COMBUSTION BEHAVIOUR AND SLAGGING TENDENCIES OF KAOLIN ADDITIVATED PELLETS FROM FEN PALUDICULTURES IN A SMALL-SCALE BIOMASS BOILER

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ABSTRACT: Fuel quality and combustion behaviour of agricultural pellets from paludiculture straw were tested within the research project “MOORuse”. Pellets were produced from *Typha ssp*., *Phragmites australis*, *Phalaris arundinacea* and *Carex ssp*..Additivation of pellets with kaolin was applied to reduce particle emissions and slagging. Physical fuel properties of pellets met the requirements of ISO 17225-6. Chemical fuel properties(e.g.K and Na content) indicated high TPM emissions for *Typha ssp*. Distinct slagging for the other species were predicted (e.g. by Si/K-index). During combustion in a small-scale biomass boiler (30 kW), CO and TPM emissions were high for *Typha ssp*. (CO: 292 mg/m^3, TPM: 115 mg/m^3, STC) but were reduced by additivation with 2.3 w-% kaolin (CO: 143 mg/m^3, TPM: 94 mg/m^3, STC). Slagging was high for *Phragmites australis, Phalaris arundinacea* and *Carex ssp*. with >40 w-% of total ash consisting of particles >8 mm. Additivation had no positive effect on slagging. In conclusion, paludiculture pellets are challenging fuels that require sufficient fuel upgrading, e. g. by additivation or fuel blending, and a suitable boiler technique that fulfils the legal requirements for the combustion of agricultural fuels in Germany. These requirements are easier met by medium sized combustions plants >100 kW.
Keywords: agricultural pellets, kaolin additivation, combustion, emissions, slagging

1 INTRODUCTION

The research project “MOORuse” aims at developing innovative and sustainable utilization strategies for fen peat lands. 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 in regional value chains. Thereby, one suitable utilization strategy might be the use of the harvested material for heat production in decentralized, small to medium sized boilers.

Paludiculture species such as *Typha ssp*., *Phragmites australis*, *Phalaris arundinacea* and *Carex ssp*. are classified as straw fuels within the fuel section “herbaceous biomass” according to ISO 17225-1 [1]. Straw fuels usually incorporate physical and chemical fuel properties that are considered unsuitable for the combustion in small to medium sized boilers (≤100 kW_{th} to 1 MW_{th}) [2, 3], e. g. a lowered net calorific value, a high ash content, low ash melting temperatures and high shares of chemical elements that are deemed critical for combustion, such as nitrogen (N), potassium (K), chloride (Cl) or sulphur (S).High N in fuels can lead to elevated NO_X emissions. High amounts of aerosol forming elements such as K and Na may increase total particle matter (TPM) emissions by forming mineral aerosols.High shares of Cl may lead to high temperature corrosion [2].Consequently, paludiculture biomass might be challenging for failure-free and low emission combustion compared to conventional fuels such as wood pellets.

Aim of this study was to test fuel quality and combustion behaviour of biomass pellets from the four above mentioned fen paludiculture species. To improve combustion behaviour in a small-scale boiler, additivation of pellets with the clay mineral kaolin was applied.

2 MATERIALS & METHODS

2.1 Selected fuels

Four biomass fuels from the MOORuse test area “Freisinger Moos” (48°22'43.6"N, 11°41'00.4"E), i. e. *Typha spp*., *Phragmites australis, Phalaris arundinacea* and *Carex spp*., were harvested in February 2018 (only for fuel analysis) and February 2019 (for fuel analysis and combustion tests). After each harvest, the biomass was transferred into containers (each 6 m^3) in which ambient air venting rapidly reduced the moisture content of the fresh material. After two weeks of drying, the biomass was chopped and stored for several weeksin a roofed open storage building (Figure 1).

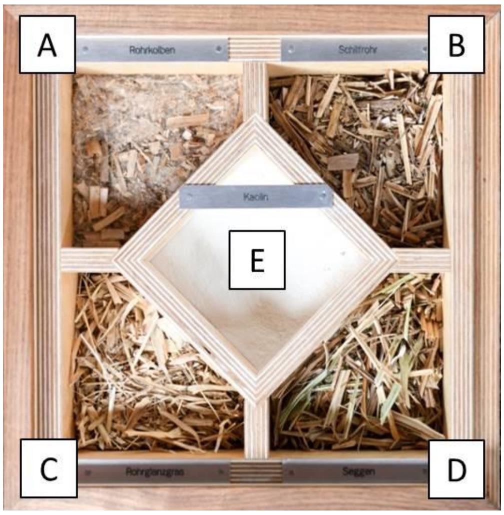

Figure 1: Chopped paludiculture biomass and additive (A = *Typhassp*., B = *Phragmites australis*, C = *Phalaris arundinacea*, D = *Carex ssp*., E = kaolin) (© Tobias Hase, StMELF)

All raw materials from the 2019 harvest were milled in an Amandus Kahl 33-390 pellet mill. Portions of each fuel were additivated using kaolin at levels that were calculated according to the guideline from the ERANET-Project "BIOFLEX!" [4]. This calculation is mainly based on the mass fraction of potassium (K) and sodium (Na) in the fuels, resulting in a kaolin additivation for the 2019 fuels of 2.3 w-% for *Typha ssp.*, 0.6 w-% for *Phragmites australis*,1.2 w-% for *Phalaris arundinacea* and 1.5 w-% for *Carex ssp.*, respectively. Mixing of the milled straw with the additiveand adjustment of the fuel moisture content for pelletization was done manually in a mixer (Stockmann Landtechnik GmbH, type 500 ESK,Fig. 2).

Figure2: Manual additivation of milled straw fuels with kaolin in an extract mixer (© Tobias Hase, StMELF)

Fuels were pelletized to a pellet diameter of 6 mm (pure and with kaolin) (Fig. 3). Standard wood pellets (EN*plus* A1) from the German pellet market and wheat straw pellets from the ERANET-project "BIOFLEX!" [3] were used as reference material.

Figure 3: Pellets of *Carex ssp*. additivated with 1.5 w-% of kaolin (© Tobias Hase, StMELF)

Pellets and unpelletized straw were analysed for their physical and chemical fuel properties according to international standards for solid biofuels, i. e. for moisture content, ash content, net calorific value, mechanical durability, bulk density, concentration of chemical elements, and ash melting behaviour (Table I).Fuel quality was classified according to the specifications of ISO 17225-6 for non-woody pellets.

Table I: Analysis methods for fuel properties of solid biofuels (a.r. = as received, d.b. = dry basis)

Fuel quality parameter	Unit	ISO-standard
Moisture content	w-%	18134-2
Ash content	w-% d.b.	18122
Net. calorific value	MJ/kg d.b.	18125
Bulk density	kg/m³ a.r.	17828
Durability	w-%	17831-1
CHN	w-% d.b.	16948
Cl, S	w-% d.b.	16994
Minor elements	mg/kg d.b.	16967
Heavy metals	mg/kg d.b.	16968
Ash melting temperatures	°C	21404

2.2 Stoichiometric calculation of the required kaolin amount following the BIOFLEX! guideline

According to the literature [2–4], aerosol forming elements are the alkali elements potassium (K) and sodium (Na), the trace elements zinc (Zn) and lead (Pb) as well as sulphur (S) and chloride (Cl). Usually, the most relevant element for aerosol formation in biomass fired conversion systems is potassium (K). 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 is a clay mineral and consists mainly of the mineral kaolinite ($Al_2(Si_2O_5)(OH)_4$). Alkali compounds like potassium can react according to equation 1 to 3 to high-melting crystalline products such as kalsilite ($KAlSiO_4$) as well as to leucite ($KAlSi_2O_6$) (equation 4 to 6) if kaolinite is present.

$$2\ KOH + Al_2Si_2O_5(OH)_4 \rightarrow 2\ KAlSiO_4 + 3\ H_2O \quad (1)$$

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

$$K_2SO_4 + Al_2Si_2O_5(OH)_4 \rightarrow 2\ KAlSiO_4 + SO_3 + 2\ H_2O \quad (3)$$

$$2\ KOH + Al_2Si_2O_5(OH)_4 + 2\ SiO_2 \rightarrow 2\ KAlSi_2O_6 + 3\ H_2O \quad (4)$$

$$K_2SO_4 + Al_2Si_2O_5(OH)_4 + 2\ SiO_2 \rightarrow 2\ KAlSi_2O_6 + SO_3 + 2\ H_2O \quad (5)$$

$$2\ KCl + Al_2Si_2O_5(OH)_4 + 2\ SiO_2 \rightarrow 2\ KAlSi_2O_6 + 2\ HCl + H_2O \quad (6)$$

Following equation 1 to 6 it is obvious that for the fixation of 2 mol potassium 1 mol of $Al_2Si_2O_5(OH)_4$ is needed. From this context, the amount of kaolinite required for the stoichiometric fixation of potassium can be calculated using the molar weights of the elements and the potassium content of the biomass (see section 2.1). Thereby, the kaolinite content of the kaolin (here: 78 %) must be considered as well.

2.3 Test stand and combustion trials

The boiler used for the combustion trials was a moving grate boiler (GUNTAMATIC Heiztechnik GmbH, Powerchip 20/30, constructed in 2010) with a lateral fuel insertion (fig.4, left). The ash is removed via the moving grate to a screw conveyor which transports the ashes into the ash box. 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. A square storage tank with a slanted floor and a screw conveyor was used for fuel feeding. 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.

Fig.4(right) shows a schematic drawing of the test stand and the arrangement of the measurement devices. The heat consumption was permanently regulated to a nominal load of 30 kW (± 8 %) following DIN 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 DX4000N) was used. The recording interval for the continuous measurement was set to 10 seconds. The total particulate matter (TPM) was isokinetically sampled following VDI 2066-1 applying a filtration temperature during sampling of 160 °C and the filter pre- and post-treatment temperature of 180 °C and 160 °C, respectively. The boiler was operated at a constant flue gas draught of -15±2 Pa as suggested by the boiler manufacturer. The diameter of the flue gas duct and the connection pipe was 150 mm. The flue gas velocity was continuously measured using a vane anemometer (Höntzsch GmbH, ZS25/25-ZG4) positioned in a narrowed stretch of the measurement section with a diameter of 100 mm (see Fig.4, right).

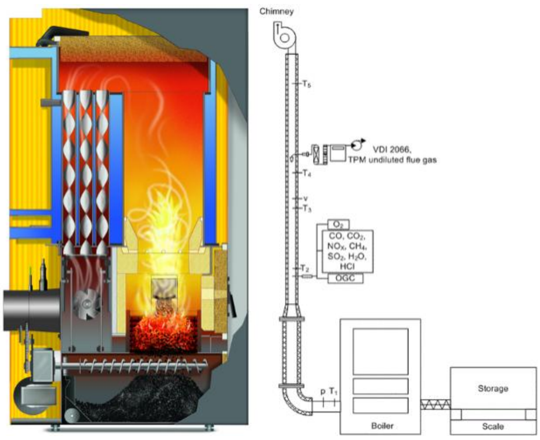

Figure4: Schematic drawing of the boiler (source: GUNTAMATIC, left) and a schematic drawing of the test stand (right)

For each combustion trial, the boiler was pre-heated to nominal load for approx. 2 h followed by a continuous 6 h nominal load operation. Emission measurements were distributed evenly throughout the 6 h operation.

2.4 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 as developed in the EU project "AshMelT" applying slight improvements. First, a 2D-sievingwas performed for 1 minute at 200 rounds per minute using a sieve with 8 mm round holes. The fraction >8 mm was weighted, and the mass was recorded. All ash particles smaller than 8 mm were sieved using a 3D-sieving machine while applying an amplitude of 0.5 for 5 minutes. The metal wire cloth sieves had opening widths of 0.5, 1.0 and 2.0 mm.

3 RESULTS & DISCUSSION

3.1 Fuel quality of straw and pellets

After drying and storage, the unpelletized straw of the four fen cultures had a moisture content of approx. 8.8 to 11.0 w-% (Table II).Moisture content of paludiculture straw that is harvested during winter mainly depends on the rainfall during this season and ranges from <15 w-% to 60 w-% [5]. Before transport to TFZ, all fuels were actively dried and stored in an open storage building for several weeks (see section 2.1) leading to sufficient pre-drying of the biomass. No further active or passive drying was required before pelletization or combustion. At low moisture contents<20 w-%, degradation of the biomass by bacteria and fungi during storage is strongly inhibited allowing for even longer storage periods of the dried material [2].

Bulk density of the straw fuels was 23.1 to 95.3 kg/m^3 (a.r. = as received) and therefore in a typical range for reed straw (<40 to 120 kg/m^3, a.r.) [6].Bulk density of fuels in 2018 was always higher compared to the respective material in 2019 (Table II), probably due to different harvesting techniques that were applied for chopping and retrieval of the biomass. Overall, bulk density was considered too low for direct use in small-scale boilers <100 kW due to a low energy density (MJ/m^3),and fuels would require some method of compaction such as pelletization or the use as bales.

In seven of eight cases, ash content for the pure fuels ranged from 3.9 w-% (d.b. = dry basis) to 6.0 w-% (d.b., see Table II),exhibiting a typical range for paludiculture biomass [5, 6]. Most straw fuels in this study complied with the ash requirements for fuel class A according to ISO 17225-6 (i. e. ≤6.0 w-% d.b.). The highest ash content was measured for *Phalaris arundinacea* straw from the harvest of 2019 (9.9 w-% d.b.)indicating some contamination of the biomass with either fibrous peat during harvesting from the field or with soil material during storage (see also chemical composition, below) [7, 8, 9]. At the same time, net calorific value of *Phalaris arundinacea* from 2019 was decreased to 16.88 MJ/kg d.b., also suggesting a high share of inorganic material in the biomass whereas the net calorific value of all other fuel samples was within the typical range for paludiculture species of 17.61 to 17.90 MJ/kg d.b. [5, 6].

The chemical composition of the straw fuels is given in Table II. Similar to ash content and net calorific value, results on chemical fuel properties of *Phalaris arundinacea* from the 2019 harvest indicate a contamination of the sample with soil material or fibrous peat as Si content increased from 11,000 mg/kg (d.b.) in 2018 to 19,000 mg/kg (d.b.) in 2019.Although grass species usually have high Si contents of 3,000 to 12,000 mg/kg [1], *Phalaris arundinacea* exceeded this range by the factor1.6. At the same time, Al content of *Phalaris arundinacea* 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 [10]. At the same time, both Si and Alcan be enriched in fibrous peat [9]. Consequently, results of the 2019 *Phalaris arundinacea* sample indicate that the material was indeed contaminated during processing with either soil or peat.

Table II: Fuel properties of the chopped raw materials (a.r. = as received, d.b. = dry basis)

Parameter	Unit	*Typha ssp.*		*Phragmites australis*		*Phalaris arundinacea*		*Carex ssp.*	
		2018	2019	2018	2019	2018	2019	2018	2019
Moisture content	w-% a.r.	10.3	9.1	8.8	9.3	10.1	9.8	10.3	11.0
Ash content	w-% d.b.	5.2	6.0	4.7	4.8	3.9	9.9	5.0	5.1
Bulk density	kg/m³, a.r.	35.2	23.1	95.3	48.5	66.2	42.7	78.0	36.5
Net calorific value	MJ/kg, d.b.	17.61	17.78	17.89	17.89	17.83	16.88	17.67	17.90
C	w% d.b.	47.0	48.4	47.3	48.4	46.7	46.2	46.8	48.8
H	w% d.b.	5.9	5.9	5.9	5.9	5.9	5.7	5.8	5.8
N	w% d.b.	0.95	0.99	0.82	0.59	0.88	1.24	1.12	1.17
Cl	w-% d.b.	0.16	0.20	0.07	0.07	0.09	0.07	0.28	0.19
S	w-% d.b.	0.06	0.09	0.06	0.07	0.11	0.12	0.12	0.12
Al	mg/kg d.b.	165	262	71	171	129	1,290	54	172
Ca	mg/kg d.b.	14,500	13,300	2,050	1,800	2,590	5,270	4,330	4,660
K	mg/kg d.b.	1,730	1,420	1,620	740	1,080	1,910	3,370	2,460
Mg	mg/kg d.b.	1,980	1,740	457	637	775	611	3,300	2,530
Na	mg/kg d.b.	2,350	1,750	119	277	199	369	589	401
Si	mg/kg d.b.	836	681	14,700	11,800	11,200	19,600	9,840	9,070

Table III: Fuel properties of the produced test fuel pellets (a.r. = as received, d.b. = dry basis)

Parameter	Ash content	Moisture content	Net calorific value	Durability	Bulk density
Unit	w-% d.b.	w-% a.r.	MJ/kg d.b.	w-% a.r.	kg/m³ a.r.
Wood pellets	0.3	7.9	18.9	99.3	683
Wheat straw pellets	4.2	8.8	17.5	96.4	625
Typha ssp.	6.8	7.8	17.62	99.0	781
Typha ssp. + 2.3 w-% kaolin	6.8	5.9	17.25	98.8	787
Phragmites australis	4.8	5.5	17.92	98.7	796
Phragmites australis + 0.6 w-% kaolin	5.2	5.4	17.76	99.3	790
Phalaris arundinacea	4.3	11.8	18.22	99.0	787
Phalaris arundinacea + 1.2 w-% kaolin	7.1	7.7	17.47	98.9	747
Carex ssp.	5.6	6.0	17.98	98.6	780
Carex ssp. + 1.5 w-% kaolin	7.1	8.3	17.67	99.0	772

Table IV: Minor and trace elements of the produced pellets (d.b. = dry basis, concentration of minor and trace elements of the additivated fuels were calculated from the analyses of the raw materials and the additive applying the respective mixing ratios; * = additional analyses of pure *Phalaris* pellets were performed and used for calculation as results of Table II indicate contamination of the raw material sample with either peat or soil)

Parameter	N	S	Cl	Al	Ca	K	Mg	Na	Si
Unit	w-% d.b.	w-% d.b.	w-% d.b.	mg/kg d.b.	mg/kg d.b.	mg/kg d.b.	mg/kg d.b.	mg/kg d.b.	mg/kg d.b.
Wood pellets	0.10	0.005	0.006	25	811	414	131	15	166
Wheat straw pellets	0.44	0.071	0.210	145	2,860	8,450	767	42	9,460
Typha ssp.	0.99	0.092	0.202	262	13,300	1,420	1,740	1,750	681
Typha ssp. + 2.3 w-% kaolin	0.97	0.090	0.197	4,062	13,020	1,661	1,748	1,733	5,246
Phragmites australis	0.59	0.071	0.071	171	1,800	740	637	277	11,800
Phragmites australis + 0.6 w-% kaolin	0.58	0.069	0.069	1,128	1,795	805	645	281	12,885
*Phalaris arundinacea**	1.27	0.139	0.094	568	4,230	2,150	1,140	292	8,460
Phalaris arundinacea +1.2 w-% kaolin*	1.24	0.136	0.092	2,568	4,191	2,268	1,152	301	10,773
Carex ssp.	1.17	0.116	0.185	172	4,660	2,460	2,530	401	9,070
Carex ssp. + 1.5 w-% kaolin	1.14	0.113	0.181	2,654	4,606	2,602	2,524	410	11,925

Table V: Fuel indices to predict combustion behaviour of paludiculture pellets, calculated using minor and trace elements

Parameter	K+Na+Pb+ Zn+Cl+S	Molar (Si+P+K)/ (Ca+Mg+Al)	Molar Cl/Si	Molar Si/K	Molar 2S/Cl
Unit	mg/kg, d.b.	-	-	-	-
Wood pellets	554	0.69	0.31	0.56	1.79
Wheat straw pellets	11,306	5.29	0.18	1.56	0.76
Typha ssp.	6,138	0.15	0.24	0.67	1.01
Typha ssp. +2.4 w-% kaolin	6,295	0.42	0.03	4.39	1.01
Phragmites australis	2,470	5.67	0.00	22.19	2.21
Phragmites australis +0.6 w-% kaolin	2,506	4.23	0.00	22.28	2.21
Phalaris arundinacea	4,827	2.05	0.01	5.48	3.27
Phalaris arundinacea + 1,2 w-% kaolin	4,901	1.79	0.01	6.61	3.27
Carex ssp.	5902	1.70	0.02	5.13	1.39
Carex ssp. + 1.5 w-% kaolin	5984	1.55	0.01	6.38	1.39

N content of the paludiculture biomass was 0.59 to 1.24 w-% d.b. (Table II), exhibiting a typical range for straw fuels. K content (740 to 2,460 kg/m^{3}d.b.) was lower than typical values for non-woody biomass (2,000 to 26,000 mg/kg) [1, 2]. Overall, concentrations of N and K were close but slightly increased to values reported for fuels from coniferous forest residues [11]. High N in fuels might lead to elevated NO_X formation during combustion while K leads to the formation of mineral aerosols [2]. Thus, for combustion of paludiculture biomass, higher NO_X or TPM emissions were expected compared to forest residue wood chips as it is often observed during the combustion of herbaceous fuels such as wheat straw [3].

For *Typha ssp*., Na content exceeded K content in fuels and provided approx. 66 % of aerosol forming elements that are relevant for PM_1 emissions (K, Na, Pb, Zn). Especially for *Typha ssp*., the high shares of Na must be considered by calculating the necessary amount of kaolin according to the “BIOFLEX!” guidelines [4].

Correct determination of all aerosol forming elements is even more relevant in *Typha ssp.*, as Si was extremely low (<840 mg/kg d.b.) compared to typical values in herbaceous biomass. Very low Si concentrations in fuels might inhibit fixation of K and Na into the ash [2]. Consequently, high shares of both major aerosol forming elements in *Typha ssp.* might be emitted as mineral aerosols during combustion.

Highest S concentrations were detected for *Phalaris arundinacea* and *Carex ssp*. but values never exceeded thresholds of ISO 17225-6 class A (≤0.20 w-% d.b.) and remained within the typical range for straw and grass fuels (0.05 to 0.20 w-% d.b.) [1, 2]. Highest Cl values were measured for *Typha ssp.* and *Carex ssp.*, exceeding the limits of ISO 17225-6 class A (≤0.10 w-% d.b.) but not of class B (≤0.30 w-% d.b.). Overall, Cl concentrations were within the typical range for straw and grass fuels (0.2 to 1.3 w-% d.b.) [1, 2]. Unpublished results from the “MOORuse” project on the use of the harvested materials for peat substitutes indicate a strong decline in Cl concentrations when the straw is harvested in winter compared to summer. The same effect was observed in literature [5, 6]. Thus, to minimize fuel related problems with high temperature corrosion or HCl emissions during combustion, paludiculture biomass should be harvested during winter.

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 III summarizes the results on physical fuel properties of the paludiculture pellets. Mean moisture content of pellets was 5.5 to 11.8 w-% and complied with fuel class A of ISO 17225-6 (≤12.0 w-%). Mean bulk density was 747 to 796 kg/m^3, which is a significant increase towards the reference fuels (wood and wheat straw pellets). At the same time, mechanical durability was as high as 98.6 w-%. Results indicate a very good densification of the material with the process parameters selected for pelletization. No trend in bulk density or mechanical durability could be detected depending on the additive, probably due to the rather low additivation levels of <2.4 w-%.

Ash content of paludiculture pellets ranged from 4.3 to 7.1 w-% d.b. (Table III). Thereby, four pellet fuels met the ash requirements of fuel class A (≤6.0 w-% d.b.), while the other fuels met the requirements of fuel class B according to ISO 17225-6 (≤10 w-% d.b.). In three of four cases, additivation with kaolin (ash content = 89.7 w-% d.b.) increased ash content in fuels.

Especially for *Phalaris arundinacea*, results on ash content of pure pellets (4.3 w-% d.b.) were close tovalues of straw fuels from 2018 (3.4 w-% d.b.) and to results from literature [5, 6]. Consequently, results of the 2019 straw sample of *Phalaris arundinacea* with an ash content of 9.9 w-% d.b.(see Table II) must be considered non-representative for the whole batch.

To minimize uncertainties due to sampling of the inhomogeneous biomass, results on chemical fuel properties of additivated pellets were calculated rather than measured (Table IV). This procedure is commonly used when additivation or experimental contamination of pellet fuels is performed [3, 12]. Thus, concentrations of chemical elements in pellets were achieved by using the element concentrations of the pure raw materials and of the additive by applying the respective mixing ratios. For pure *Phalaris arundinacea*, chemical element concentration was measured once again from the pure pellets directly, as results on ash content of straw fuels indicated non-representative sampling of the biomass (see above). The new values were also used for the calculation of the additivated *Phalaris arundinacea* pellets (Table IV).

Compared to certified wood pellets (EN*plus* A1), pure paludiculture pellets had higher shares of all chemical elements that are considered critical for combustion. Apart from K, this was also true when pure paludiculture pellets were compared to pellets from wheat straw that were produced in the ERANET-project “BIOFLEX!” [3].As K is highly relevant for aerosol formation, higher TPM emissions are 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 IV). 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 inthe additive such as N, Cl and S did not change much in the additivated fuels as the additivation level was rather low (<2.4 w-%), leading to almost no dilution effect in the biomass.

Fuel indices to predict combustion behaviour, i. e. to predict NO_Xor TPM emissions, slagging or high temperature corrosion, were calculated from the chemical element concentrations in the fuels(Table V).

A high molar (Si+P+K)/(Ca+Mg+Al) ratio indicates slag formation during combustion [2, 13]. With exception of *Typha ssp*., additivation decreased the index indicating an improvement in slagging behaviour. Still, the lowest slagging can be expected during combustion of *Typha ssp*., due to the overall low amount of Si in fuels, while for *Phragmites australis* results were close to wheat straw. During the ERANET-project “BIOFLEX!”, combustion of pure wheat straw pellets resulted in the shutdown of the GUNTAMATIC Powerchip boiler due to severe slag formation [3]. According to the index, this can also be expected during combustion of pure *Phragmites australis* pellets when they are applied to the same boiler.

The sum of aerosol forming elements (K, Na, Pb, Zn, Cl, S) are an indicator for TPM emissions [13]. According to the index, highest TPM emissions are expected for *Typha ssp*. (Table V). However, additivation with kaolin strongly increased Si in *Typha ssp*. pellets and, as predicted by an increased molar Si/K ratio that serves as an indicator for K fixation during combustion, higher shares of K might be fixed in the ash by forming potassium aluminium silicates [3, 13]. Thus, especially for *Typha ssp*., additivation with kaolin is expected to strongly improve TPM emission behaviour of the boiler during combustion.

3.2 Combustion trials

During the combustion of paludiculture pellets, gaseous and particulate matter emissions of the GUNTAMATIC Powerchip 20/30 were often similar compared to the combustion of certified wood pellets and only increased in individual cases. For the pure paludiculture pellets, mean CO emissions ranged from 13.7 mg/m^3 for *Phragmitesaustralis* to 291.7 mg/m^3 for *Typha ssp.*at standard testing conditions (STC, i. e. dry flue gas at 0 °C, 1,013 hPa and 13% O_2) (Fig.5).Mean CO values remained below the emission threshold for 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 boilers <100 kW, 1. BImSchV). Moreover, CO emissions of both *Phragmites australis* and *Carex ssp.* resembled that of the reference fuel, i. e. of EN*plus* A1 wood pellets.

Elevated CO emissions would indicate an incomplete combustion of the fuel [2, 14]. By trend, additivation of pellets with kaolin led to a decrease of CO emissions for *Typha ssp.* and *Phalaris arundinacea* (Fig.5). This effect was reported in previous studies [3, 15]. So far, no distinct cause for the decreased CO emissions due to additivation 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 fuels [3]. Another explanation can be a more porous structure of the already charred pellets during charcoal burnout caused by kaolin, which enhances the penetration of oxygen into the charcoal leading to a better burnout of the gaseous components. Further studies are required to explain this effect in more detail.

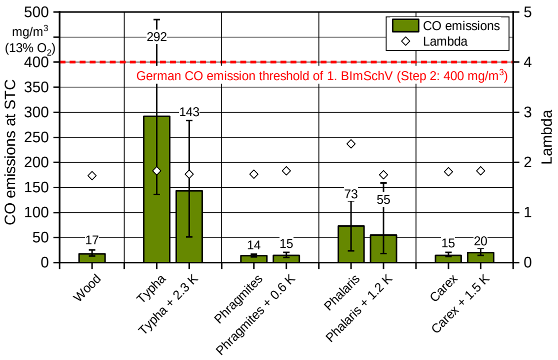

Figure 5: Mean CO emissions during combustion of wood and paludiculture pellets (with and without kaolin (K)) in a 30 kW wood chip boiler (n = 5, whiskers indicate minimal and maximal values)

Results on organic gaseous carbon (OGC) emissions followed the same trend as for CO emissions (Fig.6). Mean OGC values were below the emission threshold of the European eco-design directive (15 mg/m^3 at 13 % O_2). However, a direct comparison with this threshold is not possible as the eco-design directive relates to a mixture of full load (15 %) and part load operation (85 %) whereas during this study, only full load operation trials were performed. As expected for automatically fed boilers the OGC emissions are on a rather low level.

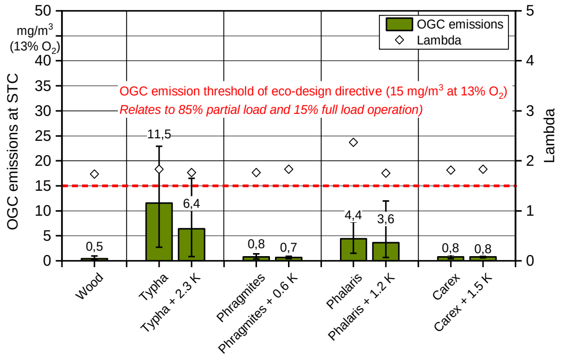

Figure 6: Mean OGC emissions during combustion of paludiculture pellets with and without kaolin (K) in a 30 kW wood chip boiler (n = 5, whiskers indicate minimal and maximal values)

NO_X emissions of paludiculture pellets were higher compared to the combustion of wood pellets (i. e. 103.7 mg/m^3), ranging from 351.9 mg/m^3 for pure *Typha ssp.* to 595.5 mg/m^3 for pure *Phalaris arundinacea*(Fig.**7**). All values exceeded the NO_X emission threshold of the European eco-design directive of 145 mg/m³ (converted to @13 % O_2). However, like OGC, the NO_X emission threshold of eco-design also relates to both part and full load operation and results cannot be compared directly.

NO_X emissions increased linearly with N content in fuels (R^2 = 0.77). This was expected as N content is considered a good indicator for NO_X [13] and the effect was frequently observed in previous studies [3, 7, 14]. Additivation with kaolin often led to a slight increase in NO_X formation. Thus, other solutions to decrease $NO_X$are necessary, e.g. a mixing of N-rich fuels (e. g. paludiculture straw) with fuels that are generally low in N (e. g. coniferous wood) [3, 4]. Alternatively, fuel gas recirculation can be effective, or technical measures during combustion such as selective catalytic reduction(SCR) and selective non-catalytic reduction (SNCR)might be applied, although these techniques are only available and economical feasible for larger biomass plants[2].

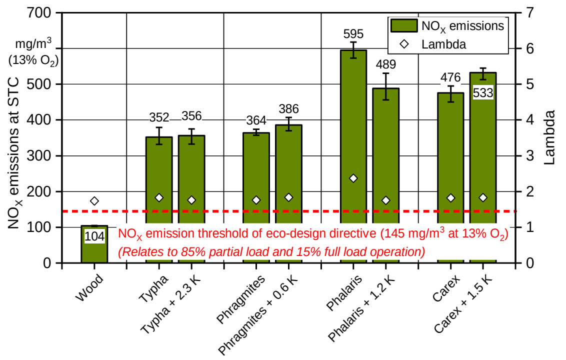

Figure 7: Mean NO_X emissions during combustion of paludiculture pellets with and without kaolin (K) in a 30 kW wood chip boiler (n = 5, whiskers indicate minimal and maximal values)

Both HCl and SO_X emissions were increased when paludiculture pellets were combusted instead of wood pellets (data not shown). HCl emissions ranged from 68 to 174 mg/m^3 (at STC) and correlated well with Cl in fuels (R^2 of linear regression = 0.85). SO_X emissions ranged from 146 to 243 mg/m^3(at STC) and increased linearly with S content in fuels (R^2 = 0.85). In contrast to previous studies [3], additivation with kaolin had no negative effect on HCl or SO_X, probably due to the overall low additivation level. Only for *Typha ssp.*, additivation led to a significant increase of HCl from 119 to 174 mg/m^3 ($p \leq 0.001$). This effect is due to equation 2 and 6 (see section 2.2) as KCl reacts with kaolinite, resulting in the emission of HCl instead of the aerosol.

TPM emissions of pure pellets were below the emission threshold of 20 mg/m^3 of 1. BImSchV for *Phragmites australis* (13.9 mg/m^3) and for *Phalaris arundinacea* (14.0 mg/m^3), while both *Carex ssp.* and *Typha ssp.* were above this threshold with 31.2 mg/m^3 and 115.3 mg/m^3, respectively (Fig.8). High TPM emissions may result from the formation of mineral aerosols but also from incomplete combustion [2, 14]. As indicated by the sum of aerosol forming elements in fuels, highest TPM emissions could be expected for *Typha ssp.* followed by *Carex ssp.* (see Table V). Additivation decreased TPM emissions for both fuels significantly ($p \leq 0.05$, Fig.8). However, in the case of *Typha ssp.*, the decrease in TPM due to additivation was only minor and TPM emissions were still 94 mg/m^3 for additivated pellets. One possible explanation is a cooccurring effect from incomplete combustion and soot formation on TPM as it was also indicated by the emission values for CO and OGC (Fig.5 and 6), probably caused by the very fluffy physical structure of the *Typha ssp.* raw material [2].

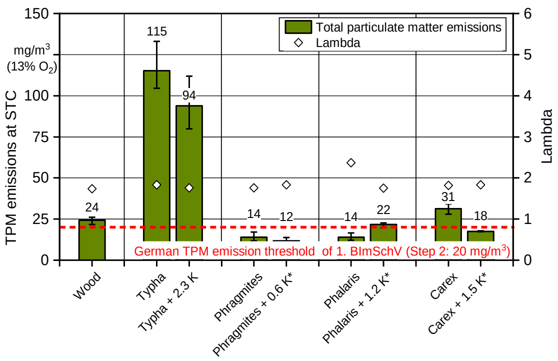

Figure 8: Mean total particulate matter (TPM) emissions during combustion of paludiculture pellets with and without kaolin (K) in a 30kW wood chip boiler (*n* = 5, * indicates *n* = 2, whiskers indicate minimal and maximal values)

Compared to the combustion of certified wood pellets, no definite steady state operation of the boiler could be achieved with any of the tested paludiculture fuels (data not shown). Consequently, the heat output of the boiler was highly fluctuating between 20 and 34 kW. At the same time, the fluctuations of O_2 concentrations in the flue gas during combustion varied between 6.4 % and 14.7 % and these variations were very high compared to the combustion of certified wood pellets.

3.3. Slagging tendencies

Ash melting and ash deformation temperatures of pellets were measured according to ISO 21404 and results are given in Fig.9. Deformation temperature (DT) is the parameter most widely used to characterize ash melting behaviour of solid biofuels. According to ISO 17225-6, this parameter is not limited by a threshold but should be stated in the fuel declaration. According to the EN*plus* certification for wood pellets, DT should be above 1,200 °C for fuel quality A1 as temperatures above 1,000 °C often occur in boilers [2]. If DT is lower than 1,200 °C, slagging might lead to problems during combustion.

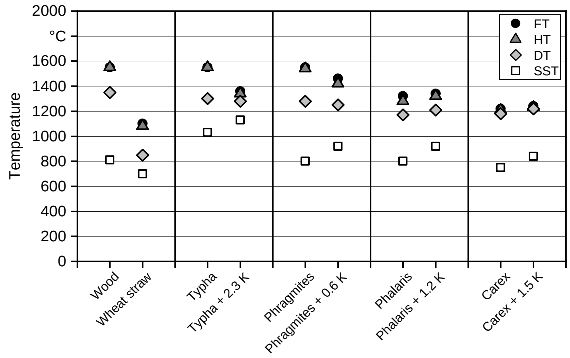

Figure 9: Ash melting temperatures of paludiculture pellets with and without kaolin (K) according to ISO 21404 (SST = shrinkage starting temperature, DT = deformation temperature, HT = hemisphere temperature, FT = flow temperature)

For all paludiculture pellets, DT was at approx. 1,200 to 1,300 °C and no trend could be observed regarding additivation of pellets with kaolin (Fig.9), except that the shrinkage starting temperature (SST) was constantly higher with additives. For pure *Phalaris arundinacea* and pure *Carex ssp.*, DT was slightly below 1,200 °C indicating that these fuels might be considered critical in terms of slagging behaviour. Especially for the reference fuel wheat straw pellets from the ERANET-project “BIOFLEX!”, severe slagging has to be expected as DT was even below 900 °C. In the “BIOFLEX!” project, this prediction proofed true as wheat straw pellets had led to a boiler shutdown due to slagging [3].

In addition to DT, the molar (Si+P+K)/(Ca+Mg+Al) ratio might also be used to predict slagging behaviour in fuels [13]. As observed in previous studies [12], DT did not correlate well with the molar (Si+P+K)/(Ca+Mg+Al) ratio (Table V). Still, the index indicated high slagging risk for *Phragmites australis* and for wheat straw. In contrast to wheat straw, however, pure *Phragmites australis* did not lead to boiler shut down during combustion in the GUNTAMATIC Powerchip 20/30 boiler. Consequently, the molar (Si+P+K)/(Ca+Mg+Al) ratio might be deemed not suitable for paludiculture fuels.

Depending on the pellet fuel used for combustion, the total mass of ash per trial ranged from 202 g (wood pellets) to 5.1 kg (pure *Phalaris arundinacea*). In most cases, strong slagging occurred during combustion of pure paludiculture pellets. The ash of each trial was screened separately following the updated procedure developed in the EU project “AshMelT” [16]. In each ash sample, particles of different particle sizes could be detected after performing an automated sieving procedure as described in section 2.4 (Fig. 10). However, particle size distribution of boiler ashes showed strong differences among the fuels (Fig. 11).

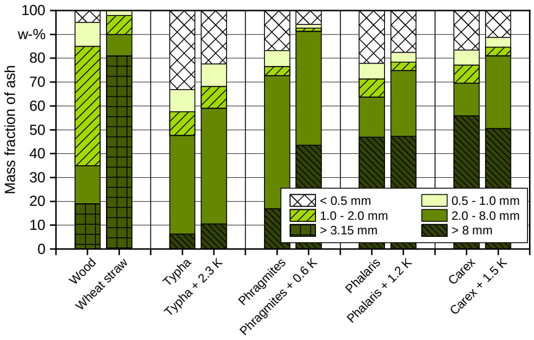

Figure 10: Mass fractions after screening of ash from combustion of paludiculture pellets with and without kaolin (K) in a 30 kW wood chip boiler

As expected, the lowest slag formation occurred during combustion of *Typha ssp*., resulting in ash particles that kept their pellet structure. In contrast, all other paludiculture fuels led to severe slagging with large shares (>40 w-%) of particles >8 mm. In these cases, ashes tended to melt and form large solid ash blocks on the moving grate after cooling of the boiler. This could lead to severe damages to the boiler when it is not cleaned in-between operation times, as it was done during this study.

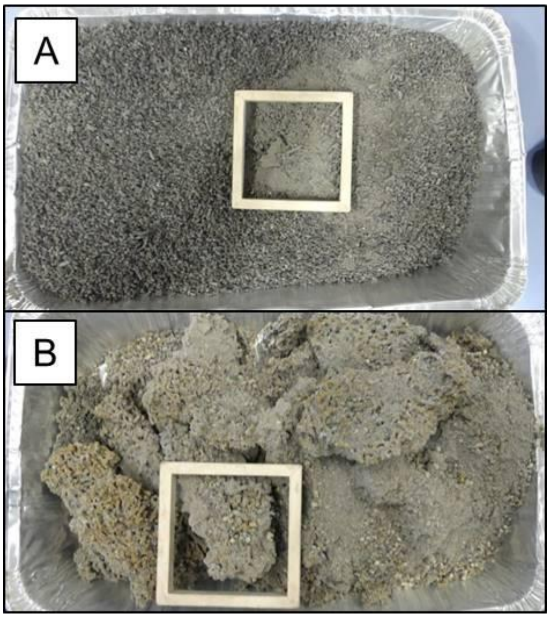

Figure 11: Ash or slag from combustion of pure paludiculture pellets (A = *Typha spp*., B = *Phalaris arundinacea*, wooden frame = 10 × 10 cm)

In contrast to the results from Mack et al. [3], no positive effect of the additive on slagging could be observed, probably due to the overall low additivation level. Calculations of the mass of kaolin required according to the “BIOFLEX!” guideline focus on the reduction of TPM and not on slagging [4]. Thus, higher additivation levels or another additive such as MgO might be required to reduce slagging in the case of paludiculture fuels.

Technical solutions might help to decrease slagging problems such as an automatic cleaning of the grate after each combustion process. However, the three paludiculture fuels *Phragmites australis*, *Phalaris arundinacea* and *Carex ssp*. must be considered as generally critical for the use in the here applied small-scale boiler. Long-term use of these fuels will probably lead to frequent boiler shutdown, to high labour demand for maintenance and/or cleaning, and to damages of the grate and the screw conveyors for ash transport.

4 CONCLUSION

The utilization of paludicultures for combustion might, in theory, be an innovative option even in small-scale boilers but their use as a fuel is limited. The here presented results show large differences in the combustion behaviour of *Typha ssp*, *Phragmites australis*, *Phalaris arundinacea* and *Carex ssp*. compared to certified wood pellets leading to the following conclusions:

- Fuel quality of paludiculture biomass meets the specifications of ISO 17225-6 if pellets are produced from the straw fuels. Thus, in theory, fuels should be suitable for combustion in boilers that are designed for agricultural biofuels.
- Winter should be the preferred season to harvest the fuels as some chemical elements, e. g. Cl, might be increased during summer.
- During combustion, NO_X emissions were increased for all four biomasses compared to the use of certified wood pellets. Suitable measures to decrease N content in fuels (e.g. fuel blending) or technical solutions (e.g. boiler design, SCR, SNCR) need to be applied.
- Combustion of *Typha ssp*. led to high CO and TPM emissions. Additivation of fuels with kaolin can reduce CO and TPM emissions of *Typha ssp*. but this effect is not very strong when an incomplete combustion occurs simultaneously. Technical solutions such as an advanced boiler design, the use of electrostatic precipitators, etc., might be necessary to apply *Typha ssp*. biomass to a small-scale boiler.
- *Phragmites australis*, *Phalaris arundinacea* and *Carex ssp*. pellets led to severe slagging. This might be challenging especially for small-scale boilers. As additivation does not automatically improve slagging behaviour, other measures such as fuel blending or technical solutions might be required.

So far, the combustion of agricultural fuels such as paludiculture biomass in boilers <100 kW in Germany is limited as hardly any boiler is certified for these fuels according to German legislation. Consequently, the use of paludicultures as a biofuel for this boiler size class might be technically possible if sufficient fuel upgrading (e. g. the use of a higher additivation level and/or fuel blending) and a suitable boiler design with an advanced combustion technique and/or secondary emission reduction measures is applied. However, the use of paludicultures as biofuels might be more useful for larger boilers >100 kW. For this size class, individual permits are required. Technical solutions to improve combustion behaviour might be more easily implemented in larger facilities. Consequently, paludiculture biomass might be more suitable for medium sized decentralized combustion plants.

5 REFERENCES

[1] Deutsches Institut für Normung e.V. (2014): DIN EN ISO 17225-1:09-2014. Berlin: Beuth, 62 pages.

[2] Kaltschmitt, M. et al. (2016): Energy from Biomass. 3rd. Edition, Berlin: Springer, 1867 pages.

[3] Mack, R. et al. (2019): Combustion behavior and slagging tendencies of kaolin additivated agricultural pellets and of wood-straw pellet blends in a small-scale boiler. Biomass and Bioenergy 125, p. 50–62.

[4] Brunner, T. et al. (2019): Guidelines for advanced fuel and boiler design. Report within the scope of the ERA-NET Bioenergy Project "BIOFLEX!" – Clean and flexible use of new difficult biomass fuels in small to medium-scale combustion. Graz: BIOS BIOENERGIESYSTEME GmbH, 31 pages.

[5] Wichtmann, W. et al. (2014): Combustibility of biomass from wet fens in Belarus and its potential as a substitute for peat in fuel briquettes. Mires and Peat, Volume 13, Article 06, p. 1–10.

[6] Dahms, T. et al. (2017): Halmgutartige Festbrenn-stoffe aus nassen Mooren. Universität Greifswald, 68 pages.

[7] Kuptz, D. et al. (2019): Evaluation of combined screening and drying steps for the improvement of the fuel quality of forest residue wood chips - results from six case studies. Biomass Conversion and Biorefinery 9 (1), p. 83-98.

[8] Smeja-Krol, B. et al (2014): Quantitative determination of minerals and anthropogenic particles in some Polish peat occurrences using a novel SEM point-counting method. Environmental monitoring and assessment, 186, p. 2573–2578

[9] Sutejo, Y. et al. (2017): Physical and chemical characteristics of fibrous peat. Proceedings of the 3rd International Conference on Construction and Building Engineering, 9 pages.

[10] Dietz, E. et al. (2016) New Indexes for the contamination of wood chips with mineral soil. Proceedings of the 24th European Biomass Conference. Amsterdam, p. 630–633.

[11] Dietz, E. et al. (2016): Qualität von Holzhack-schnitzeln in Bayern. Gehalte ausgewählter Elemente, Heizwert und Aschegehalt. Straubing: Berichte aus dem TFZ, No. 46, 150pages.

[12] Kuchler et al. (2018): Contamination of wood pellets with selected mineral soils – fuel quality and combustion behaviour. Proceedings of the 27th European Biomass Conference. Lisbon. p. 673–680.

[13] Sommersacher P.et al. (2011). Fuel Indexes: A Novel Method for the Evaluation of Relevant Combustion Properties of New Biomass Fuels. Energy Fuels26(1):380–390

[14] Schön, C. et al. (2019): Influence of wood chip quality on emission behaviour in small-scale wood chip boilers. Biomass Conversion and Biorefinery 9, p. 71-82.

[15] Huelsmann, T. et al. (2019): Influence of kaolinite on the PM emissions from small-scale combustion. Biomass Conversion and Biorefinery 9 (1), p. 55-70

[16] Schön, C. et al. (2019): New Experimental evaluation strategies regarding slag prediction of solid biofuels in pellet boilers. Energy & Fuels 33, p. 11985–11995

6 ACKNOWLEDGEMENTS

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