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IMPACT OF FUEL MODIFICATION METHODS ON THE SLAGGING BEHAVIOR OF PULP PELLETS

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ABSTRACT

Due to the limited availability of woody biomass for the energetic utilization alternative solid biofuels, like agricultural and industrial residues have become important. In contrast to woody biomass these biogenic residues have different mechanical, calorific and reaction technical fuel properties. When using these biogenic residues in existing energy facilities especially the main ash forming elements lead to operational problems like slagging, fouling and corrosion. In addition to an adjustment of the firing technology to the changing fuel properties a modification of the raw material to influence the fuel properties is also possible. This article focuses on the impact of fuel modification methods on the slagging behavior of pulp pellets produced from residues of the diaper industry. Based on the fuel properties the reasons for an unfavorable ash melting behavior are presented. With the aid of laboratory investigations the effect of different fuel modification methods on the ash melting behavior is demonstrated. In addition to the experimental investigations, thermochemical equilibrium calculations were used.

KEYWORDS: *slagging, ash melting behavior, pulp, fuel modification, biogenic residues, thermochemical equilibrium calcultaion*

1 INTRODUCTION

To substitute fossil fuels the energetic use of biomass has been intensified during the past years. Mainly in decentral biomass boilers of small and middle thermal capacity an increasing acceptance can be observed in the domestic and industrial sector. 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 adverse fuel properties is the modification of the raw material. For this purpose several process engineering basic operations are available [1]. These can be divided into mechanical, physical, chemical and biological operations. Therefore a treatment at low or high temperatures is possible. Methods how biogenic residues can be modified are listed in Table 1.

Table 1: Methods of fuel modification

Method	**Effect**
Mechanical operation (low temperature) Addition of biomass to the raw material [2], [3]	The **addition of favorable ash forming components** leads to changes in the ash and gas phase chemistry
Mechanical operation (low temperature) Addition of additives to the raw material [4], [5]	
Chemical operation (low temperature) Extraction/Leaching of the raw material [6], [7]	The **removal of unfavorable ash forming components** leads to changes in the ash and gas phase chemistry
Chemical operation (high temperature) Thermal pretreatment of the raw material (e.g. pyrolysis of the raw material) [8]	

By appropriate laboratory, pilot and field investigations the most suitable method (listetd in Table 1) for the corresponding residue has to be determined. For a better understanding how these methods influence the fuel properties (e.g. the ash transformation process) thermochemical equilibrium calculations can be useful.

This paper focuses on experimental and theoretical studies to compare the effect of different fuel modification methods with the example of pulp residues from the diaper manufacturing. During the recycling process plastic fractions of the diaper are separated from the material stream and used for the production of different plastic products. As residue fibrous pulp material of soaker pad remains which no further material use can be supplied. After pelletizing this pulp material it should be used in small or medium scale pellet boilers. In the following section the fuel modification methods listed in Table 1 are investigated in lab scale experiments. To interpret the effect of the different methods thermochemical equilibrium calculations are used.

2 PROPERTIES OF THE RAW MATERIAL

To obtain the fuel properties of the pulp residues, first the actual state of the raw material was determined by a conventional fuel analysis. In comparison to wood pellets the results of the laboratory analysis are shown in Table 2. It becomes clear that the low softening temperature (847 °C) and the much higher ash content (9.53%) of the pulp residues significantly deviate from wood pellets. When used in a conventional wood pellet boiler especially the bad ash melting behavior would probably lead to slagging and fouling of the grate and the heat exchanger surfaces. Due to the high ash content it can be also assumed that an increased release of fly ash and salts from the fuel bed occurs. This can lead to increased deposit formation on heat transfer surfaces and to an increase in particulate matter emissions. Because of the deposit formation the efficiency of the boiler would be reduced and the risk of corrosion would increase. To ensure a trouble free operation of the furnace mainly the ash melting behavior respectively the slagging behavior is important. Therefore, the following discussion will focus on methods to influence the ash melting behavior.

Table 2: Fuel properties of the pulp in comparison to wood pellets

Fuel properties	**Unit**	**Pulp**	**Wood pellets**
Moisture	wt% w.b.	5.27	4.56
Ash (550 °C)	wt% d.b.	9.53	0.34
Volatiles	wt% d.b.	74.50	84,04
Nitrogen	wt% d.b.	0.01	0.17
Carbon	wt% d.b.	44.20	51.27
Hydrogen	wt% d.b.	5.80	6.03
Oxygen	wt% d.b.	40.43	42.19
Sulphur	wt% d.b.	0.03	0.01
Chlorine	wt% d.b.	0.008	0.05
Calorific value	MJ/kg, d.b.	16.8	19.36
Shrinkage starting temperature (SST)	°C	835	959
Deformation temperature (DT)	°C	847	1044
Hemisphere temperature (HT)	°C	854	> 1450
Flow temperature (FT)	°C	861	> 1450

The ash melting behavior is influenced by the existence of main ash forming elements in the fuel. The chemical reactions taking place during the combustion lead to the formation of pure mineral compounds and mixtures of these components which may have a complex phase behavior. On the basis of the trace analysis a direct conclusion on the ash melting behavior and thus on the slagging risk is impossible. However, the knowledge of the content of different elements allows an initial qualitative statement for the possible behavior. Thus, for example high potassium and sodium contents reduce the ash fusion temperature. In contrast other elements such as calcium and magnesium improve the ash melting behavior. In Table 2 selected trace elements of the pulp residues are shown in comparison to wood pellets. It becomes clear that the unfavorable ash melting behavior is caused by a high amount of sodium in the raw material.

Table 3: Main ash forming elements of pulp residues in comparison to wood pellets

Element	**Symbol**	**Unit**	**Pulp**	**Wood pellets**
Aluminium	Al	mg/kg (d.b.)	231.3	150.0
Sodium	Na	mg/kg (d.b.)	38510.0	711.7
Potassium	K	mg/kg (d.b.)	38.2	391.2
Calcium	Ca	mg/kg (d.b.)	444.1	896.1
Magnesium	Mg	mg/kg (d.b.)	123.5	171.5
Iron	Fe	mg/kg (d.b.)	98.0	75.3
Silicon	Si	mg/kg (d.b.)	253.6	398.7
Phosphorus	P	mg/kg (d.b.)	234.0	86.1
Titanium	Ti	mg/kg (d.b.)	67.6	11.1

With a further XRD analysis of the ash (produced at 550 °C) it was shown that this consists of 91 wt.-% of sodium carbonate (Na_2CO_3). In order to determine the origin of sodium in the fuel scanning electron microscopy investigations (SEM-EDX) were used. The comparison of the experimentally determined softening temperature (847 °C) and the melting temperature of Na_2CO_3 (851 °C) shows a fairly good agreement. The SEM and SEM-EDX results are shown in Figure 1 and 2.

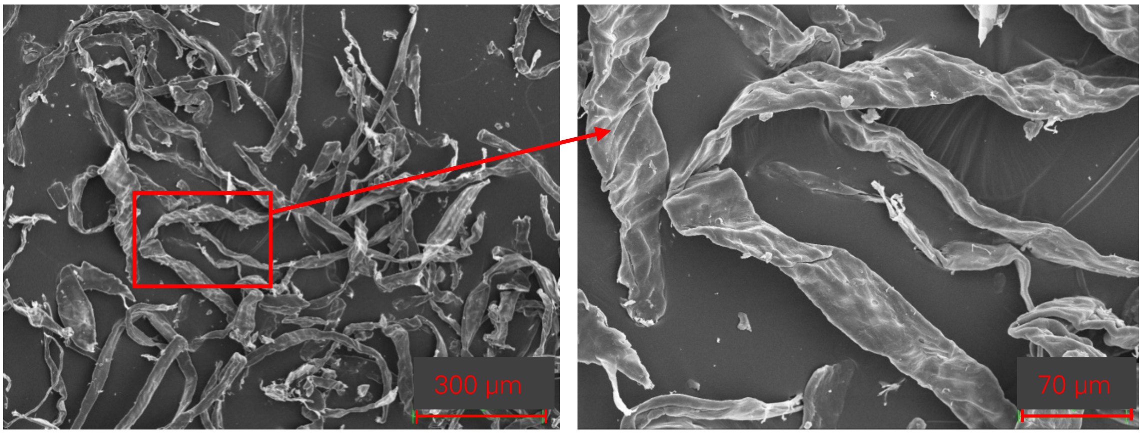

Figure 1: Overview and detail view of pulp fibers (SEM)

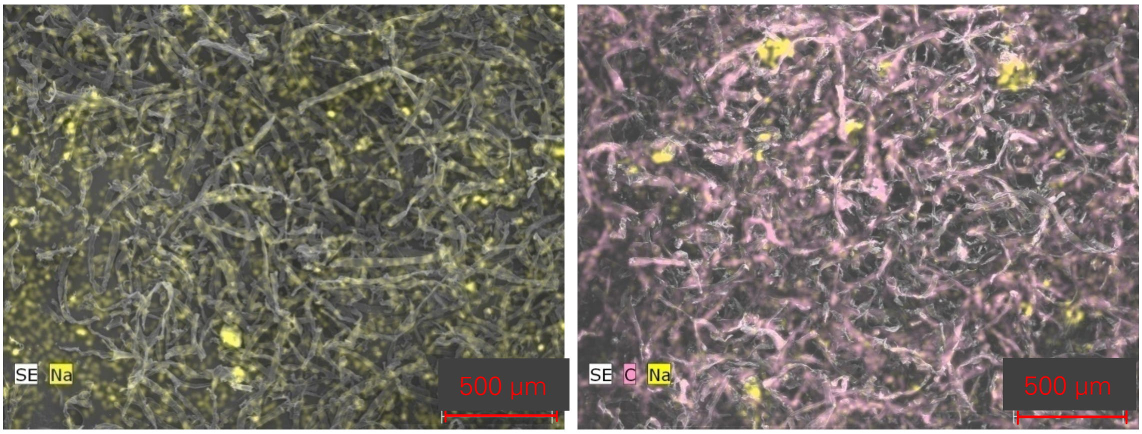

Figure 2: Overview of pulp fibers for the elements carbon and sodium (SEM-EDX)

As shown in Figures 1 and 2, the samples consist of a composite structure of individual pulp fibers. It can be seen, that sodium is mainly concentrated in small particles which are located between the pulp fibers. These sodium-containing particles were identified as Superabsorbent polymers (SAP). They are used to improve the fluid absorption in the diaper material.

3 EXPERIMENTAL INVESTIGATIONS AND THERMOCHEMICAL EQUILIBRIUM CACLULATIONS

3.1 Laboratory Investigations

After the reason for the unfavorable ash melting behavior was determined, in the next steps the influence of the different fuel modification methods were investigated concerning this problem parameter. For this purpose further laboratory tests were performed. To evaluate the slagging risk the modified pulp material was combusted according to DIN EN 14775 in an oxidizing atmosphere at 550 °C in a muffle furnace. To obtain a quick result if the modification method has a significant impact on the slagging risk or not, a quick test was developed. This quick test is based on the standardized method to determine the ash melting behaviour (DIN CEN/TS 15370-1) of biomass fuels. Therefore, the laboratory ashes were pressed to three cylindrical specimens. These specimens were heated up in a muffle furnace starting from room temperature in 50 K increments up to 1100 °C. After an equilibration time of 10 min the change of the specimen shape was observed. In case of a positive effect the four characteristic ash melting temperatures (SST, DT, HT and FT) were determined by using the standardized method DIN CEN/TS 15370-1.

a) Addition of biomass to the raw material

To improve the unfavorable ash melting behavior of the pulp, fine powdered wood pellets were mixed with the grounded raw material (wood content: 19.8; 52.5; 87.5 and 97.5 wt%). After this the mixture was combusted by the procedure described above (DIN EN 14775) and the ash melting behavior was determined.

b) Addition of additives to the raw material

A further possibility for affecting the ash melting behavior is the addition of additives. In the past, several authors [4, 5, 9-12] have studied the influence of mineral components (e.g. clay minerals, lime and dolomite) on ash related problems during the combustion of biomass. For the laboratory studies the additives calcium hydroxide ($Ca(OH)_2$), calcium carbonate ($CaCO_3$), kaolin ($Al_2Si_2O_5(OH)_4$) and two magnesium-containing commercial additives (solid, liquid) were selected. These were added to the pulp in the mixing ratios 0.5, 2, 3, 5 und 10 wt.-%.

c) Leaching of the raw material

As the element sodium is primary bounded in the SAP as positive charged ion it should be extracted by an appropriate ion exchange agent (in the following called leaching agent). Therefore, the aim of the investigations was to determine the influence of the leaching agent, the extraction time and the pulp-leaching agent-ratio (p-l-ratio) on the ash melting behavior. As leaching agent water and organic acids (formic and acedic acid) were used. In the experiments a suspensions was prepared in the three p-l-ratios 10, 25 und 50 g/l and stirred for 30, 60 und 120 min. After this the suspension was filtered, the solid residue was dried and finally the ash melting behavior was determined as described before.

d) Thermal pretreatment of the source material (e. g. pyrolysis of the source material)

The aim of the thermal pretreatment is to release the sodium by heating up the raw material under a reducing nitrogen atmosphere. The remaining pyrolysis char can be used afterwards for the fuel production. For carrying out the pyrolysis in laboratory scale, a modified laboratory furnace with a retort was used. A detailed description of the experimental setup is given in [13]. The raw material was filled in the retort and set with a temperature controller to the pyrolysis temperature of 400 °C and 600 °C. During pyrolysis the retort was continuously purged with nitrogen. After this, a trace analysis of the pyrolysis residue and the ash melting behavior was determined.

3.2 Thermochemical equilibrium calculations

In addition to experimental investigations thermochemical equilibrium calculations are a powerful tool to evaluate the slagging behavior of fuels [14, 15]. 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 the melt fraction was used, which is calculated from the equilibrium composition as follows

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

To simulate the addition of wood and the mineral additives the elemental composition (Table 2) and the main ash forming elements (table 3) of the experimental investigated mixtures were used as input data. The leaching of the pulp was simulated by varying the sodium leaching degree from 0 – 100 %. For these three methods the calculation was performed in an oxidizing air atmosphere with an air ratio of λ = 2. The pyrolysis of the pulp was simulated by calculating the equilibrium composition in the above mentioned temperature range and a reducing nitrogen atmosphere. After the simulated pyrolysis process the remaining solid and liquid resdiues were oxidized in an air atmosphere with an air ratio of λ = 2.

4 RESULTS

4.1 Laboratory Investigations

a) Addition of biomass to the raw material

Figure 3 shows the behavior of the specimen during the quick test for the four wood mixtures. The mixtures of a wood content of 19.8 wt.% and 52.5 wt.% are completely melted at 850 ° C. The specimen of the mixture 87.5 wt.% wood content exceeded the deformation temperature and have a hemispherical shape. However at 900 °C also in these mixtures a complete melting could be observed. For the samples with the highest wood content of 97.5 wt.-% up to the final temperature of 1100 °C a complete melting could not be observed. Since a significant impact on the ash melting behavior was noticed only at very high wood content, the four characteristic ash melting temperatures were not determined.

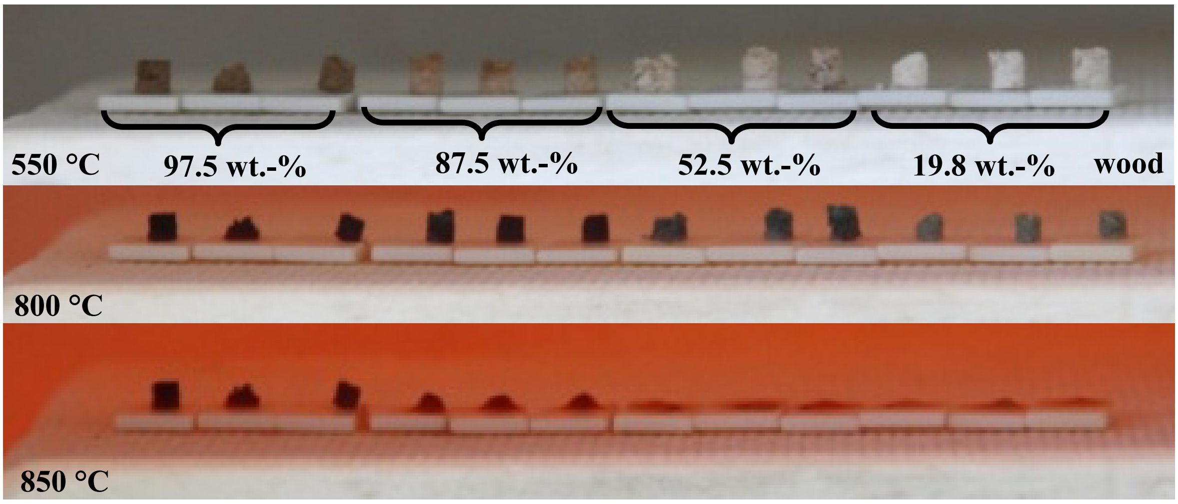

Figure 3: Behavior of ash pellets at different temperature stages

b) Addition of additives to the raw material

The quick test showed a significant impact on the ash melting behavior for the additives $Ca(OH)_2$, $CaCO_3$ and the solid commercial additive. For the other used additives no significant effect on the ash melting behavior could be observed.

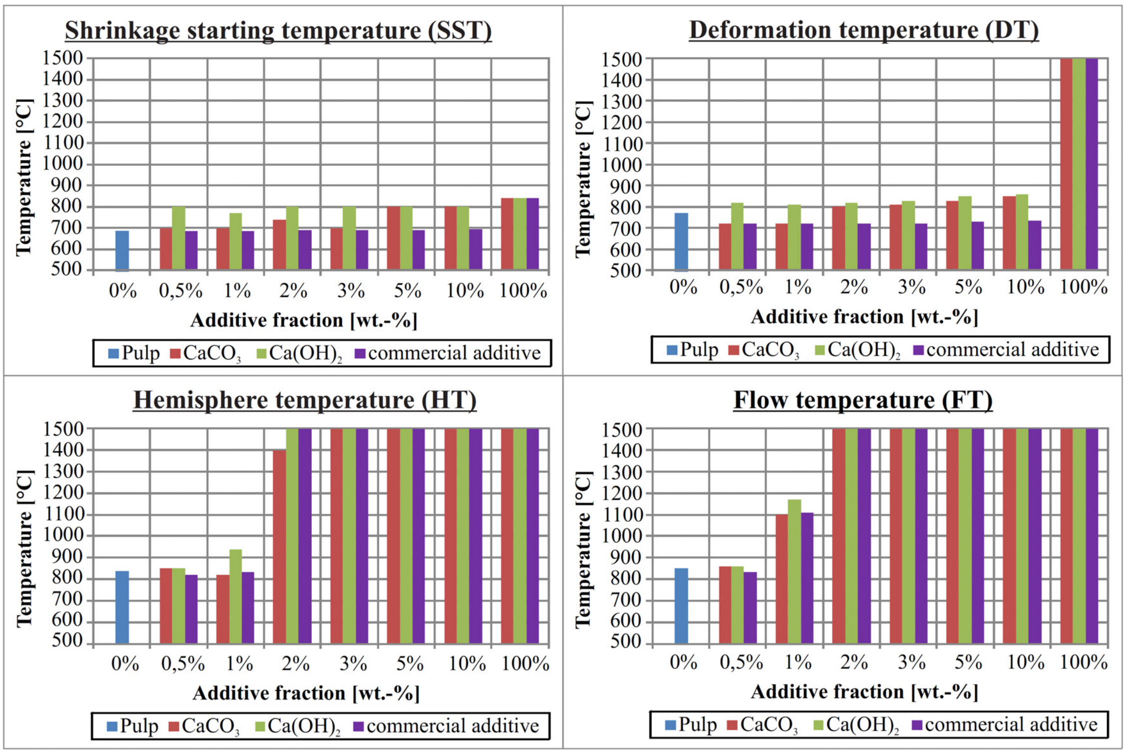

Figure 4: Impact of additive content on the ash melting temperatures (DIN CEN/TS 15370-1)

Figure 4 shows that mainly $CaCO_3$ und $Ca(OH)_2$ lead to a small increase of the deformation temperature but a significant increase of the hemisphere and flow temperature to more than 1300 °C. A considerable effect can be seen above a content of 2 wt.-%. Slightly higher temperatures are reached with the additive $Ca(OH)_2$.

c) Leaching of the raw material

The use of water as leaching agent was found to be problematic because of the SAP in the pulp. These particles absorb water, swell and thus prevent a gravity filtration. Therefore, an ion exchange effect is prevented. When using the organic acids the effect of swelling was not observed. Figure 5 shows the characteristic ash melting temperatures for the two organic acids depending on the leaching time and the p-l-ratio.

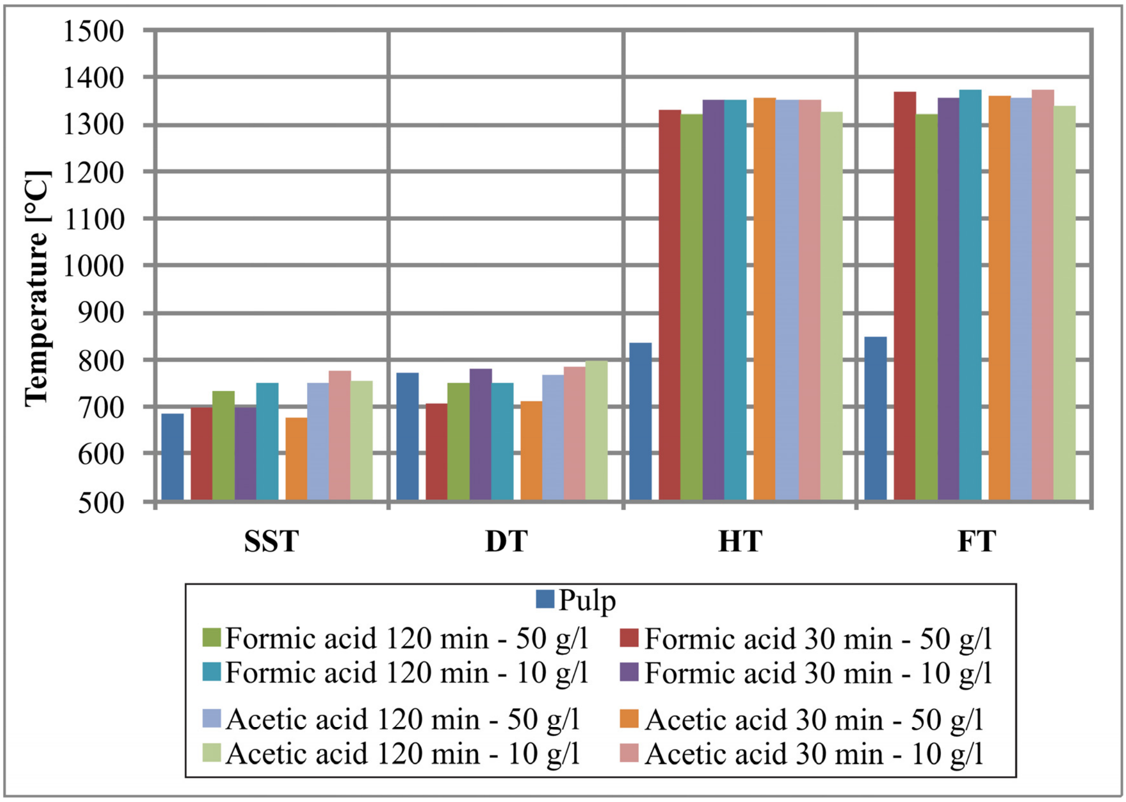

Figure 5: Impact of leaching agent, leaching time and p-l ratio on the ash melting temperatures (DIN CEN/TS 15370-1)

Based on the leaching experiments it becomes clear that both leaching agents lead to a significant increase of the hemisphere and flow temperature. An obvious impact of the leaching agent and extraction time on the ash melting behavior cannot be seen. Slightly higher temperatures can be achieved for a p-l ratio of 10 g/l.

d) Thermal pretreatment of the source material (e. g. pyrolysis of the source material)

As it can be seen in Figure 6 an increase in the ash melting temperatures could not be achieved by pyrolysis of the pulp at 400 °C and 600 °C. The main and trace analysis of the pyrolysis char showed a small reduction of the sodium content that has no impact on the ash chemistry.

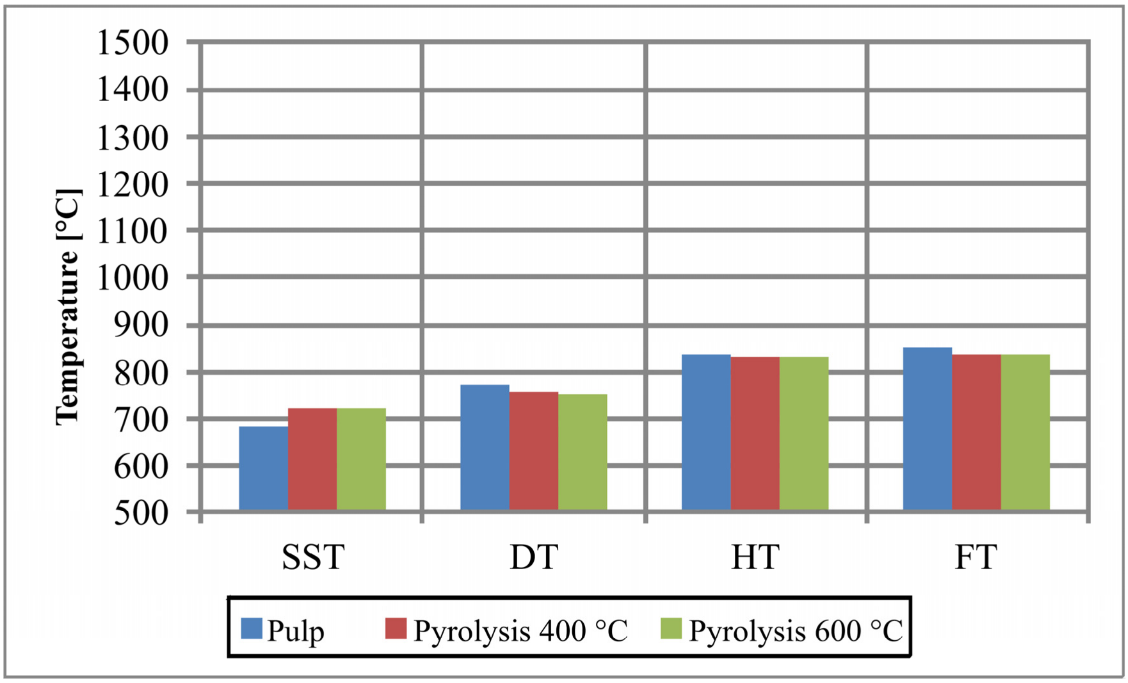

Figure 6: Characteristic ash melting temperatures (DIN CEN/TS 15370-1) of pyrolysis char

4.2 Thermochemical equilibrium calculations

a) Addition of biomass to the raw material

Figure 7 shows the calculated melt phase fraction for the pulp, wood and the experimental investigated mixtures. It can be seen that the unfavorable ash melting behavior (Table 2) is quite well reflected by the equilibrium calculation results. Up to 800 °C sodium is present as solid Na_2CO_3 which melts between 800°C and 900 °C. Above 1100 ° C the release of sodium in the gas phase (mainly as NaOH) starts. It can be seen further that the melt fraction slightly decreases with an increasing wood content. Despite a high wood content of 97.5 wt.-% the ash-forming components of the wood take only slightly affect on the ash melting behavior of the pulp ash. Therefore, the equilibrium calculation results aid to interpret the experimental results.

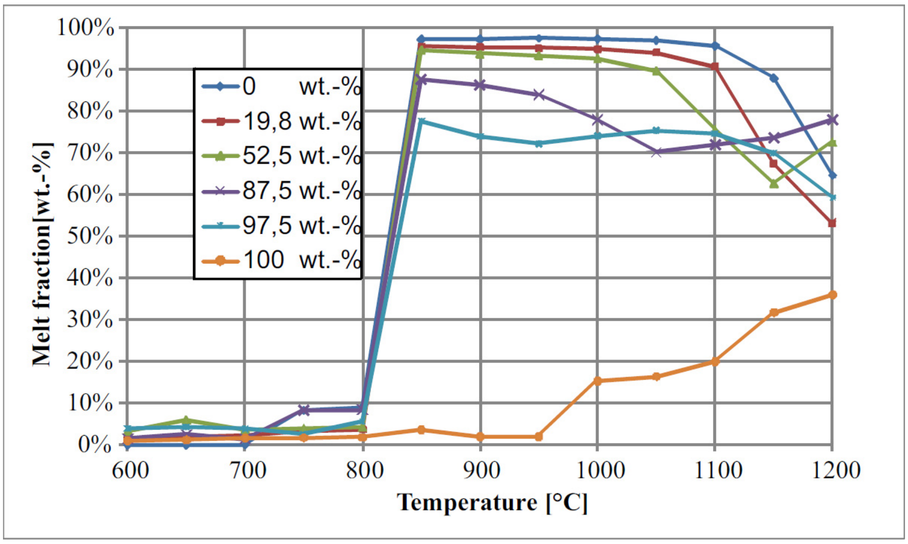

Figure 7: Calculated equilibrium melt fraction in relation to temperature and wood fraction

b) Addition of additives to the raw material

The impact of calcium-containing additives on the melt fraction is shown in figure 8 for $Ca(OH)_2$ und $CaCO_3$. It can be seen that the melt fraction decreases with an increasing additive content. According to the experimental results this effect is slightly more significant for $Ca(OH)_2$.

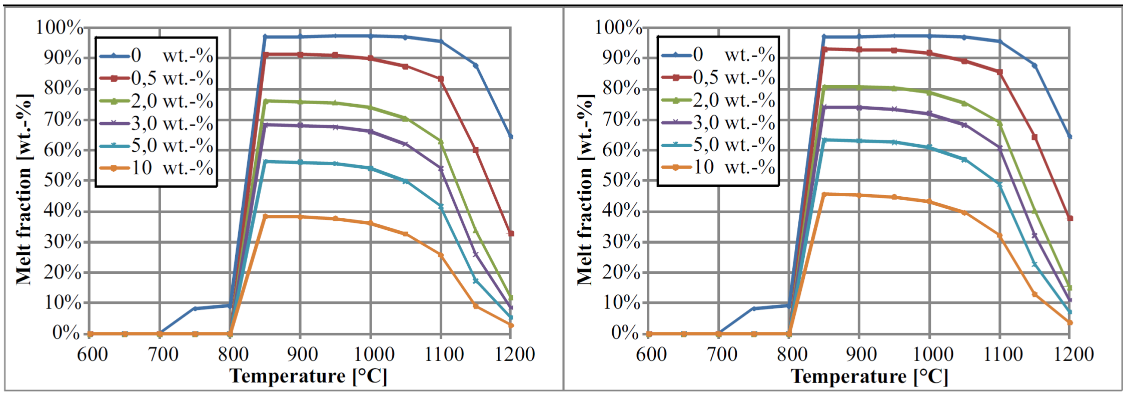

Figure 8: Calculated equilibrium melt fraction in relation to temperature and additive content(left: $Ca(OH)_2$; right: $CaCO_3$)

By plotting the maximum melt fraction against the additive fraction (Figure 9) it can be seen that the melt fraction decreases with increasing additive fraction of $CaCO_3$, $Ca(OH)_2$ and MgO. The most significant reduction of the melt fraction is obtained with kaolin, but only at a high additive fraction of 10 wt.-%.

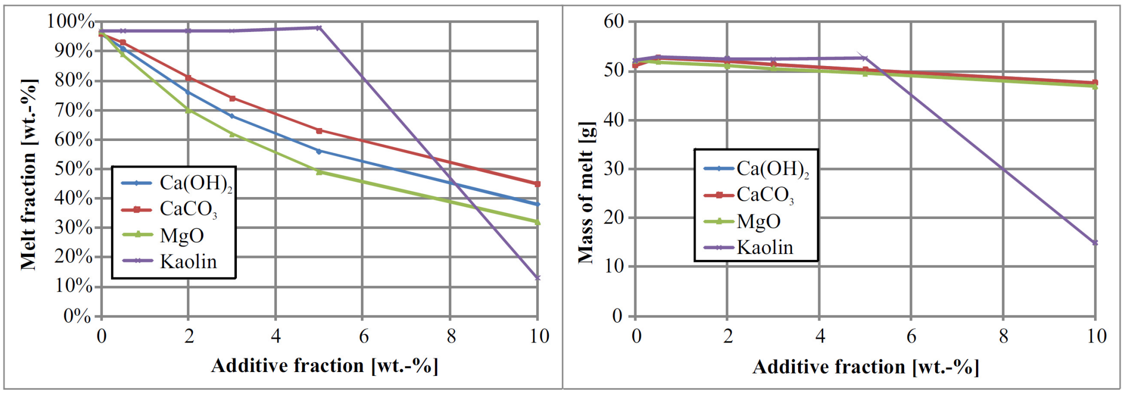

Figure 9: Maximum of calculated equilibrium melt fraction (left) and total mass of calculated equilibrium melt (right) in relation to additive fraction

If instead of the melt fraction the maximum of the total mass of melt is used it is obvious, 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 [4] 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 does not contain Na-Ca- or Na-Mg-compounds.

c) Leaching of the raw material

Figure 10 shows the influence of the sodium leaching degree on the calculated melt fraction. It can be seen that the melt fraction decreases with increasing sodium leaching degree. A significant reduction of the melting fraction only occurs at a high leaching degree more than 90%.

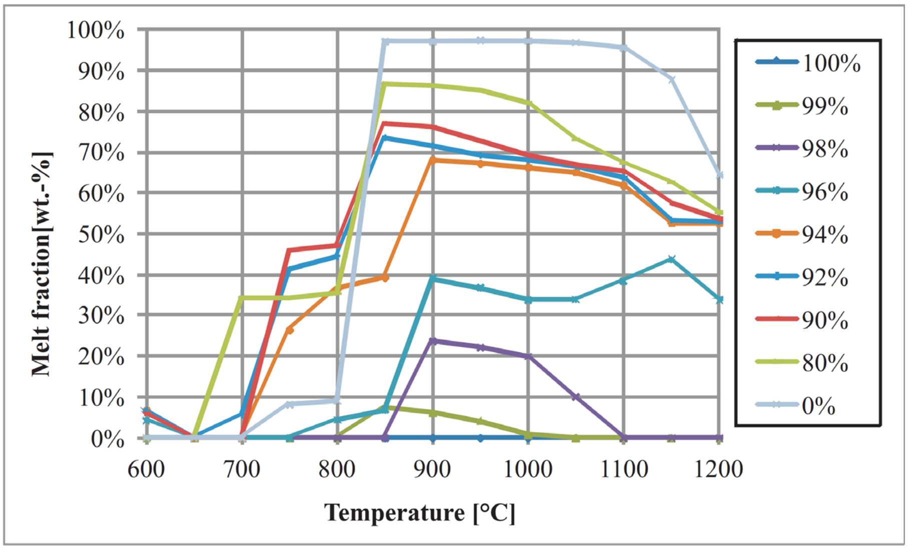

Figure 10: Calculated equilibrium melt fraction in relation to temperature and leaching degree

d) Thermal pretreatment of the source material (e. g. pyrolysis of the source material)

The phase distribution of sodium (Figure 11) shows that at temperatures greater than 850 °C a significant release in the gas phase occurs. If the solid and liquid residue is oxidized after the simulated pyrolysis it becomes apparent that a significant reduction of the melt fraction takes place at a temperature greater than 850 °C.

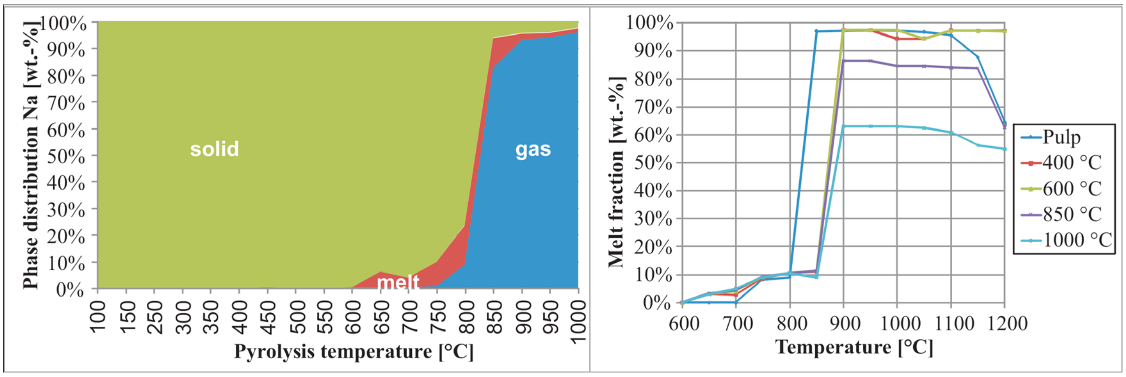

Figure 11: Calculated phase distribution of sodium (left) and calculated equilibrium melt fraction of pyrolysis char in relation to temperature and leaching degree

5 CONCLUSIONS

In this paper the impact of different fuel modification methods on the slagging behavior of pulp pellets was investigated with the aid of experimental laboratory investigations and theoretical thermochemical equilibrium calculations. It was determined that both the use of calcium containing additives (e.g. $Ca(OH)_2$ and $CaCO_3$) and the leaching of the pulp material with organic acids (formic and acetic acid) leads to a significant improvement of the ash melting behavior and therefore the slagging risk. Thus an increase in the hemisphere and flow temperature of 850 °C to more than 1300 °C was determined for an additive fraction of 2 wt.-% $Ca(OH)_2$ and $CaCO_3$. But also the leaching of the pulp leads to an increase of the hemisphere and flow temperature to more than 1100 °C by reducing the sodium. Furthermore it was found that both the blending of wood and pulp and the pyrolysis of the pulp did not lead to a significant improvement of the ash melting behavior.

The thermochemical equilibrium calculations principally support the results of the laboratory studies. By adding $Ca(OH)_2$ und $CaCO_3$ to the pulp a reduction of the melt fraction was determined for increasing additive fractions. This effect is not based on a chemical effect of bonding sodium in the additives and forming a Na-Ca-compound. It is more of a physical dilution effect. When using kaolin a significant impact on the melt fraction can be noticed for a high content of 10 wt.-%. In this case the effect is based on the chemical bonding of the sodium by forming the compound $NaAlSiO_4$, which starts melting at higher temperatures. Also the leaching of the pulp, for leaching degrees of more than 90 %, leads to a significant decrease of the melt fraction, which is in good agreement to the experimental results. Furthermore the calculation results shows that the blending of wood and pulp has only a slightly effect on the melt fraction. To influence the ash melting behavior by pyrolysis, temperatures of more than 850 °C are necessary.

6 ACKNOWLEDGEMENTS

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7 ABBREVIATIONS

w.b.	wet basis
d.b.	dry basis
DT	Deformation temperature
FT	Flow temperature
HT	Hemisphere temperature
p-l-ration	pulp-leaching agent-ratio
SAP	Superabsorbent polymers
SST	Shrinkage starting temperature

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