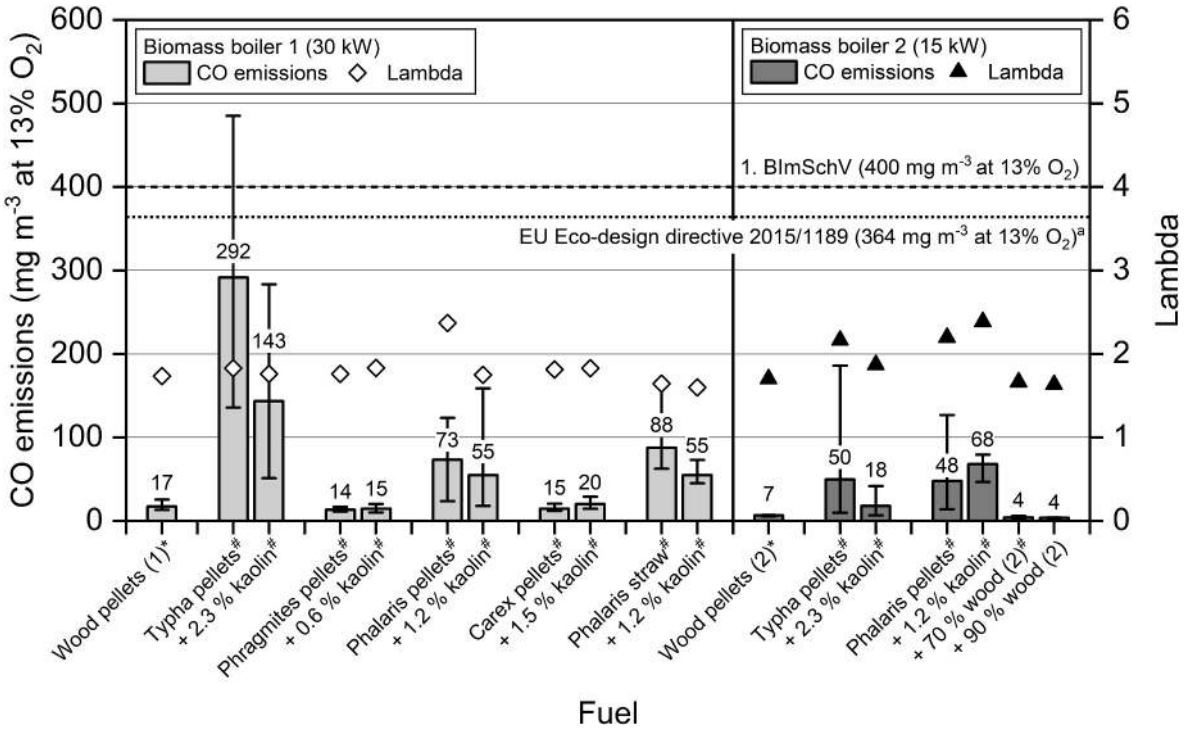


Fig. 2. Mean CO emissions during combustion of wood and paludiculture fuels in two biomass boilers ($n = 5$; whiskers indicate minimal and maximal values; * = boiler licensed for this fuel; # = no steady state boiler operation possible with this fuel; [a] = eco-design threshold relates to 15% nominal load and 85% part load).

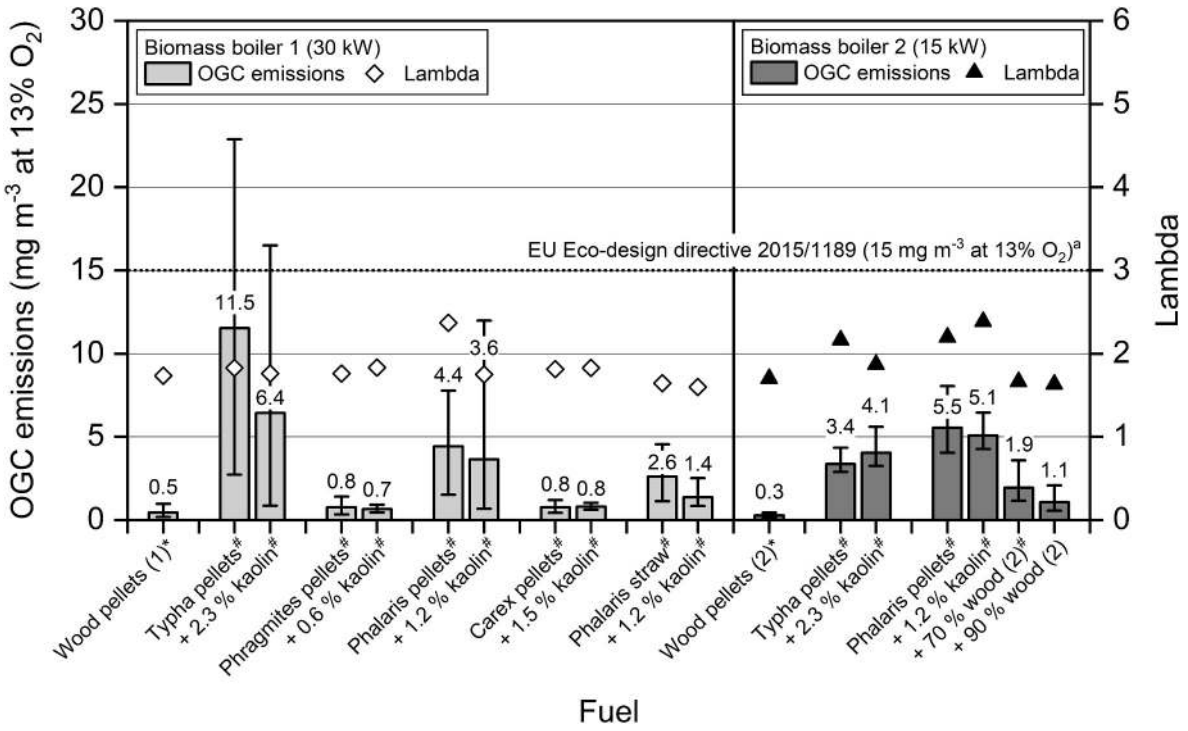


Fig. 3. Mean OGC emissions during combustion of wood and paludiculture fuels in two biomass boilers ($n = 5$; whiskers indicate minimal and maximal values; * = boiler licensed for this fuel; # = no steady state boiler operation possible with this fuel; a = eco-design threshold relates to 15% nominal load and 85% part load).

solid biofuels [13]. Thus, as observed for CO, both additivation and blending resulted in lower OGC emissions in many cases. In case of blending of *Phalaris arundinacea* with wood, this effect was statistically significant ($p \leq 0.05$). No limit for OGC emissions is given by the first ordinance of the German emission control act (1. BImSchV), but mean OGC values were constantly below the emission threshold of the European eco-design directive (15 mg m^{-3} at 13% O_2, EU directive 2015/1189). However, a direct comparison with this threshold is not possible as the eco-design directive relates emissions to a mixture of nominal load (15%) and part load operation (85%) whereas during this study, only nominal load operation trials were performed.

NO_X emissions of pure and additivated paludiculture pellets were

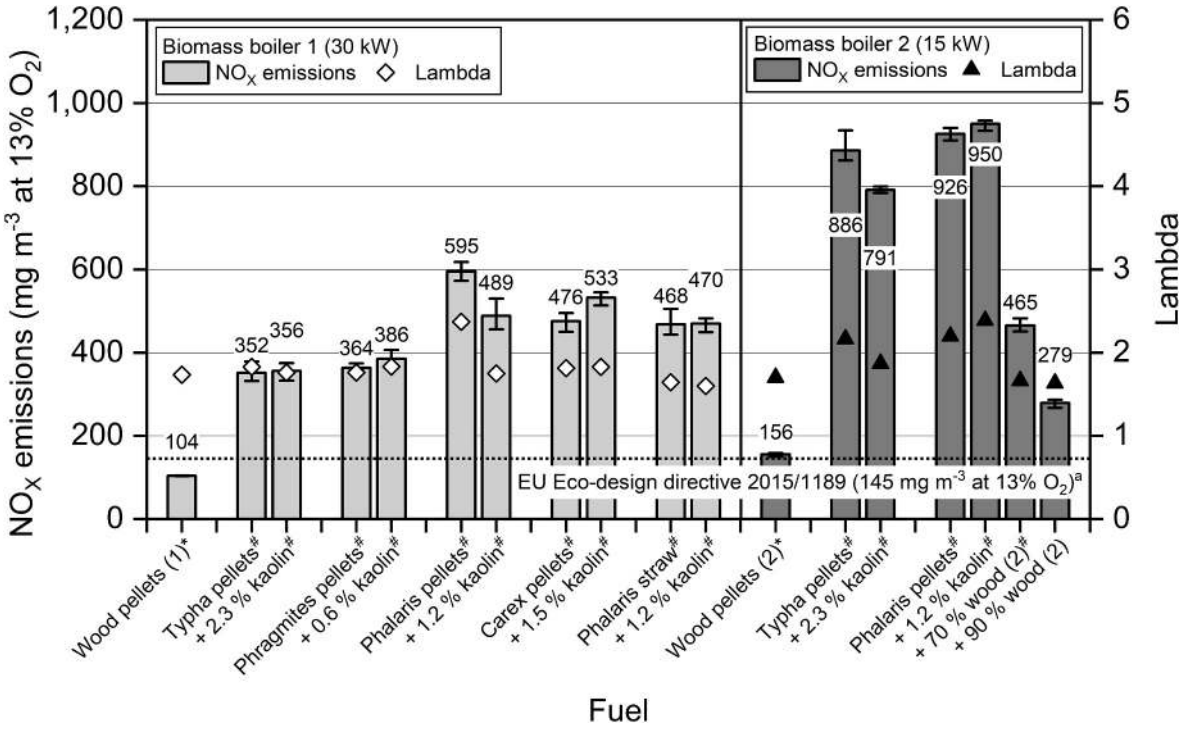


Fig. 4. Mean NO_X emissions during combustion of wood and paludiculture fuels in two biomass boilers ($n = 5$; whiskers indicate minimal and maximal values; * = boiler licensed for this fuel; # = no steady state boiler operation possible with this fuel; a = eco-design threshold relates to 15% nominal load and 85% part load).

always significantly higher ($p \leq 0.05$) compared to the combustion of wood pellets (i. e. 104 mg m^{-3} and 156 mg m^{-3} in boiler 1 and 2), ranging from 352 mg m^{-3} to 595 mg m^{-3} for boiler 1 and from 791 to 950 mg m^{-3} for boiler 2, respectively (Fig. 4). No limit for NO_X emissions is given by the first ordinance of the German emission control act (1. BImSchV). However, all values exceeded the NO_X emission threshold of the European eco-design directive of 145 mg m^{-3} (converted to 13% O_2). Like OGC, the NO_X emission threshold of the eco-design directive relates to a mixture of both nominal and part load operation and thus, results cannot be compared to this value, directly.

As expected from former studies on solid biofuel combustion [31,51,61,71–74], NO_X emissions increased almost linearly with N content in fuels (boiler 1: $R^2 = 0.77$; boiler 2: $R^2 = 0.97$). N content is usually considered a good indicator for NO_X [30–32]. Additivation with kaolin or the combustion of comminuted straw instead of pellets (only boiler 1) had no clear effect on NO_X emissions as it did not alter N content in the fuels. In contrast, mixing of *Phalaris arundinacea* with wood pellets resulted in a significant decrease of NO_X due to decreasing N ($p \leq 0.05$), as it was already observed in previous studies [21,51].

Overall, NO_X emissions during combustion of paludicultures were on a high level. Thus, in addition to fuel design, technical solutions to decrease NO_X emissions during combustion of paludiculture biomass might be recommended, e. g. flue gas recirculation in the combustion chamber, air staging, selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) [75]. While flue gas recirculation and air staging might be applied in small-scale boilers [69,76,77], both SCR and SNCR are usually only available and economical feasible for larger biomass plants [13,75]. However, first studies already focussed on applicability of SCR for small-scale application [78].

Both HCl and SO_X emissions were significantly increased when paludiculture biomass was combusted instead of wood pellets in both boilers ($p \leq 0.05$, data not shown). For paludiculture pellets (pure, additivated and blended variants) HCl emissions ranged from 68 to 174 mg m^{-3} for boiler 1 and from 9 to 122 mg m^{-3} for boiler 2. HCl emissions of the respective reference wood pellets were much lower with 2 mg m^{-3} for boiler 1 and < 1 mg m^{-3} for boiler 2. Thereby, HCl correlated well with Cl content in fuels (R^2 of linear regression = 0.85 for boiler 1 and 0.78 for boiler 2, only pellet fuels). In contrast to previous studies [21,38], additivation with kaolin had almost no negative effect on HCl, probably due to the overall low additivation level. Only for *Typha* ssp., additivation led to a significant ($p \leq 0.05$) increase of HCl from 119 to 174 mg m^{-3} in boiler 1 and from 63 to 122 mg m^{-3} in boiler 2. This effect is most likely due to the equations presented in section 1 [33] whereby KCl reacts with kaolinite during combustion, resulting in the emission of Cl as HCl instead of as a mineral aerosol. As expected from previous studies [21,51], blending of *Phalaris arundinacea* led to a significant decrease in HCl ($p \leq 0.05$) due to overall lower Cl contents in fuels as a result from mixing of the paludiculture biomass with wood pellets.

SO_X emissions of paludiculture fuels (pure, additivated, blended) ranged from 146 to 243 mg m^{-3} for boiler 1 and from 27 to 236 mg m^{-3} for boiler 2, respectively. For the reference wood pellets, SO_X emissions were always significantly lower compared to paludiculture fuels ($p \leq 0.05$) with 2 mg m^{-3} (boiler 1) and 3 mg m^{-3} (boiler 2). In both furnaces, SO_X increased linearly with S content in fuels ($R^2 = 0.85$ for boiler 1 and 0.99 for boiler 2, only pellet fuels) as it was also reported in previous studies [51]. However, in contrast to recent literature [21,38], no negative effect of kaolin additivation of fuels on SO_X emissions could be observed during this study whereas blending of *Phalaris arundinacea* pellets with wood resulted in a clear decrease in S content of fuels and therefore in a significant ($p \leq 0.05$) decrease in SO_X from 236 mg m^{-3} (pure *Phalaris*) to values of 70 mg m^{-3} (mixing ratio 30:70) and 27 mg m^{-3} (mixing ratio 10:90). Thus, the same effects as for HCl apply for SO_X.

TPM emissions during combustion of pellets ranged from 12 to 115 mg m^{-3} for boiler 1 and from 8 to 91 mg m^{-3} for boiler 2 (Fig. 5). Thereby, TPM emissions of pure paludiculture pellets were below the emission threshold of 1. BImSchV of 20 mg m^{-3} (i. e. for combustion of both wood or agricultural fuels at 13% O_2) for *Phragmites australis* and for *Phalaris arundinacea* in both boilers, while both *Carex* ssp. and *Typha* ssp. were above this threshold with 31 mg m^{-3} (*Carex* ssp.) and 115 mg m^{-3} (*Typha* ssp.) in boiler 1 and with 91 mg m^{-3} in boiler 2 (only *Typha*

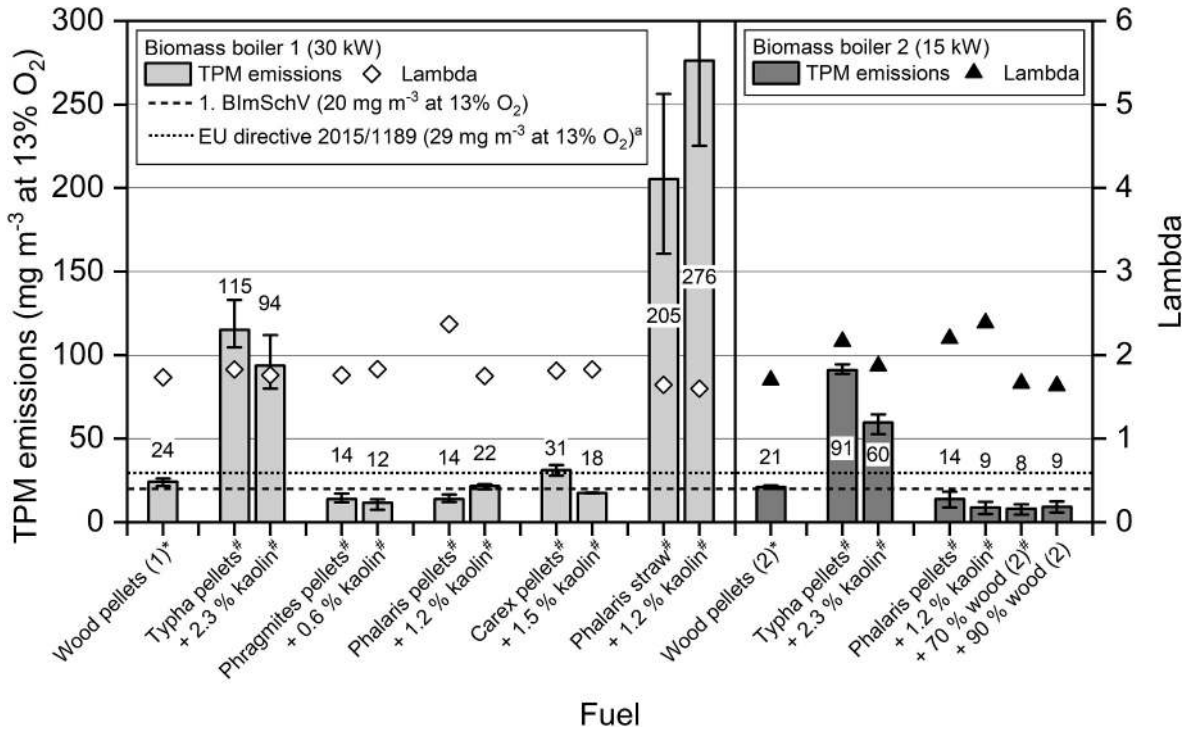


Fig. 5. Mean TPM emissions during combustion of wood and paludiculture fuels in two biomass boilers ($n = 5$; whiskers indicate minimal and maximal values; * = boiler licensed for this fuel; # = no steady state boiler operation possible with this fuel; a = eco-design threshold relates to 15% nominal load and 85% part load).

ssp.), respectively. TPM emissions of *Typha* ssp. pellets were significantly increased compared to wood pellets in both boilers ($p \leq 0.05$).

High TPM emissions may result from the formation of mineral aerosols but also from incomplete combustion [13,32,34]. As expected by the sum of aerosol forming elements in fuels, highest TPM emissions of pure pellets were measured for *Typha* ssp. followed by *Carex* ssp. While for *Phragmites australis* and *Phalaris arundinacea*, the lowest emissions could be detected (see Table 8). However, in contrast to previous studies [48,51,70], no good correlation was found between the sum of aerosol forming elements in the here investigated pellet fuels (pure, additivated and blended) and TPM emissions ($R^2 = 0.34$ for boiler 1 and 0.30 for boiler 2) excluding the combustion tests using *Phalaris arundinacea* straw.

Both the molar Si/K ratio and the molar Cl/Si ratio indicated a good fixation of K into the ash for *Carex* ssp., *Phragmites australis* and *Phalaris arundinacea* probably resulting in the much lower TPM emissions compared to *Typha* ssp. pellets. In addition, additivation of pellets with kaolin decreased TPM emissions for *Typha* ssp. and *Carex* ssp. in both boilers. For *Typha* ssp. pellets in boiler 2, this effect was statistically significant ($p \leq 0.05$). Still, the absolute decrease in TPM emissions of *Typha* ssp. due to additivation must be considered as small and TPM emissions were still above the threshold of 1. BImSchV with 94 mg m^{-3} (boiler 1) and 60 mg m^{-3} (boiler 2) for the additivated pellets. One possible explanation might be a cooccurring effect from aerosol formation and incomplete combustion such as soot formation on TPM emissions as it was also indicated by the higher emission values for CO and OGC of *Typha* ssp. fuels (Figs. 2 and 3).

Blending of *Phalaris arundinacea* with wood pellets resulted in no clear changes in TPM emissions due to the already significantly lower emission level ($p \leq 0.05$) of the pure *Phalaris arundinacea* compared to wood pellets. Still, as demonstrated by several studies [21,40,51], blending of agricultural fuels with wood might be a suitable measure to decrease TPM emissions due to a decrease in aerosol forming elements and might therefore be especially interesting for *Typha* ssp. fuels. Another approach as proposed by Höfer et al. [49] might be to combine fuel blending and additivation by selecting suitable additives in respect to different blending ratios of agricultural fuels and woody biomass, individually.

Interestingly, highest TPM emissions were measured for comminuted straw of *Phalaris arundinacea* in boiler 1. These values also significantly exceeding TPM emissions of the respective pellet fuels ($p \leq 0.05$). Fournel et al. [18] reported a decrease in CO and TPM emissions when pelletized agricultural crops were combusted compared to the respective chopped fuels. However, in the here presented study, due to the low CO and OGC emissions of the *Phalaris arundinacea* straw fuel (see Figs. 2 and 3) and the overall very low TPM emissions of the respective pellet fuels, this difference might not be attributed to either aerosol or soot formation but to entrainment of very small particles (e. g. comminuted biomass, kaolin) with the flue gas. Similar effects were observed for the same boiler during combustion of wood chips that were artificially contaminated with mineral soil using the same setup with a separate dosing screw [53]. During the cited study, chemical analyses of the filters used for gravimetric TPM measurements indicated that small soil particles were transported with the exhaust gas through the chimney. Thus, the here observed very high TPM emissions >200 mg m^{-3} might not be attributed to the paludiculture biomass but could depend on the experimental setup of the combustion trials.

Although somewhat promising in terms of rather low emission values, combustion of paludiculture biomass in both boilers must be considered challenging. Compared to the combustion of certified EN*plus* A1 wood pellets, no definite steady-state operation could be achieved with either boiler 1 or boiler 2 with any of the tested pure or additivated paludiculture fuels. Consequently, the heat output of both boilers was highly fluctuating (Fig. 6). At the same time, O_2 concentrations in the flue gas varied strongly during combustion (data not shown). This was especially pronounced for boiler 2 resulting in a continuously and constant drop of the heat output directly after nominal load was achieved. Similar effects were observed during combustion of agricultural fuels by Carvalho et al. [16] or by Kuchler et al. [56,58] using contaminated wood pellets. This high fluctuation was a direct result of the overall high

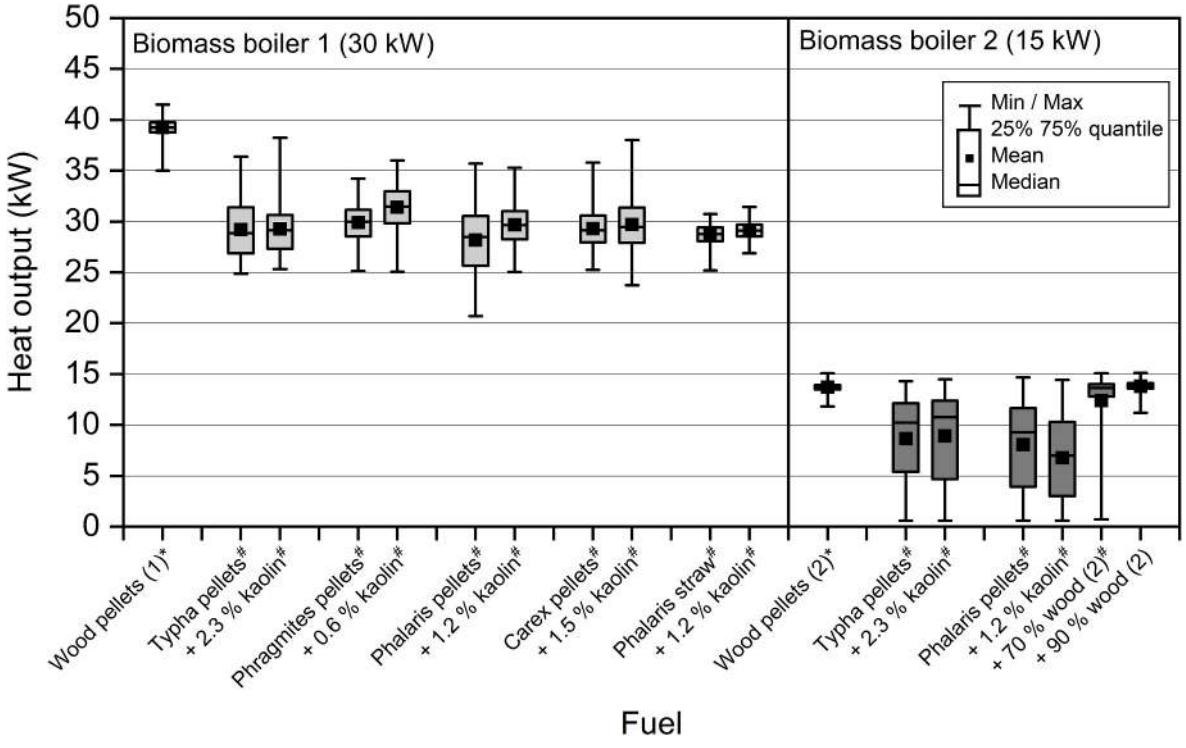


Fig. 6. Mean heat output during combustion of wood and paludiculture fuels in two biomass boilers (* = boiler licensed for this fuel; # = no steady state boiler operation possible with this fuel).

ash contents in the paludiculture fuels and, in case of *Phragmites australis*, *Phalaris arundinacea* und *Carex* ssp., of sever slag formation (see section 3.4). The same effect was observed during combustion of wheat straw pellets in boiler 1 resulting in a boiler shutdown during the respective combustion trial [21]. Consequently, results indicate that both boilers cannot be operated with paludiculture biomass efficiently and that boiler malfunction and even boiler shutdown must be expected during long-term operation. A frequent deashing of the boiler would be necessary.

Neither boiler 1 nor boiler 2 are constructed for the combustion of paludiculture biomass and both furnaces are not licensed for burning agricultural fuels in Germany (as indicated by * in Figs. 2–6). Thus, the constriction and selection of a more suitable boiler with a dedicated combustion technique specifically designed for paludiculture biomass might be required for failure-free and low-emission combustion of the here tested pellet fuels for small-scale application [79].

3.4. Slagging tendencies

Ash melting temperatures of pellets were measured according to ISO 21404 (Fig. 7). Thereby, deformation temperature (DT) is the parameter most widely used to characterize ash melting behaviour of solid biofuels. During this study, DT varied between 1170 °C and 1300 °C for paludiculture pellets and was therefore below DT of the reference wood pellets (1350 °C, only wood (1) was analyzed) and above the value for wheat straw (850 °C). Thus, according to these results, less slagging should be expected when paludiculture pellets were combusted compared to wheat straw. No general trends between the different paludiculture species or between pure and additivated pellets could be detected.

According to ISO 17225–6, DT is not limited by a threshold value but should be stated in the fuel declaration. In contrast, according to the EN*plus* certification for wood pellets, DT should be above 1200 °C for fuel quality A1 as temperatures above 1000 °C often occur in small-scale boilers [13]. If DT is lower than 1200 °C, slagging related problems might occur during combustion. Consequently, following the results from DT analysis according to ISO 21404, slag formation should not be an issue during paludiculture combustion.

In addition to DT, the molar (Si + P + K)/(Ca + Mg + Al) ratio might be used to predict slagging behaviour in solid biofuels [13,48]. As observed in previous studies [58], DT did not correlate with the molar (Si + P + K)/(Ca + Mg + Al) ratio here ($R^2 = 0.03$). Feldmeier et al. [66] and Vassilev et al. [80] highlighted that a high share of different fuel indices to predict slagging behaviour during biomass combustion were proposed by several studies. Applicability of these indices differs depending on whether fuels are rich in Ca, Si or P [66]. The here investigated paludiculture species differed largely in their chemical composition and might be divided into Ca-rich (*Typha* ssp.) and Si-rich fuels (*Phragmites australis, Phalaris arundinacea* and *Carex* ssp.). For Si-rich fuels, the selected index should work well [66] while for Ca-rich fuels such as *Typha* ssp., other indices such as the $(Fe_2O_3)/(K_2O + Na_2O)$ ratio or the Si/K ratio (used as a slagging index) might lead to better results. Alternatively, an updated version of the slag index as propose by Zeng et al. [67] could be applied. Still, the index calculated here indicated the highest slagging risk for *Phragmites australis* as well as for the reference fuel wheat straw.

A direct method to determine slag formation of woody and agricultural fuels is the so called PASSA method ("Pellet ash slagging and sieving assessment") that was developed in the EU project AshMelT [54]. Advantage of the PASSA method compared to ISO 21404 is that ash melting behaviour is evaluated during combustion of fuels directly on pellets themself without any further pretreatment instead of applying high temperatures to an already existing ash sample. From the results of the PASSA method, "slag indices", i. e. the share of particles >2 mm or >1 mm, can be assessed. For the paludiculture pellets, the slag index >2 mm was lowest for *Typha* ssp. (pure pellets: 0.10; additivated pellets: 0.22) and strongly increased for the other three species to values ranging from 0.33 for pure *Phalaris arundinacea* to 0.66 for additivated *Phragmites australis* (see also Fig. 9, below). Thereby, additivation of fuels always increased the slag index if PASSA is applied. No good correlations were found between the slag index by the PASSA method with either DT ($R^2 = 0.20$) or the molar (Si + P + K)/(Ca + Mg + Al) ratio ($R^2 = 0.30$). Still, like the calculated fuel index, the PASSA method indicated the highest slagging risk for *Phragmites australis*. No PASSA analyses were performed with straw fuels or with the blended biomasses.

Table 9 summarizes a granulometric analysis of the boiler ashes that were collected after the combustion trials. The total amount of ash during combustion of wood pellets was 23.9 g h^{-1} and 13.9 g h^{-1} in boiler 1 and 2, respectively, while combustion of paludiculture pellets strongly increased the total amount of ash to values for boiler 1 from 281.5 g h^{-1} (pure *Phalaris arundinacea*) to 418.2 g h^{-1} (additivated *Typha* ssp.) and for boiler 2 from 111.4 g h^{-1} (additivated *Phalaris*

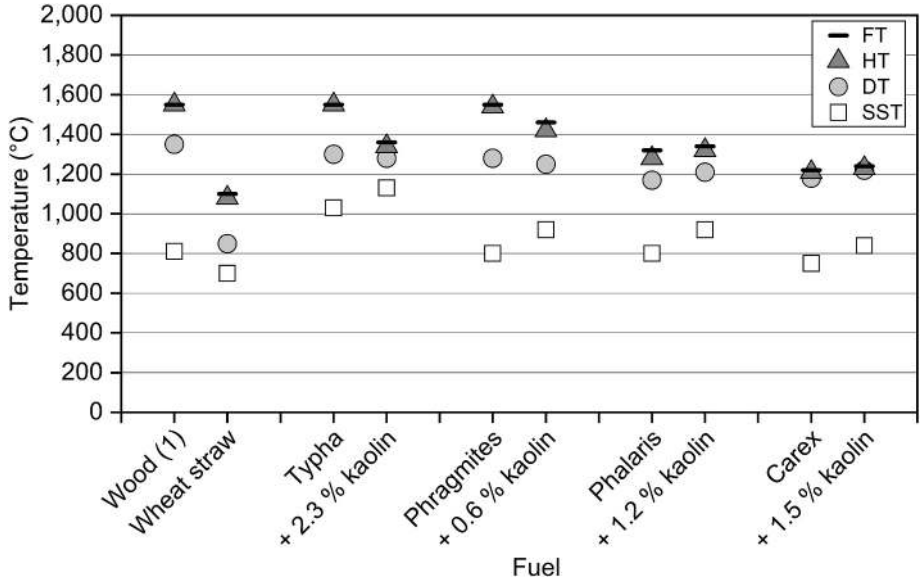


Fig. 7. Ash melting temperatures for the test fuels according to ISO 21404 (SST = shrinking starting temperature; DT = deformation temperature; HT = hemisphere temperature; FT = flow temperature).

Table 9
Fuel consumption and ash production per h boiler operation during combustion trials with paludiculture and reference fuels in two biomass boilers and ash particle size distribution of ashes after combustion ($n = 1$, ar = as received, d = dry basis).

Boiler	Fuel	Variant	Fuel	Ash	Particle size distribution of ash			
					<0.5 mm	0.5–1.0 mm	1.0–2.0 mm	>2.0 mm
			kg h^{-1} (d)	g h^{-1} (ar)	%	%	%	%
1	Wood (1)	Pellets	10.2	23.9	4.2	12.7	50.3	32.8
	Wheat straw	Pellets	7.2	294.1	0.4	1.9	7.6	90.2
	Typha ssp.	Pellets	7.1	372.3	33.1	9.3	10.0	47.6
		Pellets +2.3% kaolin	7.7	418.2	22.3	9.5	9.2	59.0
	Phragmites australis	Pellets	7.1	325.8	16.9	6.6	3.8	72.7
		Pellets +0.6% kaolin	6.5	348.8	5.8	1.6	1.3	91.2
	Phalaris arundinacea	Pellets	6.7	281.5	22.1	6.6	7.7	63.7
		Pellets +1.2% kaolin	7.7	336.4	17.6	4.0	3.5	74.9
	Carex ssp.	Pellets	6.6	380.0	16.6	6.2	7.7	69.5
		Pellets +1.5% kaolin	8.3	386.2	11.3	4.0	3.6	81.0
	Phalaris arundinacea	Straw	5.8	299.2	47.1	19.2	16.7	17.0
		Straw +1.2% kaolin	6.9	343.5	60.8	19.9	11.0	8.3
2	Wood (2)	Pellets	2.5	13.9	89.9	5.7	2.4	2.0
	Typha ssp.	Pellets	1.8	120.8	37.1	13.6	14.4	34.9
		Pellets +2.3% kaolin	2.0	129.2	26.8	11.8	15.0	46.3
	Phalaris arundinacea	Pellets	1.8	124.8	24.2	9.1	13.0	53.7
		Pellets +1.2% kaolin	1.6	111.4	24.4	8.1	10.6	56.9
		Pellets +70% wood (2)	2.4	53.3	16.4	7.3	11.1	65.2
		Pellets + 90% wood (2)	2.8	23.1	17.8	7.4	11.5	63.3

arundinacea) to 129.2 g h^{-1} (additivated *Typha* ssp.). As expected from previous studies, additivation of biomass with kaolin increased the total amount of ash due to the high ash contents of the additive in most cases while blending of *Phalaris arundinacea* with wood pellets decreased the values [21,51].

The analysis of the different ash fractions indicates that all paludiculture ashes but also the ashes from the incomplete combustion trial with wheat straw had high shares of particles >2 mm. Thereby, no clear differences could be detected between *Phragmites australis*, *Phalaris arundinacea* and *Carex* ssp. while values for *Typha* ssp. were on a generally lower level compared to the other species. Interestingly, the overall lowest share of particle >2 mm was measured when comminuted straw of *Phalaris arundinacea* was combusted instead of pellets indicating that particle form also influences slag formation.

Additivation of fuels with kaolin resulted in an increase in particles >2 mm in all cases as it was observed e. g. for pellets from grass or sunflower husk by Mack et al. [21]. Thus, results indicate that kaolin might not be the optimal choice as an additive to improve slag formation of paludiculture fuels and that other additives such a MgO, CaO, $CaCO_3$ or calcite might be more suitable [40,47,81,82].

Blending of paludiculture fuels with wood pellets had no effect on the share of ash particles >2 mm. However, blending strongly decreased the total amount of ash. Thus, although slag formation might still occur during combustion of blended fuels, the boiler benefited from the overall lower amount of ash. During the here presented trials, steady-state boiler operation was possible with the highest mixing ratio of wood pellets (90%) to *Phalaris arundinacea* (10%) in boiler 2 (see section 3.2), clearly indicating improved combustion conditions. Similar, Zeng et al. [50] indicated that a high blending ratio might be necessary to improve combustion behaviour of agricultural fuels.

For ashes from boiler 2, the two largest ash particles per sample were analyzed regarding their length, width and height separately using a calliper. Although this measurement gives only a rough estimate of the volume of the largest ash particles, clear trends can be identified. Thereby, mean volume of the two largest ash particles of *Typha* ssp. was <1 cm^3 (pure) and 1.7 cm^3 (additivated) while mean volume of particles from pure, additivated and blended *Phalaris arundinacea* ashes ranged between 28 and 46 cm^3. This indicates that although both fuels produced large quantities of ash particles with a diameter >2 mm, the much larger ash particle shape of *Phalaris arundinacea* should be more likely to lead to boiler malfunction compared to *Typha* ssp. fuels. Furthermore, an optical assessment of boiler ashes from boiler 1 and 2 indicated that biomass pellets from *Typha* ssp. kept their cylindrical shape during combustion. This was probably due to increased sintering instead of slag formation due to highly different ash chemistry of the applied biofuels [80,83] as it was e. g. observed for carbonate rich agricultural fuels [21] whereas the other three species that were low in *TIC* and Ca but high in Si produced rather large slag particles (Fig. 8). Similar, Ca-rich additives such as CaO, $CaCO_3$ or calcite were reported to supress slag formation in previous studies [35,47,81,82,84].

A direct comparison between the granulometric ash analysis of the real boiler ashes with the PASSA method revealed that although the slag index analyzed with PASSA was on a generally lower level compared to a respective slag indices of the boiler ashes (i. e. the share of particles >2 mm), the PASSA method seems highly suitable to detect general trends in ash sintering and slag formation during combustion of the investigated paludiculture fuels (Fig. 9). Thereby, the slag index determined with the PASSA method correlated well with the slag indices from both boilers ($R^2 = 0.91$ for boiler 1 and 0.78 for boiler 2, respectively) also including the additivated fuels. Consequently, for agricultural, ash rich fuels such as paludiculture species, the PASSA method can be recommended to predict slagging risks expected during combustion.

Overall, results indicate that combustion of paludiculture fuels can be associated with a high risk of sintering and slag formation. Technical solutions might help to decrease slagging related problems such as an automatic cleaning of the grate after and during each combustion process or a grate design that actively destroys the slag particles. Alternatively, grate cooling or flue gas recirculation might be applied. However, the three paludiculture fuels *Phragmites australis, Phalaris arundinacea* and *Carex* ssp. must be considered very critical for the use in small-scale biomass boilers. The use of these fuels will probably lead to frequent boiler shutdown after short operation, to high labour demand for maintenance and cleaning, and to damages of the grate and the screw conveyors for ash transport.

The here presented results on fuel quality and the combustion behaviour of the tested four paludiculture species (*Typha* ssp., *Phragmites australis*, *Phalaris arundinacea*, *Cares* ssp.) are in line with findings from previous studies focusing on pellets and straw fuels from other herbaceous species [19–21,24–26,34,36,37,40–42,45,47,49–51,67,84]. Similar effects on emission behaviour and slag formation were observed when different types of biomasses (e. g. herbaceous species that are high or low in Ca) or when upgraded fuels (additivation with kaolin, fuel



Fig. 8. Sintered ash particles after combustion of *Typha* ssp. in boiler 2 (left) and slag particle after combustion of *Phalaris arundinacea*, also from boiler 2 (right).

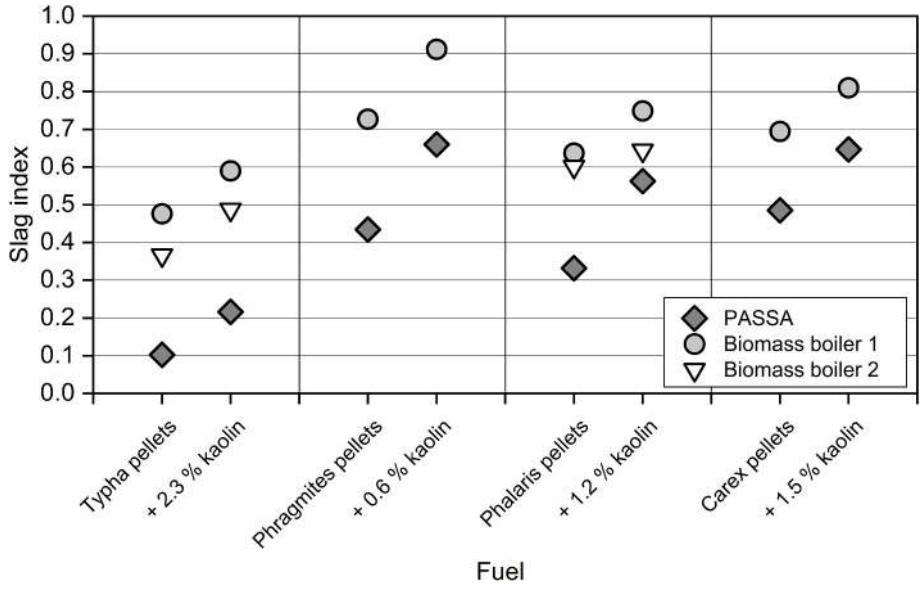


Fig. 9. Comparison of slag indices for ash particles >2 mm measured by the PASSA method and from granulometric particle size distribution of boiler ashes from biomass boilers 1 and boiler 2, $n = 1$.

blending) were combusted in small-scale boilers. Thus, this study contributes to the general understanding of the combustion of challenging agricultural biomasses and the findings are not limited to the four species investigated.

4. Conclusion

The utilization of paludiculture biomass for combustion might be an innovative option but their use as a fuel is strongly limited. This is especially true during combustion of the fuels in small-scale biomass boilers. Moreover, results showed large differences in the combustion behaviour of *Typha* ssp, *Phragmites australis*, *Phalaris arundinacea* and *Carex* ssp. compared to certified EN*plus* A1 wood pellets leading to the following conclusions:

- Fuel quality of paludiculture biomass often meets the specifications of ISO 17225–6 if pellets are produced from uncontaminated straw fuels. Thus, in theory, fuels should be suitable for combustion in boilers that are especially designed and certified for agricultural biomass.
- During this study, no steady state conditions were possible, especially for boiler 2, for the combustion of pure or additivated paludicultures due to high ash contents and slag formation. Thus, paludiculture fuels must be considered unsuitable for this boiler size class and should only be applied in less demanding, medium to large heat (and power) plants.
- NO_X emissions were significantly increased for all four paludiculture biomasses compared to the use of certified wood pellets. Suitable measures must be applied to either decrease N content in fuels (e. g. by fuel blending) or to decrease NO_X emissions by technical solutions (e. g. flue gas recirculation, air staging, SCR, SNCR [69,73,75–78]). This also applies if paludiculture fuels shall be combusted in larger heat plants following the European MCP directive or the German 44. BImSchV.
- Combustion of *Typha* ssp. led to high CO and TPM emissions. Although additivation of fuels with kaolin reduced CO and TPM of *Typha* ssp., this effect was not very strong as incomplete combustion occurred simultaneously. Technical solutions such as an advanced boiler design [76,77,79,85] or the use of electrostatic precipitators [19,86], etc., might be necessary for low emission combustion of this biofuel.
- *Phragmites australis*, *Phalaris arundinacea* and *Carex* ssp. pellets led to severe slag formation. This might be especially challenging for small-scale boilers but also applies for larger facilities. Selection of suitable

additives to improve slagging behaviour directly such as $CaCO_3$, calcite or MgO, or other measures such as fuel blending and technical solutions might be required.

Overall, results from this study indicate that paludiculture biomass is challenging for combustion in small-scale boilers and that other uses might be preferred for the feedstocks such as using them as raw materials e. g. for fiber board production. If paludiculture biomass should be combusted, it might be more suitable for medium sized, decentralized heat (and power) plants. Currently, the combustion of agricultural, ash-rich fuels such as paludiculture biomass in boilers <100 kW is limited in Germany as hardly any boiler is certified for these fuels according to German legislation. Consequently, paludicultures are mostly restricted to boilers >100 kW. For this size class, individual permits (4. BImSchV, 44. BImSchV) are required. Thereby, technical solutions to improve combustion behaviour might be more easily implemented in larger facilities.

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