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Investigation of the combustion behavior of pulp pellets in a domestic pellet boiler

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Daniel Bernhardt, Kathrin Gebauer, Martin Pohl, Michael Beckmann
Technical University Dresden, Institute of Power Engineering, Chair for Combustion, Heat and Mass Transfer, 01062 Dresden – Germany;
e-mail: daniel.bernhardt@tu-dresden.de

1 Abstract

In the last years the importance of energetic biomass utilization has strongly increased. Especially in combustion plants for the local energy supply, mostly wood based biomass like split logs, wood chips and pellets are used. It can further be assumed that the demand for woody biomass will grow in future. Parallel to this, an increasing competition of energy and material utilization can be expected. To counteract this conflict other biomasses and biogenic residues, like agricultural and industrial residues can be considered. In comparison to woody biomass, the fuel properties of these residues, however, differ considerably. In existing combustion units especially the main ash forming elements lead to operational problems like slagging, fouling and corrosion. In order to still use these alternative fuels a modification of the combustion technology or the fuel properties can be applied. Lab scale investigations have shown that the addition of calcium hydroxide to high sodium containing pulp pellets leads to a significant improvement of the ash melting behavior. The main focus of this contribution is the investigation of the combustion behavior of calcium hydroxide modified pulp pellets in a 15 kW pellet boiler. Especially the impact of the additive content on the slagging and emission behavior of the pulp pellets in comparison to wood pellets is presented.

2 Introduction

To substitute fossil fuels the energetic use of biomass has been intensified during the past years. Mainly in decentralized biomass boilers of small and middle thermal capacity an increasing acceptance can be observed in the domestic and the industrial sectors. Especially the demand for wood pellets which are mainly produced from industrial waste wood has increased. The availability of wood waste raw material constitutes a limiting factor. Due to these developments, alternative fuels come into focus. In terms of cascade utilization agricultural and industrial residues have a potential as alternative fuels if another material utilization is impossible. However, these residues are not standard fuels. For example straw and herbaceous residues have high amounts of alkali like potassium and sodium resulting in an unfavorable ash melting behavior. The combustion of potassium and sodium rich fuels often leads to operational problems like slagging and fouling. One way to influence the adverse fuel properties is the modification of the raw material. Various measures to reduce slagging behavior of different biomass fuels were examined in [1-6].
The impact of different fuel modification methods on the slagging behavior of high sodium containing pulp residues was investigated in [7] with the aid of experimental lab scale investigations. Especially the addition of calcium containing additives (e. g. $Ca(OH)_2$ and $CaCO_3$) and the leaching of the pulp material with organic acids (e. g. formic acid, acetic acid) resulted in a significant improvement of the ash melting behavior of the pulp. In contrast, the prepa-

ration of various blends of wood as well as the pyrolysis of the raw material did not lead to the same significant improvement of the ash melting behavior. The results presented in [7] represent only an estimation of the real slagging behavior when using modified pulp pellets in small scale pellet boilers. The influence of real operation conditions (e. g. local temperatures, local reducing or oxidizing conditions in solid fuel bed) can result in a different slagging behavior than determined with lab scale investigations. Therefore, combustion tests in a real combustion unit are necessary to determine the impact of the fuel modification method on the combustion behavior. In this article the impact of different blends of pulp and $Ca(OH)_2$ on the combustion behavior will be investigated in a domestic pellet boiler.

3 Fuel properties

Based on the laboratory tests carried out in [7] three mixtures of pulp and $Ca(OH)_2$ (2, 3 and 5 wt.-% $Ca(OH)_2$) were produced and finally pelletized. The fuel properties of the pellets were subsequently analyzed using standardized analytical methods. Major results of the fuel analysis are shown in Table 1 in comparison to commonly used wood pellets.

Table 1: Fuel properties of pulp pellets blended with $Ca(OH)_2$ in comparison to wood pellets

				Wood pellets	**Pulp pellets+2% $Ca(OH)_2$**	**Pulp pellets+3% $Ca(OH)_2$**	**Pulp pellets+5% $Ca(OH)_2$**
1. Chemical properties							
Moisture	w	w. b.	wt.-%	4.81	4.,43	3.15	2.,81
Ash (550 °C)	a	d. b.	wt.-%	0.34	7.24	5.92	9.30
Volatile	v	d. b.	wt.-%	84.04	81.57	82.53	80.97
Carbon	C	d. b.	wt.-%	51.27	46.41	46.99	45.45
Hydrogen	H	d. b.	wt.-%	6.03	6.34	6.61	7.03
Oxygen	O	d. b.	wt.-%	42.19	39.86	40.39	42.76
Nitrogen	N	d. b.	wt.-%	0.17	0.14	0.08	0.07
Sulphur	S	d. b.	wt.-%	0.01	0.01	0.01	0.01
Chlorine	Cl	d. b.	wt.-%	0.05	0.42	0.17	0.33
C/H	-	d. b.	wt.-%	8.50	7.32	7.11	6.47
Ash composition							
Aluminum oxide	Al_2O_3	d. b.	wt.-%	1.03	1.78	1.18	0.42
Sodium oxide	Na_2O	d. b.	wt.-%	4.25	47.07	65.06	54.18
Potassium oxide	K_2O	d. b.	wt.-%	12.44	0.01	<0.013	<0.013
Calcium oxide	CaO	d. b.	wt.-%	31.89	8.42	26.05	29.96
Iron oxide	Fe_2O_3	d. b.	wt.-%	1.95	0.33	0.28	0.63
Magnesium oxide	MgO	d. b.	wt.-%	8.66	0.42	0.76	0.66
Phosphorus oxide	P_2O_5	d. b.	wt.-%	4.42	1.03	0.88	0.85
Silicon dioxide	SiO_2	d. b.	wt.-%	5.05	0.65	1.76	1.15
Ash melting behavior							
Deformation temperature (DT)	ϑ_{DT}	-	°C	1044	780	795	1035
Hemisphere temperature (HT)	ϑ_{HT}	-	°C	>1450	885	1250	>1450
Flow temperature (FT)	ϑ_{FT}	-	°C	>1450	1000	>1450	>1450
2. Mechanical properties							
Fine fraction (<3,15 mm)	ξ_{Fine}	w. b.	wt.-%	< 1.0	2.47	4.41	5.13
3. Calorific properties							
Calorific value	h_u	w. b.	MJ/kg	18.37	16.33	16.92	16.39
		d. b.	MJ/kg	19.36	17.20	17.55	16.94

The comparison of wood pellets and the three modified pulp pellets shows, that ash and chlorine content is higher for the modified pulp pellets. In contrast the nitrogen content is lower for the modified pulp pellets. Considering the ash melting behavior the pulp pellets with a

$Ca(OH)_2$ fraction of 5 wt.-% have nearly the same deformation temperature as the wood pellets. The calorific value of all modified pulp pellets is less than the wood pellets.

4 Experimental setup and test procedure

To investigate the combustion behavior of the modified pulp pellets a pellet boiler test rig was used. The core of this test rig is a pellet boiler which is widely used in the domestic heat supply sector of Germany and Austria. The nominal heat output of the pellet boiler is 15 kW_{th}. The flue gas produced during the combustion process leaves the boiler through a connected flue gas measuring channel which is used for the measuring of the emission conditions (temperature, draft, gas velocity, particle concentration and particle size distribution). The heat which is transferred to the boiler water is then transferred to the environment by an air cooled heat exchanger. For the determination of the recovered heat quantity a flow meter and two thermocouples are installed in the heat output channel.

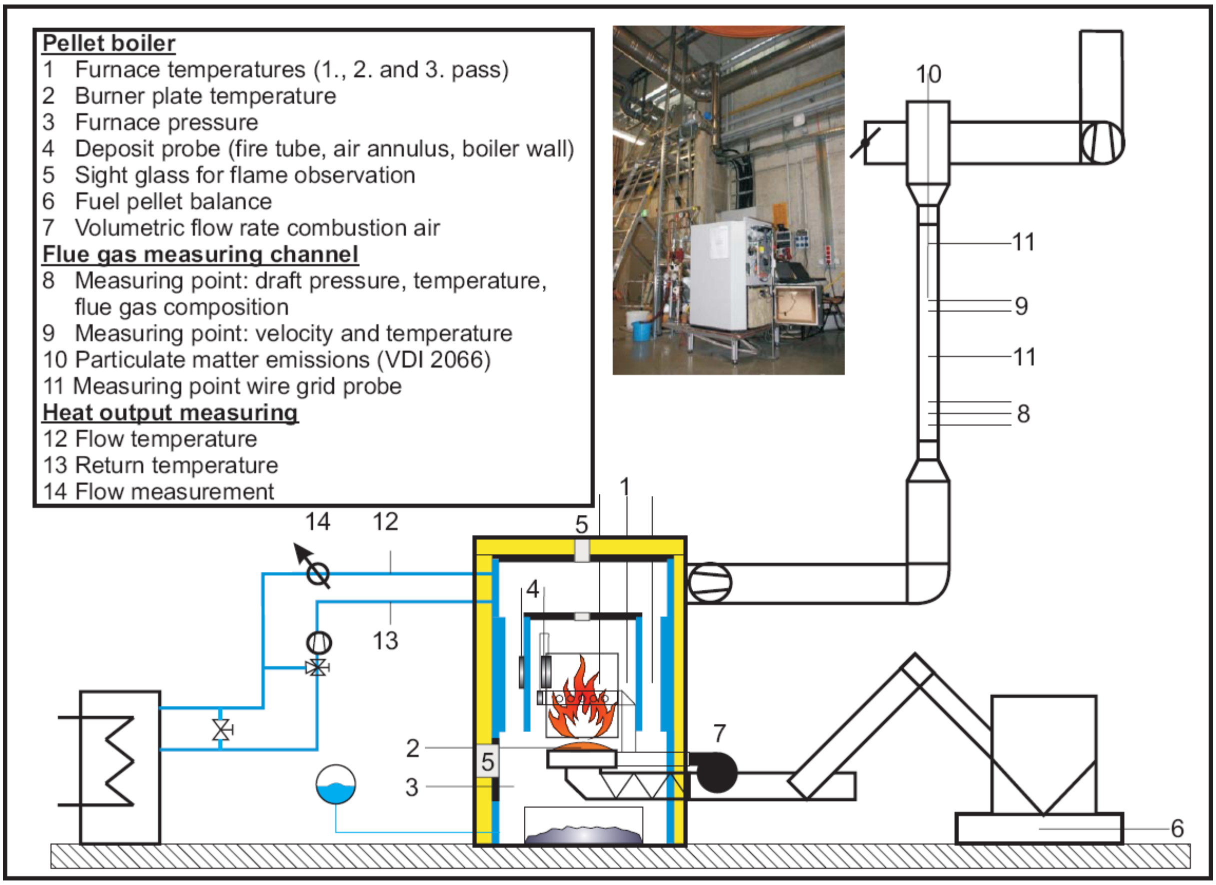

Figure 1: Pellet boiler test rig

Starting from a reservoir the pellets are fed to an underfeed burner by a stoker screw. The burner consists of a burner plate where the solid combustion takes place with the zones drying, degassing and char burn out. To realize a nearly complete solid fuel burn out, primary air is fed into the bed of embers through radially arranged holes. The ash gets discharged at the edge of the burner plate and falls into an ash box placed underneath. On the burner plate the air ratio is substoichiometric mainly to reduce the NO_x emissions since the formation of N_2 occurs preferably in substoichiometric conditions. Degassing products which are released in the primary combustion zone are finally oxidized in the secondary combustion zone which is technically achieved by a flame tube (first pass) located above the burner plate. For complete gas phase combustion, radially arranged nozzles mix the degassing products with secondary air. The heat transfer of the exhaust gas to the boiler water occurs downstream in the second and third pass. To control the combustion behavior, thermocouples are installed in all three passes. The furnace pressure is measured by a differential pressure sensor. In order to observe the fuel bed and the flame, temperature-resistant inspection glasses are installed. The control of essential furnace parameters, such as the amount of combustion air and fuel, is accomplished by a Siemens PLC. For detection of emission relevant flue gas constituents the gaseous components O_2, CO_2, NO_x and CO were continuously monitored and recorded. In addition, particulate matter emissions can be determined by a discontinuous measurement of particle concentration and particle size distribution (VDI 2066).

In order to compare the combustion behavior of the modified pulp pellets, initially experiments with wood pellets were carried out. Subsequently, modified pulp pellets with decreasing $Ca(OH)_2$ content were used. At the end of the experiments non-modified pulp pellets without $Ca(OH)_2$ were used. During the operational time the above described measurements were recorded continuously. After a quasi-stationary operating state was achieved over a period of 30 min, a partial volume flow of the flue gas was removed isokinetically. From the mass of the extracted particles the mass concentration of the particulate emission was determined. Similarly, the particle size distribution was determined by a 3-stage GMU-Cascade Impactor Johnas II (PM 10 and PM 2.5). To get information about the chemical particle composition SEM-EDX analyses were carried out. After each test run ash samples were taken from the ash box and the burner plate. From these samples the slag content was determined by a sieve analysis (DIN EN 15149-1).

5 Results combustion experiments

Process conditions and pollutant emissions

Figure 2 shows exemplarily the furnace temperatures in the three passes and the gaseous flue gas composition for the combustion of pulp pellets with 5 wt. -% $Ca(OH)_2$. For the other modified pulp pellets a similar behavior was observed. For an operational time of more than 8 h a trouple-free and stable operating state was established for all modified pulp pellets. The apparent fluctuations in the measured variables are caused by the pulsed underfeeding stoker screw. On the one hand it is noticeable that compared to wood pellets the furnace temperature (1. pass) for the pulp pellet combustion is nearly 250 °C lower. This is caused by the lower calorific value of the pulp pellets (Table 1). Also, the high residual oxygen content (14 Vol.-%) of the flue gas is noticeable. This is caused by an over-stoichiometric combustion which is typical for that kind of pellet boilers to ensure a total oxidization of the fuel. The disadvantage of that operation mode is that lower furnace temperatures are reached, since the nitrogen of the combustion air needs be heated too.

For the unmodified pulp pellets an operation time of only 3.5 h was established. The reason for this effect was the formation of a molten ash phase which was frozen on new pellets. This seriously affected the degassing of the pellets which subsequently led to the extinction of the flame.

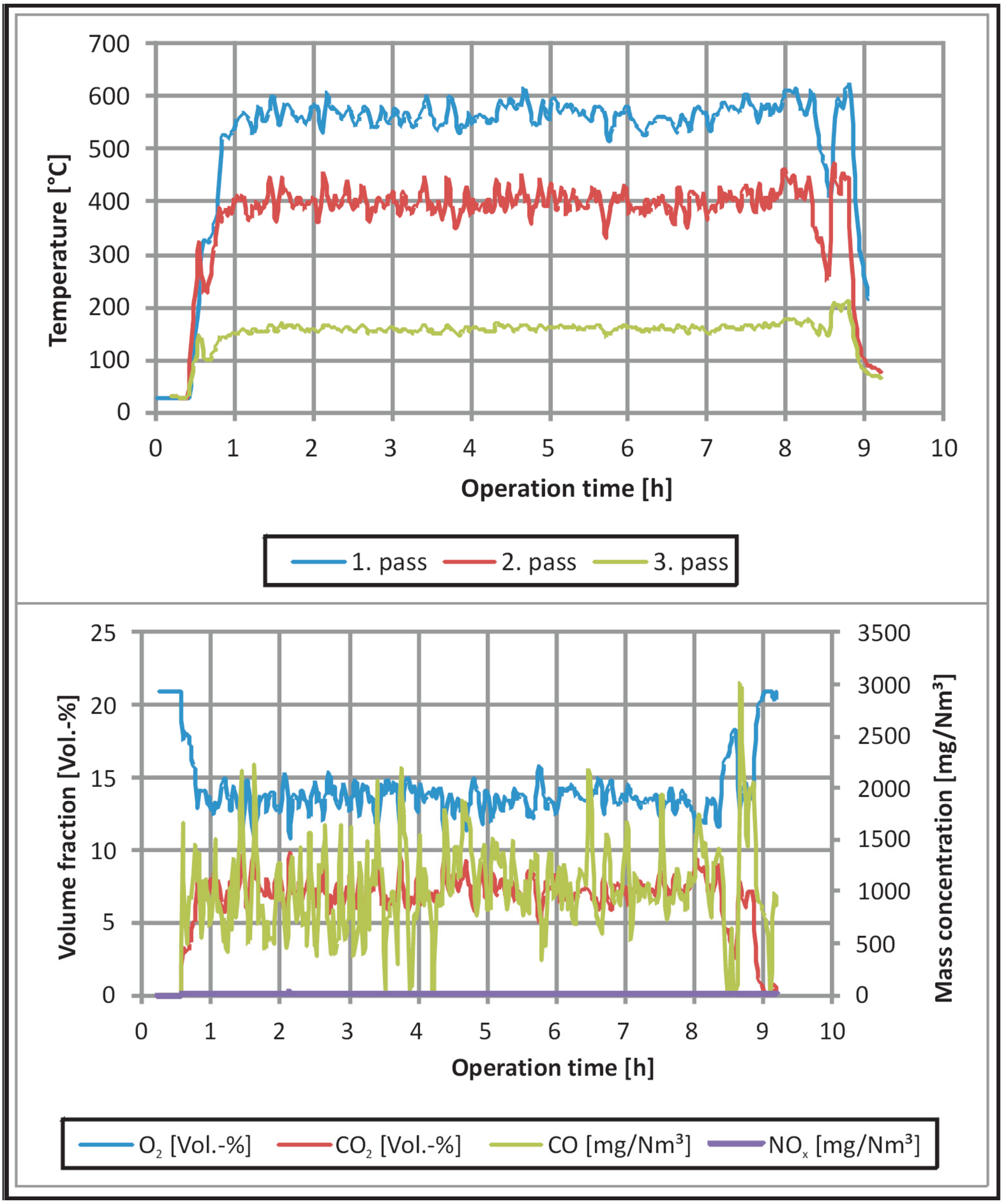

Figure 2: Furnace temperatures and flue gas composition for combustion of pulp pellets + 5 wt.-% $Ca(OH)_2$

For a better comparison of the pollutant emissions Figure 3 shows the average values of the quasi-stationary operation mode in relation to that of wood pellets and to the limit values for

German small and medium scale combustion plants (1. BImSchV) (1). It becomes clear that the pulp pellets with and without $Ca(OH)_2$ have significantly higher CO and particulate matter emissions than that of wood pellets. Both flue gas pollutants also exceed the limit values for wood pellets. For a $Ca(OH)_2$ content of 5 wt-% the CO limit value is only slightly exceeded for straw pellets. It is also noticeable that the CO emissions decrease with an increasing additive content. The NOx emissions are however lower than for wood pellets.

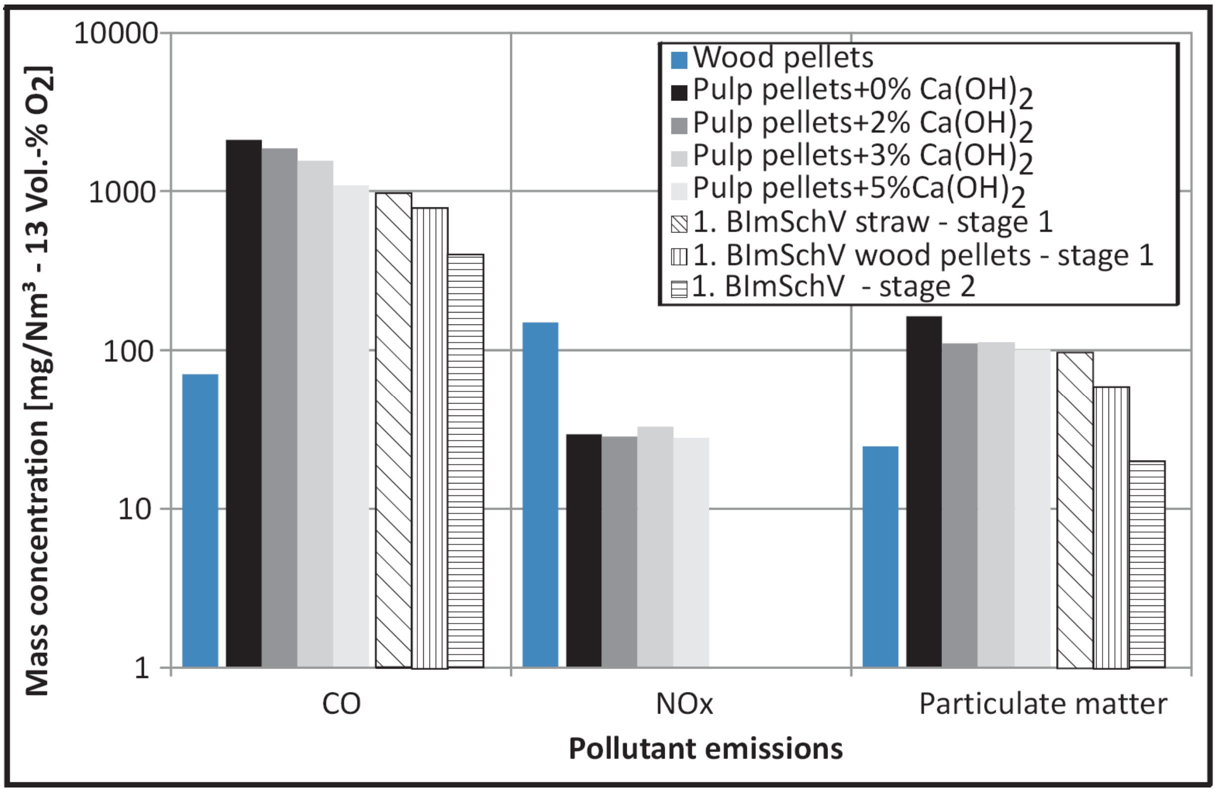

Figure 3: Average values of flue gas emission components in comparison to limit values of the 1. BImSchV

The high amounts of CO are caused by the interaction of several main influencing factors-especially the low furnace temperature (see Figure 2) and the residence time of the gases in this zone. An unfavorable distribution of primary and secondary combustion air and an unfavorable mixing of secondary air and degassing products in the flame tube are also really important. Geometric modifications to the boiler design would lead to a reduction of the CO emissions. An aerodynamically optimized and thermally insulated secondary combustion chamber would lead to better mixing of the combustion air and degassing products and to higher furnace temperatures. The high concentration of particulate matter is caused by the ash content and the high fine fraction of the pulp pellets (see Table 1).

In addition to the particle concentration, the particle size is of great importance for the hazardous effect of the particulate matter emissions. Figure 4 exemplarily shows the particle size distribution determined with a 3 stage cascade impactor for the combustion of pulp pellets+5 wt. % $Ca(OH)_2$ in comparison to wood pellets. As shown, 98 % of the particles have an

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(1) Depending on the fuel a distinction of the limit values is carried out. The lowest limit values apply to wood pellets. The highest limit values apply to alternative fuels, such as straw or grain.

aerodynamic diameter of $d_{ae} < 2.5$ µm(2). In general all particles smaller than $d_{ae} = 10$ µm are respirable and can result in negative health effects. A significant difference between both pellet fuels is not detectable.

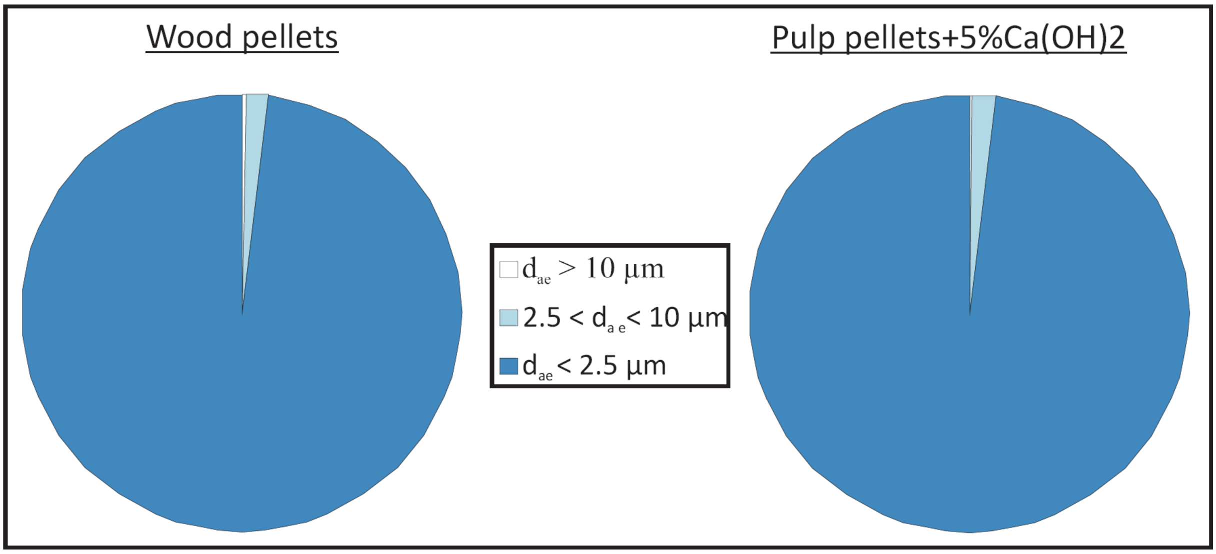

Figure 4: Particle size distribution of particulate matter emissions for wood pellets and pulp pellets + 5 wt.-% $Ca(OH)_2$

To determine the chemical composition of the particles, scanning electron microscopic studies (SEM-EDX) were carried out. For the most common particle fraction of $d_{ae} < 2.5$ µm the results are shown in Figure 5.

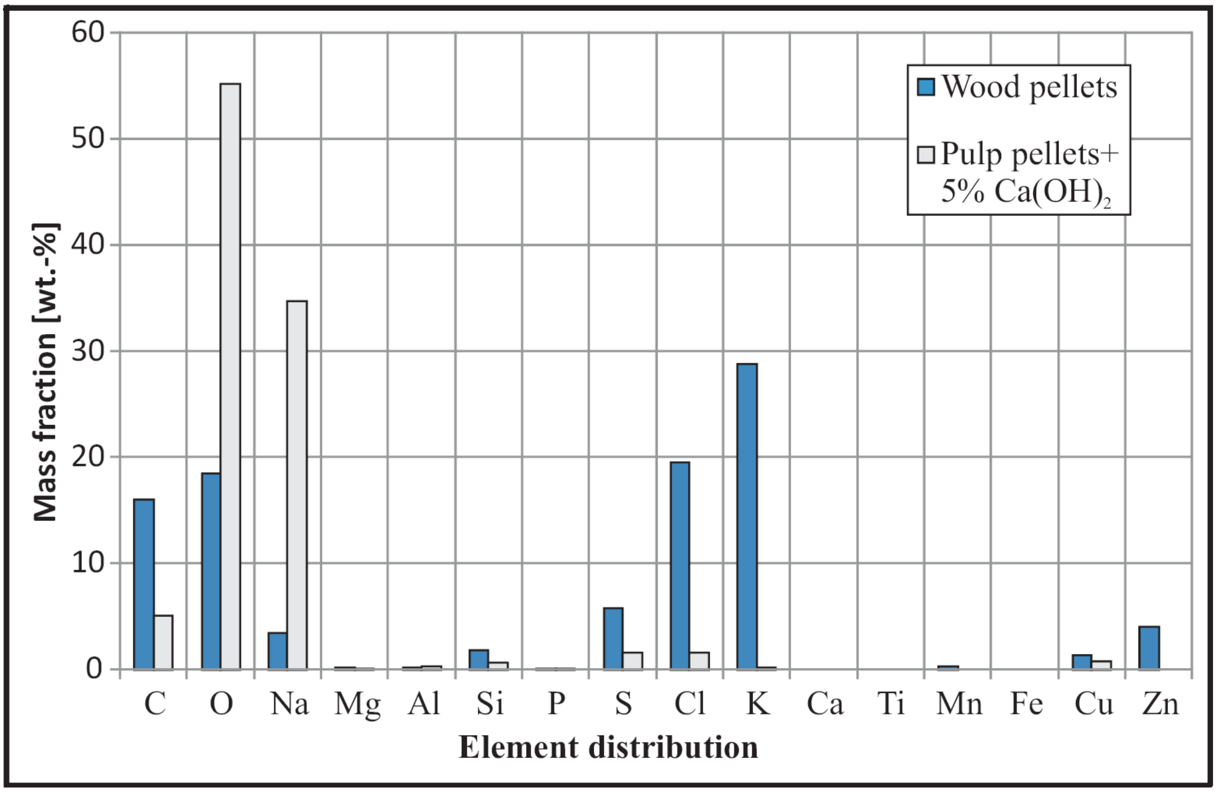

Figure 5: Element distribution for particle fraction $d_{ae} < 2.5$ µm (SEM-EDX mapping)

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(2) The aerodynamic diameter is defined as the diameter of a sphere with a normalized density of 1 g/cm³ with the same settling velocity as the particle in stationary or irrotational air.

The particle composition for the combustion of wood pellets and pulp pellets differs considerably. For the wood pellets the ash forming elements K, Cl, S,Zn as well as O and C dominates the particles. Presumably, these elements are present as K_2SO_4, KCl and $ZnCl_2$ which are typical particles for wood combustion [8, 9]. Carbon is mainly present as carbonate and soot. For pulp pellets with additive the elements Na and O dominate wherein small amounts of C, Cl and S are present. Since the laboratory ash was mainly composed of Na_2CO_3 [7] it can be assumed that it is released in the gas phase and desublimates during the flue gas cooling. In addition, the particles probably consist of Na_2SO_4 and NaCl.

Ash quality and ash composition

To evaluate the slagging behavior of the fuels, the combustion chamber ash (ash box and burner plate) was divided into 4 fractions by a sieve analysis (Figure 6). The single fractions were then examined by a visual observation.

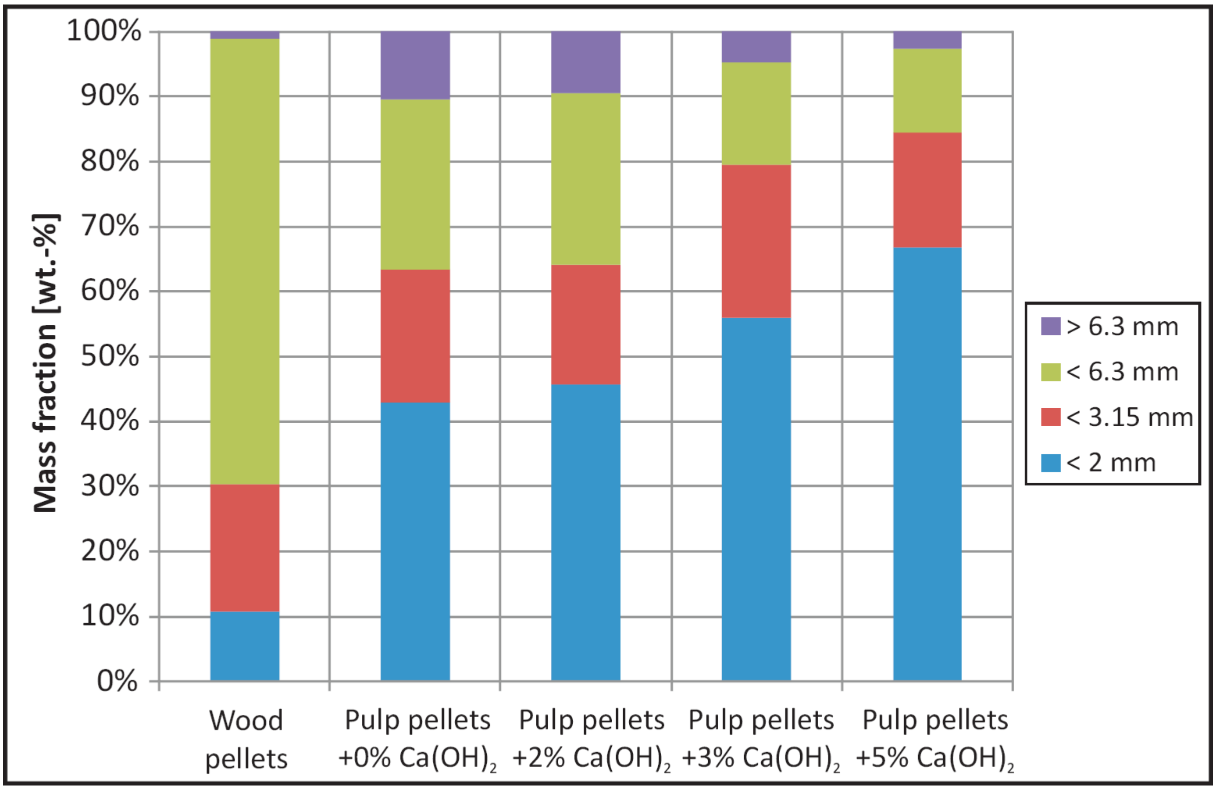
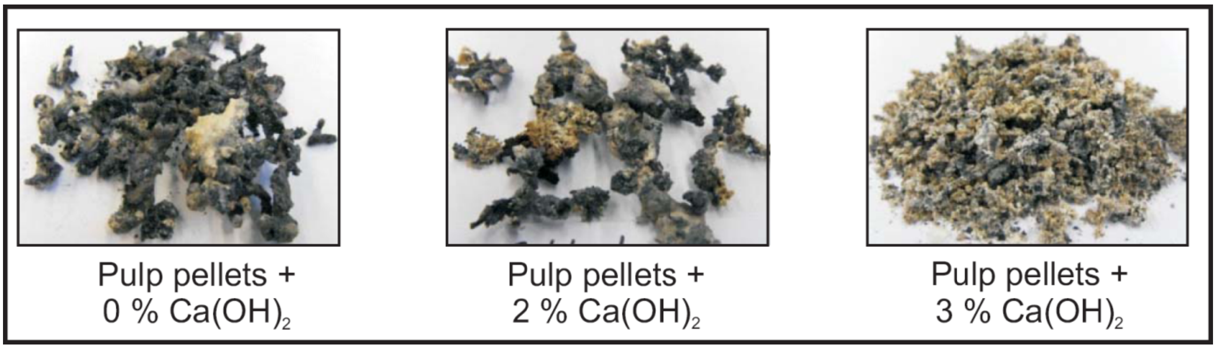


Figure 6: Sieve analysis of ash residues from ash box and burner plate

For the wood pellet ash no slag particles could be identified. The particles > 6.3 mm mainly consisted of unburned wood pellets. Unburned particles were also found in the ash of the non modified and $Ca(OH)_2$ modified pulp pellets. As it can be seen in Figure 7 the ash of the pulp pellets with +0, 2 and 3 wt.-% $Ca(OH)_2$ mainly consists of slag particles > 6.3 mm. With increasing $Ca(OH)_2$ content, the fraction of the slag particles (> 6.3 mm) decreases. This confirms the positive effect of the $Ca(OH)_2$ with respect to the slagging behavior.


Pulp pellets + 0 % $Ca(OH)_2$

Pulp pellets + 2 % $Ca(OH)_2$

Pulp pellets + 3 % $Ca(OH)_2$

Figure 7: Slag particles > 6.3 mm after combustion and sieve analysis

Besides the determination of slag content the ash composition was also determined by XRD studies. Figure 8 exemplarily shows the X-ray diffractogram of the pulp pellet ash.

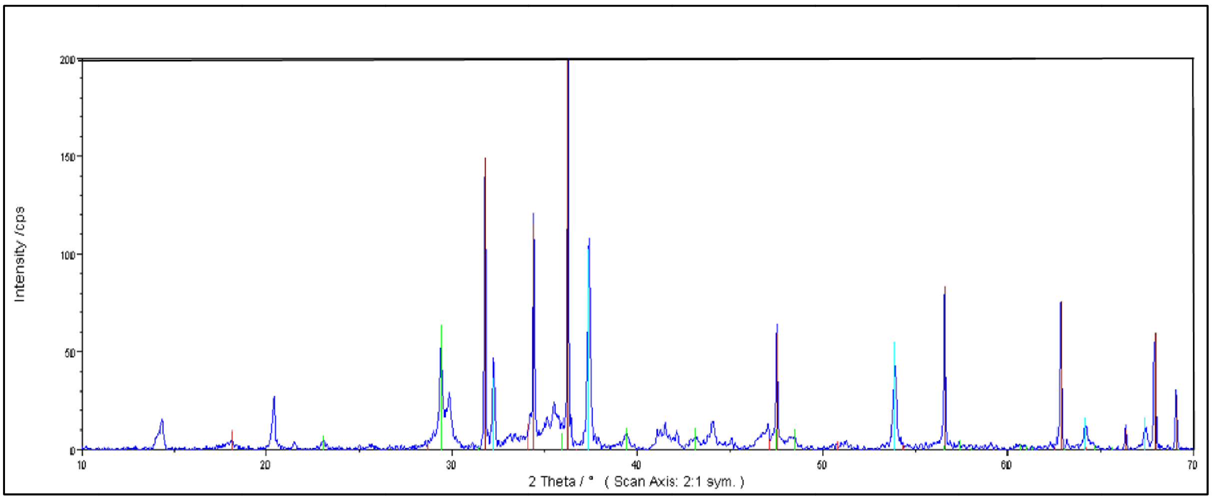


Figure 8: X-ray diffractogram of ash residue for combustion of pulp pellets+5 wt.-% $Ca(OH)_2$

The main components of the XRD analysis were identified as CaO, $CaCO_3$ and $Ca(OH)_2$. It should be emphasized that no sodium containing component was determined. This means, firstly, that the sodium is released into the gas phase, which is in good agreement to the particles found in the flue gas (see Figure 5). This means secondly, that the reduction of the slag fraction cannot be attributed to the formation of Na-Ca compounds, which have a higher ash melting temperature range.

6 Thermochemical equilibrium calculations

In addition to experimental investigations thermochemical equilibrium calculations are a powerful tool to evaluate the slagging behavior of fuels [10, 11]. To model the ash transformation process a one stage global equilibrium reactor approach was used. On the basis of the fuel composition of the modified pulp the equilibrium composition of the involved solid, liquid and gas phases is calculated by Gibbs Energy minimization. The calculations were performed in a temperature range of 600 - 1200 °C and at a reactor pressure of 1 bar. For the thermochemical equilibrium calculations the software package FactSage 6.2 was used. The formation of molten slag phases was considered by an oxide-silicate-melt (FTOxid) and a salt melt (FTSalt). To evaluate the slagging behavior usually the melt fraction is used, which is calculated from the equilibrium composition as follows

$$\xi_{melt} = \frac{\sum_{i=1}^{n} m_{liquid}}{\sum_{i=1}^{n} m_{liquid} + \sum_{i=1}^{m} m_{solid}} .$$

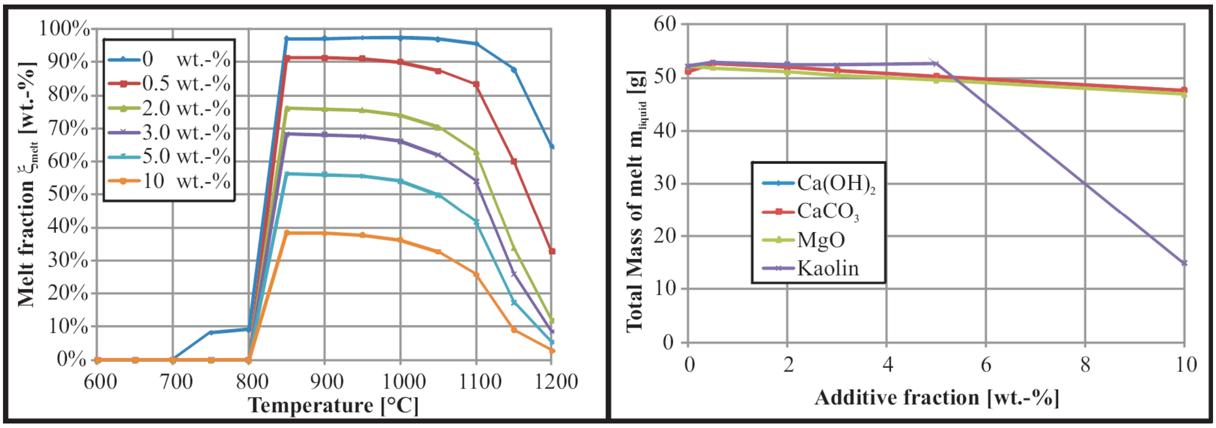


Figure 9: Calculated equilibrium results, left: melt fraction for various $Ca(OH)_2$ fractions in relation to temperature, right: maximum total mass of melt in condensed phases (ash) for various additives in relation to additive fraction

The left graph of Figure 9 shows the calculated melt fraction for various $Ca(OH)_2$ fractions in relation to temperature. It can be seen that the melt fraction decreases with increasing additive content. Between 800 and 850 °C a strong increase of the melt fraction is obvious. This is caused by the phase change of Na_2CO_3 from solid to liquid state. Between 850 and 1000 °C Na_2CO_3 is present in a salt melt. At temperatures higher than 1000 °C a strong decrease of the melt fraction occurs which is caused by the release of sodium in the gas phase (mainly as NaOH). In contrast to the melt fraction, the right graph of Figure 9 shows the maximum of total mass of melt for different additives which were used during the laboratory investigations [7]. It can be seen that it changes slightly for $CaCO_3$, $Ca(OH)_2$ and MgO. In contrast to the other additives kaolin shows a strong reduction of the total mass at an additive fraction of 10 wt.-%. This effect is caused by the bonding of sodium in the solid phase as $NaAlSiO_4$. Therefore it can be assumed that the effect described by [2] for the bonding of potassium is also applicable for this case. In contrast to that chemical effect the calcium and magnesium containing additives influences the ash melting behavior more by a physical dilution effect. The calculated compounds do not contain Na-Ca- or Na-Mg-compounds.

6 Summary and conclusions

In this paper the combustion behavior of calcium hydroxide modified pulp pellets was investigated in a 15 kW_{therm} pellet boiler. For all modified pulp pellets a stable operation state could be established over a period of more than 8 h. As expected the combustion of non modified pulp pellets resulted in slagging of the burner plate which made a stable operation mode impossible.

In terms of pollutant emissions significant higher CO and particulate matter emissions were measured for the modified pulp pellets. The reason for this is mainly the lower calorific value of the pulp pellets which leads to about 250 °C lower furnace temperatures. This lowers the reaction rate of CO burnout in the post-combustion zone. Because of the defined furnace geometry (mainly flame tube) the retention time of the flue gas in this zone is too low. A simple optimization of the furnace geometry, e. g. by a fluid dynamic optimized and thermal insulated flame tube enlargement, should lead to an improvement of the gas phase combustion and thus to a reduction of the CO emissions.

In terms of the particulate matter higher emissions were measured for the pulp pellets. The particulate mainly consisted of particles with $d_{ae} < 2.5$ µm. The chemical composition of the particles shows that these consist primarily of sodium, which was released in the gas phase during the solid combustion. To reduce the release of the particles, an additive could be used which binds the sodium in low volatile compound. Another possibility could be the leaching of pulp material which removes the sodium before the combustion.

The investigation of the ash residues showed a lowering of the slag fraction with an increasing $Ca(OH)_2$ content in the fuel. The ash residues mainly consisted of CaO, $CaCO_3$ and $Ca(OH)_2$. The experimental results were aided by thermochemical equilibrium calculations. The combination of the experimental and theoretical results suggests that the positive effect of the $Ca(OH)_2$ is more due to a physical dilution effect than a chemical bonding of the sodium in new formed compounds.

7 Acknowledgments

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