

## COMBUSTION BEHAVIOUR AND SLAGGING TENDENCIES OF KAOLIN ADDITIVATED AGRICULTURAL PELLETS AND OF WOOD-STRAW PELLET BLENDS IN A SMALL SCALE BOILER

Robert Mack, Daniel Kuptz, Claudia Schön, Hans Hartmann  
Technology and Support Centre in the Centre of Excellence for Renewable Resources (TFZ),  
Schulgasse 18, D-94315 Straubing, Germany  
Phone: +49-9421-300154, Fax: +49-9421-300211  
Email: robert.mack@tfz.bayern.de

**ABSTRACT:** The ERA-NET Project “BioFlex!” aims at the utilisation of agricultural fuels for failure free and low emission combustion in domestic biomass boilers. Within the project, the effect of kaolin additivation of four agricultural biomass fuels as well as of fuel blends of wheat straw with woody biomass was assessed regarding combustion behaviour in small scale boilers. By additivation of kaolin as well as by fuel blending, total particle emissions and CO emissions were reduced by 53 to 77 % and 69 to 95 %, respectively. In addition, slag formation (determined as amount of agglomerates > 3.15 mm) of the agricultural fuels was also reduced. Thus, additivation with kaolin or blending of agricultural fuels might be an interesting option for the utilisation of “difficult” biomass fuels. However, regarding the pelletisation process itself, a distinct increase in wearing off of the dies and the rollers of the pellet mill was observed. This also has to be considered during production.

**Keywords:** agricultural fuels, pellets, additives, blending, emissions, combustion, slagging

### 1 INTRODUCTION

The potential of woody biomass is limited. Therefore, new but challenging biomass fuels need to find their way into small and medium-scale combustion applications. These fuels are, for example, agricultural residues, by-products and energy crops that are mostly considered as “difficult” in terms of fuel quality.

Within the ERA-NET Project “BioFlex!”, fuel quality and combustion behaviour of agricultural biomass pellets were tested in a small scale boiler. To improve combustion behaviour, non-woody biomass was additivated with kaolin or blended with soft wood.

### 2 MATERIAL & METHODS

#### 2.1 Selected fuels

Fuels selected for this study included pellets of poplar, sunflower husk, wheat straw and grass. Furthermore, unpelletized poplar wood chips were used during combustion trials. All pellets were produced at TFZ using an Amandus Kahl press with exception of wood pellets, i. e. the reference fuel, that were purchased on the German market. To improve the ash chemistry regarding slagging behaviour and to reduce particle emissions by fixation of potassium into the ash (see section 2.2), the clay mineral kaolin was used as an additive in all non-woody fuels. Kaolin was purchased from the company KAMIG (Perg, Austria) and consisted to 87 w-% of kaolinite. During production, kaolin was added to poplar fuels (1.5 w-%, d. b.) wheat straw (3.45 w-%, d. b.), sunflower husk (2.8 w-%, d. b.) and grass (8.1 w-% and 10.5 w-%, d. b., respectively). Mixing ratios derived from element analysis (see below) and from stoichiometric calculation (see section 2.2).

Further trials were performed using poplar fuels that were additivated with kaolin (1.5 w-%, d. b.) after fuel production (pellets, wood chips). For these fuels, additivation was done by mixing pellets with kaolin manually in a barrel (pellets) or by adding kaolin directly into the screw feeder of the respective boiler (wood chips).

In addition to kaolin additivation, wheat straw was blended with 50 w-%, 75 w-% and 90 w-% of wood prior

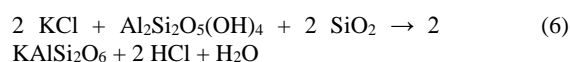
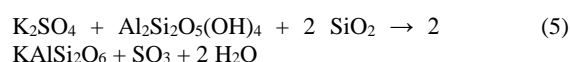
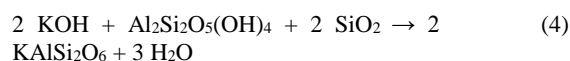
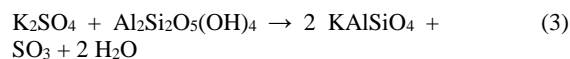
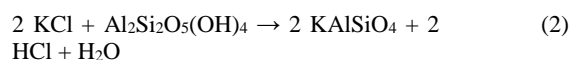
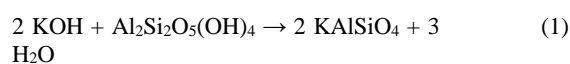
to the pelletisation. This might also be done by mixing of already produced pure wheat and wood pellets. Thus, a 50/50 mixture of premanufactured pure wheat straw pellets and pure wood pellets was generated, as well.

All pure fuels were analysed for elemental composition including heavy metals and trace elements at BIOS Bioenergiesysteme GmbH. Physical fuel parameters of all fuels were determined at TFZ. Based on the element analysis, specific fuel indexes were calculated in order to predict the ash melting behaviour (molar  $(\text{Si}+\text{P}+\text{K})/(\text{Ca}+\text{Mg})$ -ratio), the theoretical risk for aerosol formation ( $\Sigma(\text{K}, \text{Na}, \text{Pb}, \text{Zn})$ ),  $\text{NO}_x$ -emissions (N-content of the fuel), K-release (molar  $\text{Si}/\text{K}$ -ratio), high temperature corrosion (molar  $2\text{S}/\text{Cl}$ -ratio) and  $\text{HCl}/\text{SO}_x$ -emissions (molar  $(\text{K}+\text{Na})/[x(2\text{S}+\text{Cl})]$ -ratio) [1]. In contrast to these indexes which are usually used for pure wood fuels, the Al concentration of agricultural fuels or of fuels additivated with Al-based additives might be very high while ash melting temperatures might be increased. Therefore the  $(\text{Si}+\text{P}+\text{K})/(\text{Ca}+\text{Mg}+\text{Al})$ -ratio might be preferred for predicting ash melting behaviour of such fuels [2, 3]. Furthermore, the molar  $\text{Cl}/\text{Si}$ -ratio might be a better indicator to estimate the K-release [3]. This ratio was calculated, as well.

#### 2.2 Mode of action and stoichiometric calculation of the required kaolin amount

According to literature, 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 chlorine (Cl) [1,4,5]. The most relevant element for aerosol formation in biomass fired conversion systems is potassium (K) [6]. K is mainly released to the gas phase as KOH and KCl, but also to small amounts as  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{CO}_3$  [7,8].

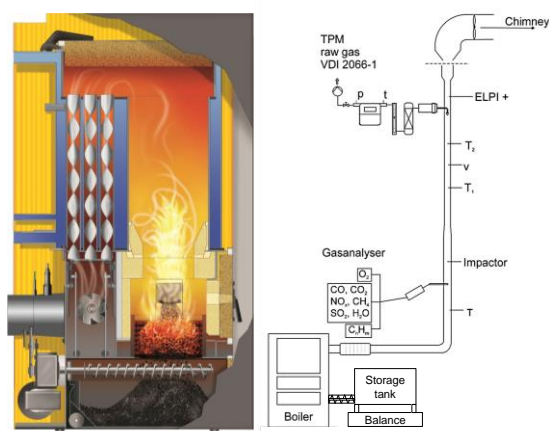
Kaolin is a clay mineral and consists mainly of the mineral kaolinite ( $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ ). Alkali compounds like potassium can react according to equation (1–3) to high-melting crystalline products such as kalsilite ( $\text{KAlSiO}_4$ ) as well as to leucite ( $\text{KAlSi}_2\text{O}_6$ ) (equation 4–6) if kaolinite is present [9,10].



Following equation 1 to 6 it is obvious that for the fixation of 2 mol potassium 1 mol of  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  is needed. From this context the amount of kaolinite needed 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 (87 %) has to 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 (Figure 1, left). The ash is removed via the moving grate to a screw conveyor which transports the ashes into the ash box. This 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. Two different fuel feeding systems were used for the test runs. For trials with pellets, a square storage tank with a slanted floor and a screw conveyor was used. For wood chips, a round storage tank with a flat spring agitator and a screw conveyor was used. 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.



**Figure 1:** Schematic drawing of the boiler (source: Guntamatic, left) and a schematic drawing of the test stand (right)

Figure 1 (right) shows a schematic drawing of the test rig and the arrangement of the measurement devices. The heat consumption was permanently regulated to a nominal load of 30 kW ( $\pm 8\%$ ) following DIN EN 303-5 [11]. The gaseous components CO, CO<sub>2</sub>, and O<sub>2</sub> were determined using a single component analyser (ABB Automation GmbH ABB AO2020), NO<sub>x</sub> by a chemiluminescence detector (Eco Physics GmbH CLD 822 Mhr Analysator) and for water vapour content, SO<sub>x</sub>, HCl and CH<sub>4</sub> an 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 measured following VDI 2066-1 [12] applying a filtration temperature during sampling and the filter pre- and post-treatment temperature of 180 °C. The boiler was operated at a constant flue gas draught of  $-15 \pm 2$  Pa as it is 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 Figure 1, right).

### 2.4 Measurement procedure

Prior to each trial, the combustion chamber, the heat exchanger and the fuel feeding system were completely cleaned using a vacuum cleaner, a brush and pressurized air. The storage tank was filled with sufficient amount of fuel and the boiler was started and heated up to steady state operation at nominal load (30 kW) within approx. 2 h. Then the measurement was performed over 8 h at nominal load operation. Within this time period, the gaseous emissions were continuously recorded but were evaluated only for the duration of the TPM measurements. Four TPM measurements were performed evenly spread over the whole 8 h (0–30 min, 150–180 min, 300–330 min and 450–480 min). All reported emissions refer to dry flue gas at 0 °C and 1,013 hPa and are based on 13 % O<sub>2</sub>.

#### 2.4.1 Visual classification of boiler ash

After each test run ashes were completely removed from the boiler and analysed regarding slag formation. As a first step, visual classification according to Table I was done.

**Table I:** Description of sintering degree for slag collected from the residual ash [13]

Category	Description
1	Non sintered ash residue, i. e. no fused ash (clear grain structure)
2a	Partly sintered ash, i. e. particles contained clearly fused ash that breaks at a light touch (distinguishable grain structure).
2b	Partly sintered ash, i. e. particles contained clearly fused ash that holds together at a light touch but is easily broken apart by hand (distinguishable grain structure).
3	(Totally) sintered ash, i. e. the deposited ash was fused to smaller blocks that still are breakable by hand (slightly distinguishable grain structure).
4	Totally sintered ash, i. e. the deposited ash was totally fused to larger blocks that not are possible to break by hand (no distinguishable grain structure).

#### 2.4.2 Slag index for boiler ash

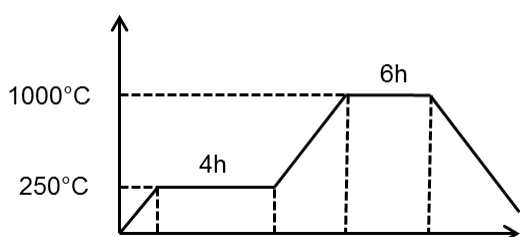
In a second step, the bottom ash, grate ash and fly ash from the heat exchanger were separately weighed on a balance with a resolution of 0.1 g (Mettler-Toledo

GmbH, PG12001-S). The bottom ash and grate ash were analysed regarding slagging using a sieving machine (AS400 control by Retsch GmbH & Co. KG), operated at 200 rpm for one minute using mesh wire cloth sieves with opening widths of 0.5, 1.0, 2.0 and 3.15 mm. The slag index was then calculated according equation 7.

$$\text{Slag index} = \frac{\Sigma \text{ of particles } > 3.15\text{mm}}{\text{mass of ash in crucible with sample} - \text{mass of empty crucible}} \quad (7)$$

#### 2.4.3 PASSA method and slag index

To predict the slagging tendency of a fuel in a biomass boiler, the PASSA (Pellets ash and slag sieving assessing assessment) method has been developed in the EU project AshMelT and it was further elaborated at TFZ. For each pelletized fuel, the PASSA method was conducted twice. Therefore, 250 g of the respective pelletized fuel were placed in a pre-weighted crucible and thermally treated applying a temperature program as shown in Figure 2 (Nabertherm GmbH, muffle furnace LT15/13/P330). The maximal temperature was 1,000 °C.



**Figure 2:** Temperature programme for the PASSA method.

After the sample had cooled down in a desiccator, it was weighted together with the crucible on an analytic balance with a resolution of 0.001 g (Kern & Sohn GmbH, 572-35). Afterwards, the sample was carefully removed from the crucible using a brush and analysed granulometrically using the sieve set and the sieving machine mentioned in chapter 2.4.2. The empty crucible was weighted again after removing the loose ash fractions. If there was some amount of the sample left sticking to the crucible due to slagging or glazing it was added to the fraction > 3.15 mm. The slag index of the PASSA method was then also calculated applying equation 7.

### 3 RESULTS & DISCUSSION

#### 3.1 Fuel properties, additivation levels and fuel indexes

The results from the fuel analyses of the raw materials are shown in Table III. The pure poplar pellets were produced from the poplar wood chips. Therefore, chemical composition of these fuels was the same.

Based on these results, the additivation levels of the fuels were calculated concerning the fixation of K in aluminium silicates in the ashes. Table II shows the results for the stoichiometric calculations regarding this fixation of K. In this study a safety factor of +12 % or +50 % was used to raise the feasibility that the reactants (potassium and kaolinite) will collide in order to react to potassium silicates. Furthermore, the relative Ca to K

level of the fuel was considered for the choice of the respective safety factor. For wheat straw, grass and sunflower husk the adjusted level I (i. e. a safety factor of +12 %) was selected. For poplar, due to a high Ca/K ratio, and also for grass, the adjusted level II (i. e. a safety factor of +50 %) was additionally applied in the combustion trials (Table II).

**Table II:** Results from the stoichiometric calculations for the fixation of K in the ashes

Parameter	Unit	Poplar	Wheat straw	Grass	Sunflower husk
K	mg/kg fuel d.b.	3,070	8,450	21,200	7,450
K	mole/kg d.b.	0.011	0.216	0.542	0.190
Stoichiometric kaolin level*	w-% d.b.	1.01	2.79	7.00	2.46
Adjusted level I (+12 %)*	w-% d.b.	n.a.	<b>3.12</b>	<b>7.84</b>	<b>2.76</b>
Adjusted level II (+50 %)*	w-% d.b.	<b>1.52</b>	n.a.	<b>10.50</b>	n.a.

\*The calculated levels are based considering that the kaolinite content in the kaolin used was 87 % as well as the moisture content of the fuels. The selected levels for the test runs are marked up in boldface. n.a. fuel not applied in combustion trials

The pelletized fuels (Table IV) showed a high durability of 94.6 to 99.3 w-%. Fines were between 0.0 and 0.3 w-%. Thus, regarding these fuel parameters, pellets were on the same level as wood pellets fulfilling the requirements for ENplus certification [14]. Sunflower husk with 2.8 w-% kaolin showed the lowest durability of 94.6 w-%, followed by pure sunflower husk and pure wheat straw.

For the pure fuels, bulk density was between 625 and 722 kg/m<sup>3</sup> which is in the range stated for ENplus pellets. However, for the additivated or blended fuels, bulk density was higher. For example for sunflower husk with 2.8 w-% kaolin, grass pellets with 8.1 w-% and 10.5 w-% kaolin and the 10 w-% wheat straw / 90 w-% wood blends, bulk density was above 750 kg/m<sup>3</sup>. This might be explained by the mean pellet length, which was shorter for the additivated fuels (data not shown). Therefore, it may be assumed that particle density does not vary significantly between pure and additivated fuels.

The ash content of the raw materials increased from conventional wood pellets (0.3 w-%) to poplar pellets (2.2 w-%), sunflower husk (2.9 w-%), wheat straw (4.3 w-%) and grass pellets I (8.5 w-%, Table IV). By additivation with kaolin, the ash content was distinctly increased for each raw material. For example, for grass pellets with 10.5 w-% kaolin the ash content increased from 8.53 w-% to 15.96 w-%. Such high ash contents can lead to problems for the deashing system of a common biomass boiler.

The gross calorific value of the reference fuel wood pellets was approx. 20,080 kJ/kg (Table IV). Sunflower husk was slightly higher (20,200 kJ/kg) while poplar (19,600 kJ/kg), wheat straw (18,880 kJ/kg) and grass (18,350 kJ/kg) were characterised by a slightly lower gross calorific value. The addition of kaolin reduced this value.

The results on minor and trace elements and on fuel indexes are given in Table V and Table VI. From the results of the produced pure fuels, element composition and fuel indexes of additivated or blended fuels were calculated, using the respective mixing ratios.

**Table III:** Fuel properties of the raw materials used for pelletizing

Parameter	Unit	Wheat straw pellets	Wood pellets	Sunflower husk pellets	Grass pellets	Poplar wood chips/ Poplar pellets
Moisture content	w% w.b.	8.53	5.5	6.9	9.7	7.87
Ash content	w% d.b.	4.27	0.3	2.9	8.5	2.2
Ash content-excl. carbonates	w% d.b.	3.96	0.3	2.4	8.2	1.7
TIC ashed fuel sample	w% d.b.	20,000	51,800	46,3	9,500	70,600
Volatile matter	w% d.b.	77.5	84.3	76.7	72.8	81.0
C	w% d.b.	47.5	50.7	51.3	45.4	49.5
H	w% d.b.	5.8	6.1	6.3	5.8	6.0
N	w% d.b.	0.44	<0.1	0.7	2.5	0.3
Gross calorific value	kJ/kg d.b.	18,880	20,080	20,200	18,350	19,600
Cl	mg/kg d.b.	2,090	64.3	383	3,600	75.0
S	mg/kg d.b.	717	52.1	1,490	2,260	384
Si	mg/kg d.b.	9,460	166	490	9,630	211
Al	mg/kg d.b.	145	25.1	27.8	988	31.2
Ca	mg/kg d.b.	2,860	811	3,810	7,560	6,010
Fe	mg/kg d.b.	117	27.5	83.2	721	55.4
K	mg/kg d.b.	8,450	414	7,450	21,200	3,070
Mg	mg/kg d.b.	767	131	1,910	3,350	554
Mn	mg/kg d.b.	22.2	134	8.6	78.3	9.0
Na	mg/kg d.b.	42.1	14.6	6.4	369	19.9
P	mg/kg d.b.	638	54.7	752	3,610	873
Zn	mg/kg d.b.	6.8	9.0	14.5	28.1	42.3

**Table IV:** Physical parameters of the produced test fuel pellets

Parameter	A <sub>d.b.</sub>	M <sub>a.r.</sub>	LCV <sub>d.b.</sub>	Durability	Fines <3.15 mm	BD <sub>a.r.</sub>	PD <sub>a.r.</sub>
Unit	[w-%]	[w-%]	[MJ/kg]	[w-%]	[w-%]	[kg/m <sup>3</sup> ]	[kg/m <sup>3</sup> ]
Wood pellets pure	0.3	7.9	18.9	99.3	0.00	684	1,316
Wood90 straw10	0.7	7.6	18.8	98.7	0.02	768	1,290
Wood75 straw25	1.3	8.6	18.6	98.0	0.04	722	1,277
Wood50 straw50	2.3	8.3	18.3	98.3	0.03	742	1,433
Wheat straw pellets pure	4.2	8.8	17.5	96.4	0.3	625	1,198
Wheat straw 3.45% kaolin	6.6	8.2	17.1	98.9	0.03	730	1,270
Poplar pure	2.3	8.4	18.4	99.1	0.01	699	1,307
Poplar 1.5% kaolin	3.1	8.6	18.2	98.0	0.04	689	1,403
Sunflower husk pellets pure	2.9	8.4	19.0	96.3	0.03	710	1,291
Sunflower husk 2.8% kaolin	4.8	7.3	18.6	94.6	0.12	766	1,327
Grass pellets pure	8.8	11.3	16.8	98.8	0.01	722	1,330
Grass 8.1% kaolin	13.9	11.0	15.7	98.4	0.03	820	1,297
Grass 10.5% kaolin	16.0	10.2	15.2	98.7	0.02	835	1,307

A: ash content; M: moisture content; LCV: lower calorific value; BD: bulk density; PD: particle density; d.b.: dry basis; a.r.: as received

**Table V:** Minor- and trace-elements of all fuels

Parameter	Si	P	K	Ca	Mg	Al	Cl
Unit	[mg/kg, 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 pure	166	54.7	414	811	131	25.1	64.3
Wood90 straw10*	1,095	113	1,218	1,016	194	37.1	267
Wood75 straw25*	2,489	200	2,423	1,323	290	55.1	571
Wood50 straw50*	4,813	346	4,432	1,836	449	85.1	1,077
Wheat straw pellets pure	9,460	638	8,450	2,860	767	145	2,090
Wheat straw 3.45% kaolin*	17,037	616	8,559	2,811	761	6,531	2,018
Poplar pure	211	873	3,070	6,010	554	31.2	75.0
Poplar 1.5% kaolin*	3,644	860	3,198	5,941	555	2,809	73.9
Sunflower husk pellets pure	490	752	7,450	3,810	1,910	27.8	383
Sunflower husk 2.8% kaolin*	6,891	731	7,567	3,743	1,873	5,214	372
Grass pellets pure	9,630	3,610	21,200	7,560	3,350	988	3,600
Grass 8.1% kaolin*	27,407	3,318	20,424	7,063	3,128	15,912	3,308
Grass 10.5% kaolin*	32,674	3,231	20,194	6,916	3,062	20,334	3,222

\*concentration of minor- and trace-elements were calculated from the analyses of the raw materials and the mixing ratio

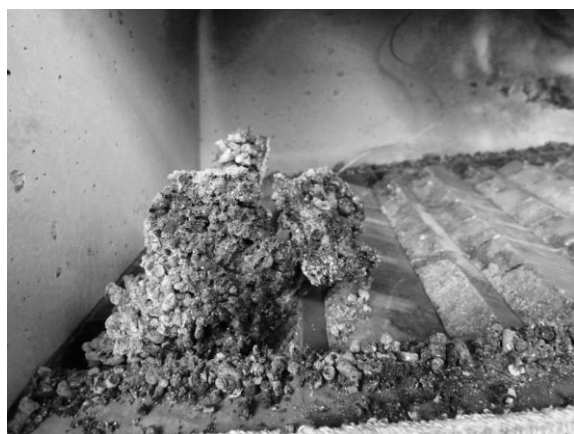
**Table VI:** Fuel indexes calculated for all fuels

Parameter	(Si+P+K)/(Ca+Mg+Al)	Cl/Si	2S/Cl	Si/K	$\Sigma$ (K, Na, Zn)
Unit	[mol/mol]	[mol/mol]	[mol/mol]	[mol/mol]	[mg/kg, d.b.]
Wood pellets pure	0.7	0.3	1.8	0.6	438
Wood90 straw10*	2.1	0.2	1.0	1.3	1,244
Wood75 straw25*	3.3	0.2	0.8	1.4	2,453
Wood50 straw50*	4.4	0.2	0.8	1.5	4,468
Wheat straw pellets pure	5.3	0.2	0.8	1.6	8,499
Wheat straw 3.45% kaolin*	2.5	0.1	0.8	2.8	8,607
Poplar pure	0.7	0.3	11.3	0.1	3,132
Poplar 1.5% kaolin*	0.9	0.0	11.3	1.6	3,259
Sunflower husk pellets pure	1.3	0.6	8.6	0.1	7,471
Sunflower husk 2.8% kaolin*	1.3	0.0	8.6	1.3	7,587
Grass pellets pure	2.8	0.3	1.4	0.6	21,597
Grass 8.1% kaolin*	1.8	0.1	1.4	1.9	20,789
Grass 10.5% kaolin*	1.7	0.1	1.4	2.3	20,550

\*concentration of minor- and trace-elements used for fuel index calculation were calculated from the analyses of the raw materials and the mixing ratio

One important fuel index regarding the combustion performance is the ash melting temperature which is calculated from the molar ratio of (Si+P+K)/(Ca+Mg+Al). This index should be below 2.5 in order to avoid severe slagging, as claimed by SOMMERSACHER et al. (2013) and BRUNNER et al. (2015) [2, 3]. For pure wheat straw, for the straw blends with 75 w-% and 50 w-% wood as well as for pure grass pellets, the index exceeded the ratio of 2.5 which may indicate slagging problems during combustion, Table VI.

Regarding the K-release, the kaolin additivated fuels showed distinctly decreased molar Cl/Si ratios compared to the raw materials for poplar, sunflower husk and grass since kaolin mainly consists of SiO<sub>2</sub>. Thus, according to the theory described by BRUNNER et al. (2015) [3], particle emissions of poplar, sunflower husk and grass with kaolin were expected to be strongly reduced. However, due to its high Si content (compared to grass), wheat straw had a low molar Cl/Si-ratio of only 0.2.



**Figure 3:** Deashing duct of the boiler, blocked by a large piece of slag formed in pure wheat straw combustion

Regarding the sum of aerosol forming elements (K+Na+Zn, only, since Pb was not analysed) the reference fuel (wood pellets) contained 438 mg/kg. Poplar contained 3,132 mg/kg, sunflower husk 7,471 mg/kg and grass pellets 21,597 mg/kg. Therefore, the prospective particle emissions from these fuels should be several times higher than during the combustion of wood pellets.

For the prediction of high temperature corrosion, the molar 2S/Cl-ratio is used and should not be below 2.0. Otherwise, severe corrosion risk may be expected [2,3]. For pure poplar, pure sunflower husk and sunflower husk with 2.8 w-% kaolin only a low risk for high temperature corrosion can be expected since the values are above 8 (Table VI).

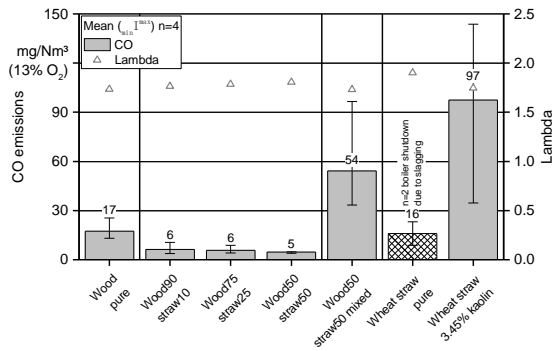
### 3.3 Results of the combustion trials

All fuels were applied in the 30 kW boiler over an 8 h full load operation with exception of pure wheat straw. The pure wheat straw test had to be interrupted due to severe slagging (Figure 3) which occurred after the second particle measurement (180 min). As a result, the boiler could not maintain steady state operation anymore. Therefore no direct comparison of the emissions from pure wheat straw (which is marked differently in the diagrams) and the additivated or blended fuels was possible.

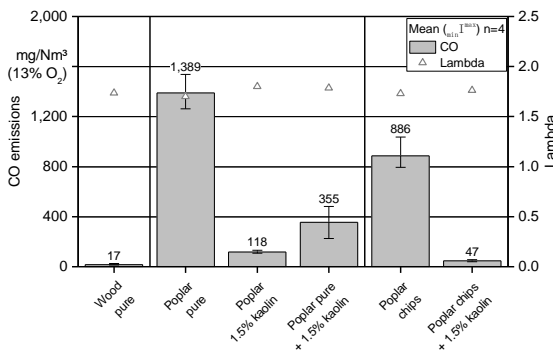
#### 3.3.1 CO emissions

The CO emissions from wood pellets as well as from the wood/wheat straw blends were on a very low level between 17 mg/Nm<sup>3</sup> for pure wood and 5 mg/Nm<sup>3</sup> for all blends (Figure 4). CO emissions even decreased with higher shares of wheat straw. The CO emissions of the blend with 50 w-% wood pellets mixed with 50 w-% pure wheat straw pellets (i. e. "Wood 50 Straw 50 mixed" in Figure 4) were 10 times higher than for the pelletized blends. Variation was also higher (see min and max values). However, results indicate that the combustion conditions were not so stable (high CO peaks spread over the whole trial) for the mixed compared to the pelletized blends. The highest CO emissions for this fuel group were measured for wheat straw with 3.45 % kaolin.

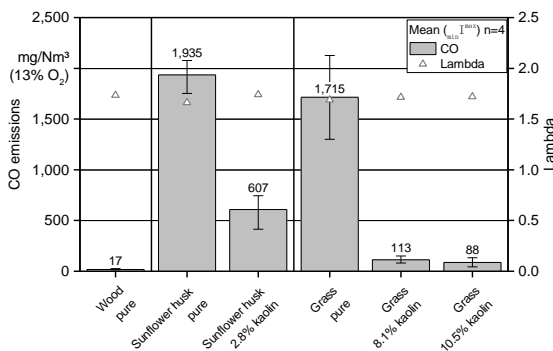
For poplar pellets the CO emissions were approx. 81 times higher and for poplar wood chips approx. 52 times higher than for wood pellets (Figure 5). By additivation of poplar with 1.5 w-% kaolin, the CO emissions were largely reduced by approx. 92 %. When kaolin was added manually to fuels after pelletizing in an additional trial (i. e. "poplar pure + 1.5 w-% kaolin", Figure 5) the CO reduction was still high, i. e. at 74 %. By dosing the kaolin directly to (unpelletized) poplar chips into the screw feeder ("poplar chips +1.5 % kaolin", Figure 5) a reduction of 95 % was observed.



**Figure 4:** CO emissions measured for all fuels containing wood and wheat straw



**Figure 5:** CO emissions measured for all poplar fuels



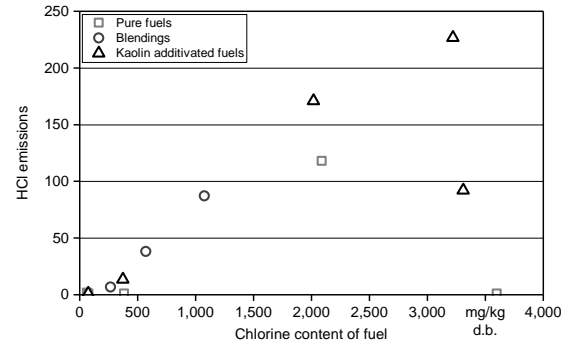
**Figure 6:** CO emissions measured for all sunflower husk and grass fuels.

The same trends were observed for sunflower husk and grass pellets which showed even higher CO levels than poplar (Figure 6). The CO emissions of sunflower husk pellets were reduced by approx. 69 % by adding 2.8 w-% kaolin. For grass pellets, the reduction was 93 % (at 8.1 w-%) and 95 % (at 10.5 w-%).

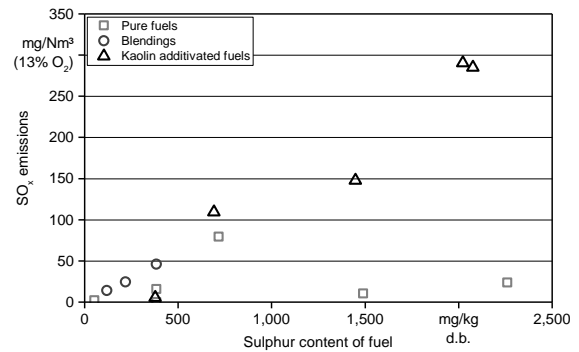
The observed reduction of CO emissions was also indicated by several other researchers using underfed cup burner, grain burner or moving grate burner [3,15,16]. Only in one case, increased CO emissions had been measured (with a cereal burner) [17]. One reason for CO reduction could be a catalytic effect of kaolin as it is used as a catalyst in other fields of application such as synthesis of 1,5-Benzodiazepines or for CO<sub>2</sub> photocatalytic reduction [18,19]. On the other hand, the fire bed structure is expected to be improved by the embedment of K-silicates in the ash and. Therefore, it can be assumed that channelling and formation of CO layers is prevented in a more homogeneous fire bed.

### 3.3.3 HCl and SO<sub>2</sub> emissions

Due to the better embedding of K in the bed ash (see chapter 2.3), less reaction partners for Cl and S during aerosol formation were available and, consequently, HCl (Figure 7) and SO<sub>2</sub> (Figure 8) emissions were increased for the kaolin additivated fuels [3,16,20].



**Figure 7:** HCl emissions as a function of chlorine content in the fuel



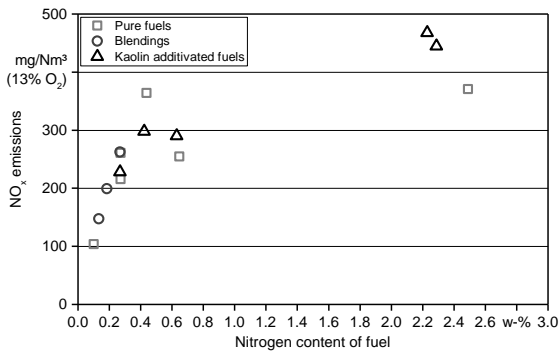
**Figure 8:** SO<sub>2</sub> emissions as a function of sulphur content in the fuel

For the fuel blends (wood / wheat straw), a dilution of the chlorine and sulphur content in the fuels was observed, resulting in lower HCl and SO<sub>2</sub> emissions compared to pure wheat straw [21].

### 3.3.4 OGC and NO<sub>x</sub> emission

For the organic gaseous carbon (OGC) emissions (data not shown) no clear trend was observed between pure and kaolin additivated fuels. The highest OGC emissions were detected for pure sunflower husk (18.8 mg/Nm<sup>3</sup>) and for sunflower husk additivated with 2.8 w-% kaolin (45.1 mg/Nm<sup>3</sup>).

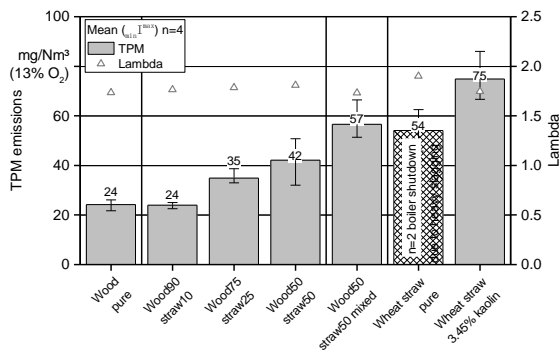
The NO<sub>x</sub> emissions (Figure 9) increased with increasing nitrogen content in the fuels. For fuels with high nitrogen contents (e. g. in grass), the conversion rate from fuel nitrogen to NO<sub>x</sub> decreased [22]. For the kaolin additivated fuels, the NO<sub>x</sub> emissions increased except for pure wheat straw. The deviation between the NO<sub>x</sub> emissions of the pure and additivated fuel is increasing with the nitrogen content of the fuel (by 5.5 to 26 %). The negative effect of kaolin on NO<sub>x</sub> emissions was also observed by other researchers [15,16] and in a previous project at TFZ when kaolin additivated beech pellets were fired in a pellet boiler. The mechanism behind this is still unknown and further investigations are needed to get a detailed explanation about the negative impact of kaolin on NO<sub>x</sub> emissions.



**Figure 9:** NO<sub>x</sub> emissions as a function of nitrogen content in the fuel

3.3.1 Total particle matte emissions

Total particulate matter (TPM) emissions of wood pellets, wheat straw blends, pure wheat straw and additivated wheat straw are summarized in Figure 10. As expected, the lowest values were achieved for wood pellets emitting 24 mg/Nm<sup>3</sup> of TPM during full load operation, which is close to the TPM emission threshold value of 20 mg/Nm<sup>3</sup>, i. e. the TPM emission limit of the 1. BImSchV (First ordinance of the German emission control act) [23].

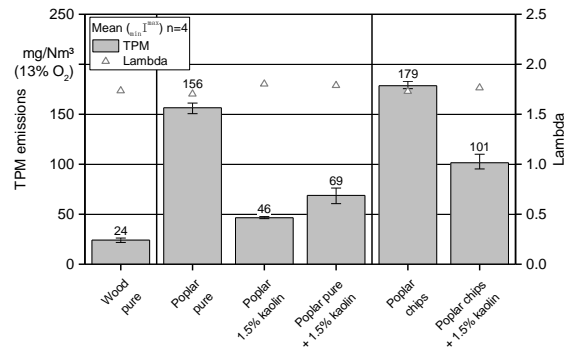


**Figure 10:** TPM emissions for all fuels containing wood and wheat straw

Blending of wheat straw with wood reduced TPM emissions compared to pure straw (Figure 10). A blend with 90 w-% pure wood caused nearly the same particle emissions as for pure wood pellets. Moreover, the process of fuel blending, i. e. whether fuel blending is performed before or after pelletization, was relevant. When already produced wheat straw and wood pellets were mixed at a ratio of 50:50 (i. e. “Wood 50 Straw 50 mixed” in Figure 10) TPM emissions of 57 mg/Nm<sup>3</sup> were released. In contrast, lower emissions of only 42 mg/Nm<sup>3</sup> were achieved, when the same fuel ratio was realized in the raw material before pelletization (i. e. “Wood 50 Straw 50” in Figure 10).

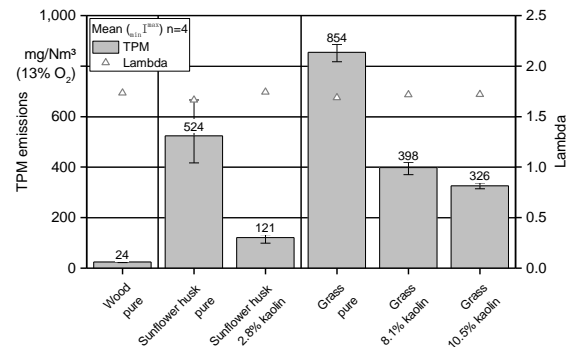
Due to the above mentioned slagging related problems with pure wheat straw pellets, no direct comparison between this test run and the blended and additivated fuels was possible. Particle emissions of wheat straw with 3.45 w.-% kaolin were 75 mg/Nm<sup>3</sup> on average, which is clearly higher than for all straw/wood blends. However, with kaolin additivated straw pellets, the boiler could be operated over 8 h without any slag related problems indicating clear benefit of additivation or blending compared to pure fuels.

For pure poplar pellets, the particle emissions were on average 156 mg/Nm<sup>3</sup> and therefore 6.5 times higher compared to wood pellets (Figure 11). By additivation of 1.5 w.-% kaolin, the particle emissions were reduced by approx. 71 % down to 46 mg/Nm<sup>3</sup>. By adding 1.5 w.-% kaolin to poplar pellets after pelletizing (i. e. “Poplar pure + 1.5 % kaolin”), TPM was reduced down to 69 mg/Nm<sup>3</sup>. During the combustion of poplar wood chips, the particle emission was slightly higher compared to poplar pellets. By the direct additivation of kaolin to poplar wood chips via dosing to the screw feeder (i. e. “Poplar chips +1.5 % kaolin”), TPM could be reduced by 44 % compared to pure poplar chips.



**Figure 11:** TPM emissions for pure wood pellets and poplar fuels

Figure 12 shows the particle emission measured for all sunflower husk and grass pellets. Compared to wood pellets, the particle emissions for pure sunflower husk pellets were 22 times and for pure grass pellets almost 36 times higher. By additivation with kaolin, the particle emissions for sunflower husk were reduced by 77 % (2.8 w.-% kaolin) and for grass by 53 % (8.1 w.-% kaolin) and 62 % (10.5 w.-% kaolin), respectively.



**Figure 12:** TPM emissions for pure wood pellets and all sunflower husk and grass pellets

At this extremely high level of particle emissions, especially for pure sunflower husk and pure grass pellets, the additivation with kaolin alone cannot be the solution for low emission combustion in small scale biomass boilers as emission levels were still very high. However, kaolin might be an option to reduce dust pollution in the raw gas entered into a dust precipitator, which could then work more effectively.

### 3.4 Ash analyses and slagging behaviour of the pelletized fuels

All ash residues were collected from each combustion trial. The total amount of ash from an 8 hours full load operation plus approx. 2 h starting and preheating phase was between 0.2 kg for wood pellets and 16.6 kg for grass pellets with 10.5 % kaolin (Table VII). To cope with such high masses of ash, the ash box of the boiler had to be emptied after approx. 4 h of full load operation when grass containing fuels were applied. This means that for such fuels a boiler should be equipped with a large ash box or a powerful deashing system.

Table VII shows the particle size distribution of the collected ashes. For the wood / straw blends, the fraction of particles larger than 3.15 mm increased gradually with higher shares of wheat straw, i. e. from 18.9 w-% for pure wood pellets up to 81.4 w-% for pure wheat straw. Additivation with kaolin reduced the fraction > 3.15 mm for pellets from wheat straw, poplar and sunflower husk. In contrast, for grass containing pellets this ash fraction increased with higher kaolin content.

**Table VII:** Results from the granulometric analysis of the boiler ashes (grate ash + fly ash)

	Total amount of ash kg <sup>a, w.b.</sup>	> 3.15 mm	> 2.0 mm	> 1.0 mm	> 0.5 mm	< 0.5 mm
		w-% w.b.				
Wood pure	0.20	18.9	15.8	50.1	10.3	4.9
Wood90 straw10	0.52	43.3	9.2	38.8	6.7	2.0
Wood75 straw25	0.98	71.4	5.7	16.0	5.3	1.7
Wood50 straw50	1.85	78.8	5.5	11.2	3.4	1.0
Wheat straw pure	2.42	81.4	8.8	7.6	1.9	0.4
Wheat straw 3.1% kaolin	6.08	58.9	14.3	13.6	8.6	4.7
Poplar pure	1.42	72.6	7.4	12.6	4.9	2.4
Poplar 1.5% kaolin	2.48	49.8	10.7	31.5	6.4	1.6
Sunflower husk pure	1.70	70.9	8.7	10.2	6.4	3.8
Sunflower husk 2.8% kaolin	3.69	65.4	5.5	22.6	5.1	1.4
Grass pure	6.77	61.0	9.7	14.7	7.5	7.2
Grass 8.1 % kaolin	13.46	71.6	5.2	7.1	6.5	9.6
Grass 10.5 % kaolin	16.64	85.1	2.0	2.4	3.3	7.3

<sup>a</sup> values are presented on as received basis; w.b.: wet basis

In direct comparison, the slag index calculated by the PASSA method and the slag index calculated by the boiler ashes (Table VIII) are showing very similar results for wood pellets. For pure agricultural fuels, the wood / straw blends and the kaolin additivated fuels, the slag index calculated for the boiler ashes seems to distinguish more precisely between the different fuels than the slag index according to the PASSA method. This could be due to a lower bed temperature in the boiler due to cooling by the primary air through the grate. As a consequence, for some fuels, the PASSA method (in the current stage of development) is indicating contrary slagging tendencies compared to the slag index for the boiler ashes regarding the effect of kaolin.

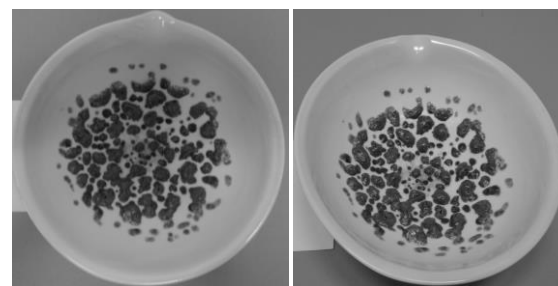
The results of the visual classification of the ashes from the boiler tests (Table VIII) are very subjective and depend largely on the person who performs the test. Nevertheless, these results are more in line with the slag index for the boiler ashes. Still, visual inspection did not allow for any differentiation between the wood / straw blends and the pure straw pellets. It also leads to contrary results regarding the additivation of poplar with kaolin.

One interesting aspect is the share of slag which remains sticking to the crucible after performing the

PASSA method. While in case of pure wheat straw and pure grass pellet approx. 100 w-% of the sample remained sticking to the crucible (Figure 13), this share was drastically reduced to only 1 w-% (Figure 14) when additivation with kaolin was applied (Table VIII). This was due to the fact that for wheat or grass fuels that were additivated with kaolin, the residues after the PASSA treatment in the crucibles did not turn into a small heap of loose particles but they rather retained their original cylindrical pellet shape while having been transferred into a very fluffy and soft mode with no particles sticking to the crucible (Figure 13, Figure 14). These sintered “ash pellets” were hard enough to not fall apart by a light touch (sintering degree 2a) but they were at the same time easily breakable by hand (sintering degree 2b–3, see definitions in Table I).

**Table VIII:** Sintering degree and slag index for boiler ashes and slag index and share of ash sticking to the crucible for the PASSA method

	Visual classification of boiler ash	Slag Index boiler	Slag index PASSA	PASSA: Slag share sticking to crucible w-% w.b.
Wood pure	2a	0.24	0.26	19
Wood90 straw10	4	0.43	1.00	100
Wood75 straw25	4	0.71	1.00	100
Wood50 straw50	4	0.79	1.00	100
Wheat straw pure	4	0.81	1.00	100
Wheat straw 3.1% kaolin	3	0.59	0.97	1
Poplar pure	2a	0.73	0.49	24
Poplar 1.5% kaolin	2b	0.50	0.70	1
Sunflower husk pure	2b	0.71	0.41	26
Sunflower husk 2.8% kaolin	2a	0.65	0.69	1
Grass pure	2a	0.61	1.00	100
Grass 8.1% kaolin	3	0.72	0.99	1
Grass 10.5% kaolin	3	0.85	0.99	0



**Figure 13:** Pure wheat straw after performance of the PASSA test (left) and after cleaning the crucible by brush (right)



**Figure 14:** Wheat straw with 3.15 % kaolin after performance of the PASSA test (left) and after cleaning of the crucible by a brush (right)



For moving grate boilers or boilers with a comparable effective deashing system only a low risk of operational disturbance is to be expected even for fuels with such "severe" sintering classification into class 2b or 3. However, if such fuels are applied in cup burners or fixed grate burners, their performance could be limited, as those softly sintered ash pellets might be problematic for the deashing system, as they could lead to bridging or piling up in the burner or be blocking the air inlet nozzle. Therefore, the evaluation methods of slagging tendencies such as the PASSA method should be revised to distinguish between the complete melting of the sample (share of slag sticking to the crucible) which could cause trouble in all kinds of boilers (as seen for pure wheat straw) and the loose but sintered fraction > 3.15 mm which is not sticking to the crucible and should, thus, be uncritical for moving grate or comparable boilers.

Slagging of fuel blends was also assessed (Table VIII). Blending of wheat straw with wood pellets can slightly reduce slagging problems. However, only for a blend with high wood content (90 w-%) a distinct reduction of slagging was observed [24].

#### 4 CONCLUSIONS

The following conclusions can be drawn from the presented findings.

- Additivation of "difficult" agricultural fuels with kaolin is an interesting option to reduce CO emissions and total particulate emissions (TPM) from aerosol forming elements as they occur in complete combustion of agricultural fuels.
- However, for many agricultural fuels, additivation alone will usually not be a sufficient enough measure to reduce TPM below strict emission threshold limits of national legislation. Still, performance of any additional particle precipitator will be strongly improved by kaolin additives.
- The CO- and TPM reduction is associated with some disadvantages. Kaolin additivation has the effect that at a lower degree of the chlorine and sulphur content in the fuel will be embedded into the ash. As a consequence, Cl and S will rather be released as HCl and SO<sub>2</sub>, respectively. In the presented study, the threshold for SO<sub>2</sub> emissions by the European MCP (medium plant combustion) directive (200 mg/Nm<sup>3</sup> based on 6 % O<sub>2</sub>, resp. 107 mg/Nm<sup>3</sup> based on 13 % O<sub>2</sub> [25]) is exceeded for wheat straw, sunflower husk and grass pellets, if pellets were additivated with kaolin. For HCl emissions, there is no threshold at the given moment [25].
- The increased HCl and SO<sub>2</sub> release will raise the risk of high temperature corrosion which needs to be considered in plant design where corrosion resistant materials need to be chosen.
- Consequently the use of additives in fuels for small scale furnaces seems most promising for problematic but low chlorine and low sulphur containing wood fuels, such as poplar fuels from short rotation coppices.
- For the wheat straw fuels, fuel blends seem to

be a better option than additives, as by blending the negative impact of higher HCl and SO<sub>2</sub> emissions can be avoided. This was also confirmed by other researchers [21].

- The results display a moderate increase of NO<sub>x</sub> emissions for the additivated fuels, except for wheat straw. This increase might lead to a violation of European NO<sub>x</sub> emission limits. From the results shown here, the threshold for NO<sub>x</sub> emissions of the EU MCP directive for new combustion plants (500 mg/Nm<sup>3</sup> based on 6 % O<sub>2</sub> resp. 267 mg/Nm<sup>3</sup> based on 13 % O<sub>2</sub>) would be exceeded for most fuels except for pure wood pellets. This means that for new plants, an advanced NO<sub>x</sub>-reduction measure is needed for nearly all agricultural fuels.
- The additivation of the fuels with kaolin reduces slagging in terms of the formation of larger slag agglomerates. At the same time, the remaining ash keeps the original pellet shape. This may be no problem for moving grate boilers or boilers with an adequate deashing system as such systems are generally expected to have a minor problem with extremely high ash contents in fuels. However, the formation of softly sintered "ash pellets" might create problems in cup burners (as applied in pellet stoves) or in fixed grate burners.
- Blending of wheat straw with wood is a weak measure to reduce slagging of pellets substantially. Only for a blend with very high wood content (i. e. 90 w-% wood) a distinct reduction of slagging is expected.
- The PASSA method seems to be a suitable simplified method for the prediction of slagging tendencies of wood and agricultural fuels. However, further development and specifications are necessary to avoid misleading interpretation of results for additivated agricultural fuels.
- Regarding the pelletisation process, heavy wear of the dies and rollers was observed which was caused by kaolin additives (data not shown). This will lead to higher costs for fuel processing.

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## 6 ACKNOWLEDGMENTS

- This research was funded by Federal Ministry of Agriculture by decision of the German Bundestag with the Fachagentur Nachwachsende Rohstoffe e. V. (FNR) as project executing organization.

Gefördert durch:



aufgrund eines Beschlusses  
des Deutschen Bundestages

- We thank our colleagues Benedikt Haas, Albert Maierhofer, Elisabeth Rist and Stefan Winter for their support during this study.
- We also thank our project partners for the good support and cooperation within the project BioFlex!.

## 7 LOGO SPACE



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