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Biogenous residues for the use as wood pellet equivalent fuels

Paper # 8

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1 Abstract

Over 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 mainly pellets are used. Up to now basically saw mill waste of the wood processing industry is used for the production of wood pellets. Because of rising energy costs and the increasing energetic utilization in boilers and stoves the demand of wood pellets has become of more interest. If this trend proceeds there will be a supply shortfall in future. To guarantee a stable supply the use of alternative biogenous residues become in focus. Because of different fuel properties in comparison to wood pellets it has to be verified if existing combustion technology can be used for the thermal treatment of these biogenous residue pellets. In case of unsuitable fuel properties, so that existing combustion technology cannot be used, there are two options. If e.g. slagging, fouling and emission behavior would lead to technical problems then the combustion technology or the fuel could be modified.

The main focus of this work is to study possibilities to affect the slagging behavior of biogenous residue pellets. Often high fractions of sodium and potassium are the reason for low ash melting temperatures. The aim of this work is to present possibilities and methods how biogenous residues can be modified to make wood pellet equivalent fuels. Thereby the results of different modification methods will be described and discussed.

2 Introduction

To substitute fossil fuels the energetic use of biomass was 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 mainly produced from sawdust of the wood processing industry has increased. The availability of wood waste as 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 the material cannot be used in other applications. However, these residues are no standard fuels. For example straws and herbaceous residues have high amounts of alkalis 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 source 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. In Table 1 selected methods of fuel modification are shown.

Table 1: Methods of fuel modification

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

To determine which of the in Table 1 listed methods of fuel modifications is suitable for the corresponding residue, then appropriate laboratory, pilot and field investigations have to be undertaken. This means that the impact of the modification method on the combustion behavior should be examined in 3 steps:

1. The impact on the fuel properties (e.g. ash melting behavior and ash content) must determined by laboratory scale investigations.
2. For a process-oriented evaluation the combustion behavior is investigated in a pilot plant (e.g. slagging, fouling and corrosion) [9].
3. Finally, the use of the modified fuel under real conditions is examined by field investigations in a pellet boiler.

In this paper, the authors limit to laboratory scale investigations with the aim to compare different modification methods on the example of cellulose residues. These cellulosic residues are a waste product of diaper production. During the recycling process plastic fractions are separated from the material stream and used for the production of different plastic products, like pallets. As residue cellulosic material of the suction zone remains which no further material use can be supplied. In the following explanations the shown fuel modification methods are summarized and discussed for the cellulosic residues in Table 1.

3 Properties of the unmodified source material

To obtain the fuel properties of the cellulose residues, first the actual state of the source 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%) significantly deviate from the requirements of 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 discharge 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 the influence of the ash melting behavior.

Table 2: Comparison of fuel composition of cellulose with requirements for wood pellets
Abbreviations: d.b. = dry basis; w.b. = wet basis.

Fuel properties	**Unit**	**Cellulose**	**Requirements for wood pellets (DIN EN 14961-2)**
Moisture	wt% w.b.	4.61	≤ 10
Ash (550 °C)	wt% d.b.	9.53	≤ 0.7 (A1); ≤ 1.5 (A2); ≤ 3.0 (B)[1]
Nitrogen	wt% d.b.	0.01	≤ 0.3 (A1); ≤ 0.5 (A2); ≤ 1.0 (B)
Hydrogen	wt% d.b.	5.8	Not specified
Carbon	wt% d.b.	44.2	Not specified
Sulphur	wt% d.b.	0.03	≤ 0,03 (A1) / (A2); ≤ 0.04 (B)
Chlorine	wt% d.b.	0.008	≤ 0.02 (A1) / (A2); ≤ 0.04(B)
Calorific value	MJ/kg, d.b.	16.8	16.5 – 19,0 (A1); 16.3 – 19.0 (A2); 16.0 – 19,0 (B)
Softening temperature	°C	847	≥1200 (A1) / (A2); ≥1100(B)

The ash melting behavior is influenced by the existence of certain trace 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. Other elements such as calcium and magnesium improve, however, the ash melting behavior. In Table 3 selected trace elements of the cellulose residues are shown in comparison to wood pellets. With a further XRD analysis it could be shown that the ash (produced at 550 °C) mainly consist of so-

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[1] A1, A2 and B represent a classification of wood pellets in 3 different quality levels.

dium carbonate (Na_2CO_3) with a mass fraction of 91 wt.%. Based on these results it can be assumed that the main cause for the unfavorable ash melting behavior is the high sodium content in the source material.

Table 3: Trace Analysis of cellulose residues in comparison to wood pellets

Element	**Symbol**	**Unit**	**Cellulose**	**Wood pellets**
Aluminium	Al	mg/kg (d.b.)	231.3	n.d.
Sodium	Na	mg/kg (d.b.)	38510.0	2,2
Potassium	K	mg/kg (d.b.)	38.2	91,3
Calcium	Ca	mg/kg (d.b.)	444.1	42.9
Magnesium	Mg	mg/kg (d.b.)	123.5	18.1
Iron	Fe	mg/kg (d.b.)	98.0	10.5
Silicon	Si	mg/kg (d.b.)	253.6	14.0
Phosphorus	P	mg/kg (d.b.)	234.0	n.d.
Titanium	Ti	mg/kg (d.b.)	67.6	n.d.

In order to determine the origin of sodium in the fuel scanning electron microscopy investigations (SEM, SEM-EDX) were performed. The comparison of the experimental 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.

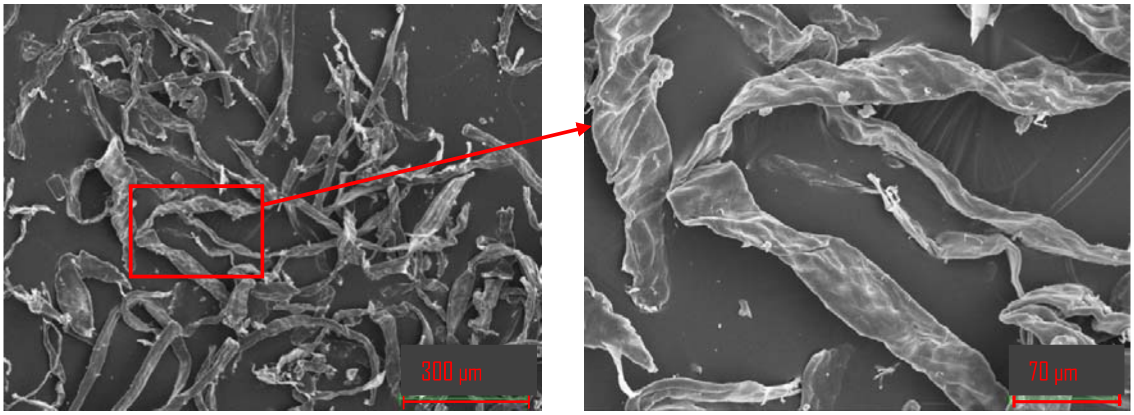


Figure 1: Overview and detail view of cellulose fibers (SEM)

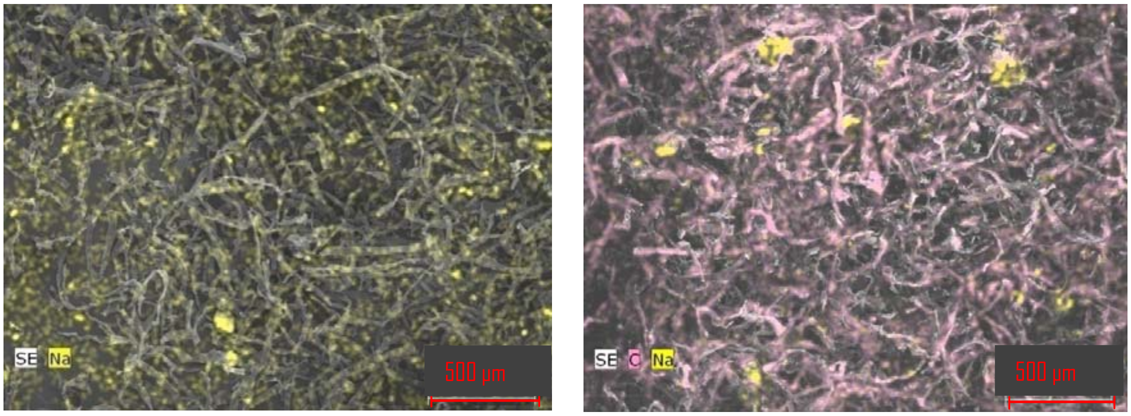


Figure 2: Overview of the cellulose fibers for the elements carbon and sodium (SEM-EDX)

As shown in Figures 1 and 2, the samples consist of a composite structure of individual cellulose fibers. On the one hand sodium is extensively distributed on the cellulose fibers, suggesting that it is added during the manufacturing process. On the other hand the samples include single sodium-containing particles which were identified as Superabsorbent polymers (SAP). They are used to improve fluid absorption in the diaper material.

4 Experimental investigations to influence the source material

After the reason for the unfavorable ash melting behavior was determined, in the next steps the influence of the modification methods shown in Table 1 were investigated concerning this problem parameter. For this purpose further laboratory tests were performed.

Addition of biomass to the source material

The addition of an additional fuel should change the ash composition in a way that this leads to a change in the ash melting behavior. For this purpose defined mixtures of the cellulose material and fine powdered wood pellets were produced (wood content: 19.8; 52.5; 87.5 and 97.5 wt%) and then the ash melting behavior was determined. To limit the experimental efforts, the standard method for determining the ash melting behavior in the melting microscope (DIN 51730) was modified. Therefore the mixed samples were incinerated in accordance with DIN 51719 and pressed to each of 3 cylindrical specimens. These were then heated up in a muffle furnace from room temperature in 50 K increments up to 1100 ° C. Figure 3 shows the behavior of the specimen during the test.

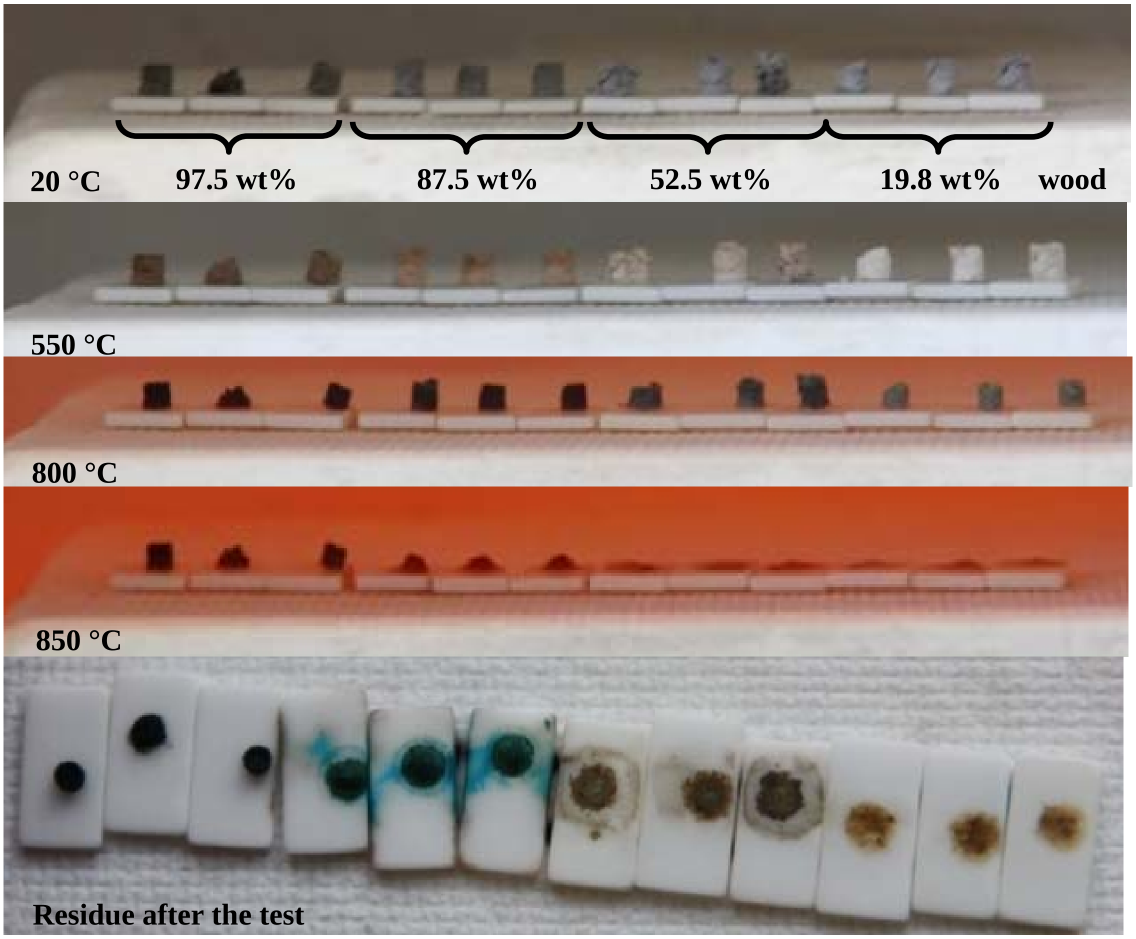


Figure 3: Behavior of ash pellets at different temperature stages

As shown in Figure 3, the mixtures of wood with a 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 softening point 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.

Addition of additives to the source material

A further possibility for affecting the ash melting behavior is the addition of additives. Thereby chemical compounds are added including elements that have high melting temperatures. During combustion these compounds form solution phases which have a higher melting temperature than the pure fuel ash. In the literature related to the unfavorable ash melting behavior of straw-based fuels such as rape, wheat and barley the influence of calcium, aluminum and silicon-containing additives was investigated [3]. Therefore, the additives calcium hydroxide ($Ca(OH)_2$), calcium carbonate ($CaCO_3$), Kaolin ($Al_2Si_2O_5(OH)_4$) and 2 commercial magnesium-containing additives (solid, liquid) were selected. These were each in the mixing ratios 0.5, 2, 3, 5 and 10 wt.% added to the fuel. Subsequently, to investigate the ash melting behavior, the same method as used for the mixing of biomass was applied (see Figure 3). As a result of the experiments it was determined that all additives with a content greater than 2 wt.% expect kaolin and the liquid commercial additive had a positive influence on the ash melting behavior. With a mass fraction of greater than 3 wt.% no melting of the ash pellets could be observed to the final temperature of 1100 °C. A clear preference additive was not determined in this review experiment because all ash pellets at the appropriate temperatures had almost the same morphological characteristics. According to the modified method then the standard procedure for the determination of ash melting behavior (DIN 51730) with the commercial additives was determined in the melting microscope. In figure 4 the effect of the commercial additives on the ash melting behavior (sintering, softening, hemispherical and flow temperature) is shown.

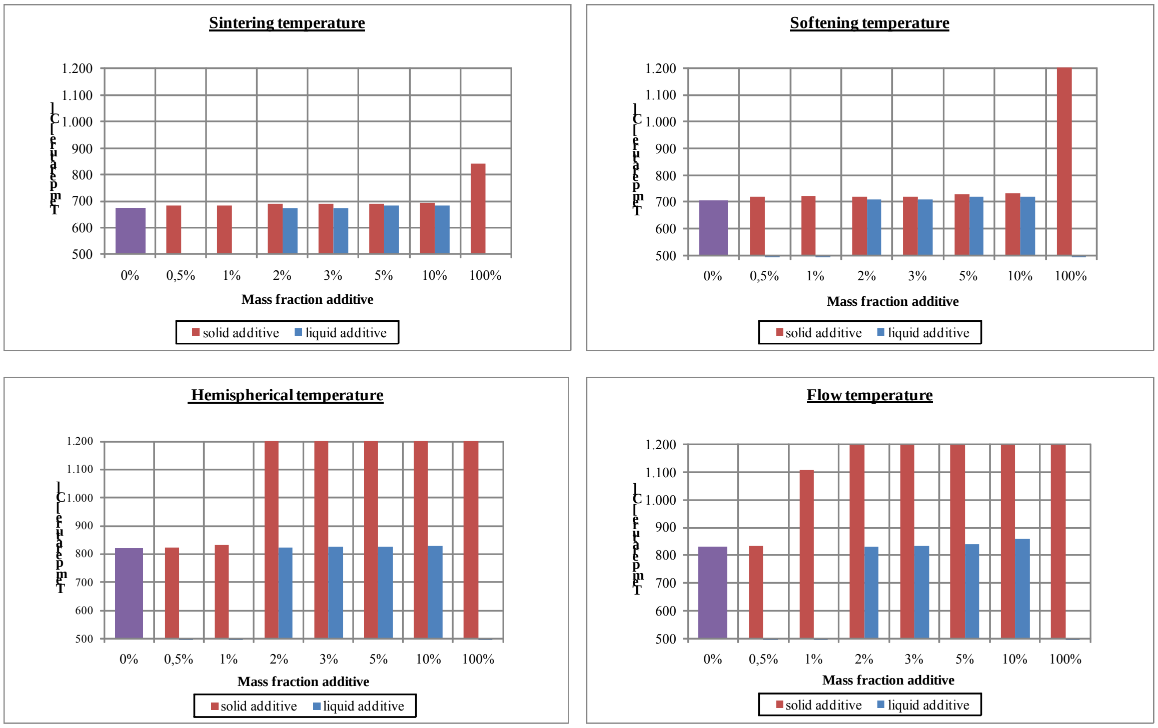


Figure 4: Impact of the mass fraction of additive on the ash melting behavior

As Figure 4 illustrates, by the addition of the solid additive a significant increase in the hemispherical and flow temperature to about 1200 ° C is achieved from up to 2 wt.%. The use application of the liquid additive, however, shows no significant improvement of the ash melting behavior. The addition of further mineral components however has the disadvantage that they lead to an increasing of the ash content.

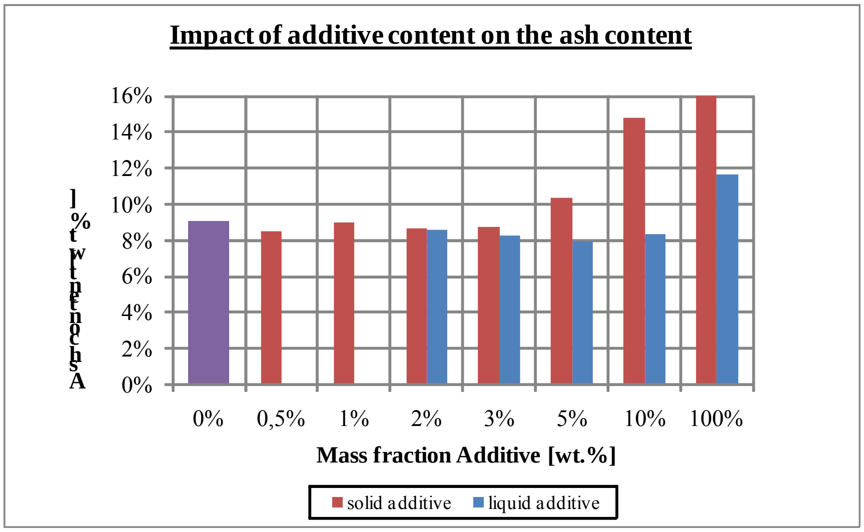
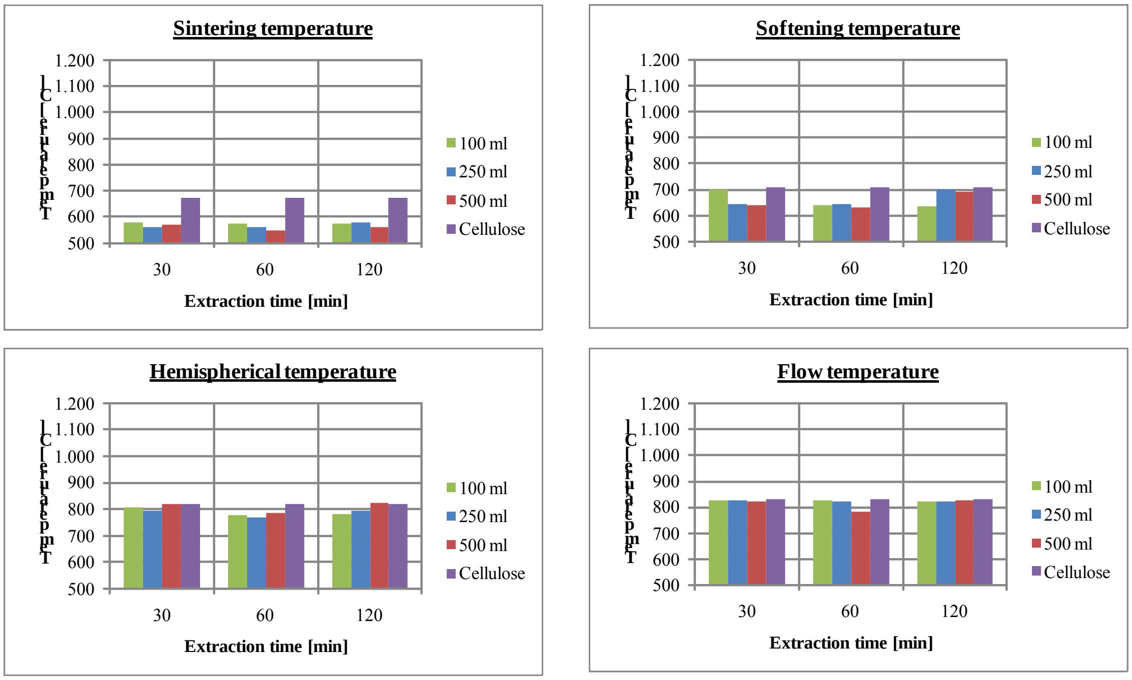


Figure 5: Impact of the additive mass fraction on the ash content

In figure 5 the impact of the additive mass fraction on the ash content is presented. Thereby a significant increasing of the ash content from an addition of 5 wt.-% of the solid additive was determined. In contrast, with the liquid additive no significant impact on the ash content could be observed. This is also the reason why the ash melting behavior could not be influenced.

Extraction/Leaching of the source material

With the fuel leaching method the fuel is mixed with an appropriate extraction agent. Through contact with the fuel individual components dissolve in the extraction agent. In the context of the laboratory examinations water and 1 M acetic acid were selected as extraction agent. The influence of the extraction agent volume and the extraction time were investigated. After leaching the cellulose residues the suspension was filtered. The composition of laden extraction agent was then determined by ion-chromatography. The residue was dried, ashed and analyzed for the ash melting behavior in the melting microscope. The use of water as extraction agent was found to be problematic because of the SAP in the cellulose. These particles absorb water, swell and thus prevent a gravity filtration. When using acetic acid the effect of swelling was not observed. In Figure 6 and 7 the ash melting behavior is shown after the extraction with water and acetic acid.

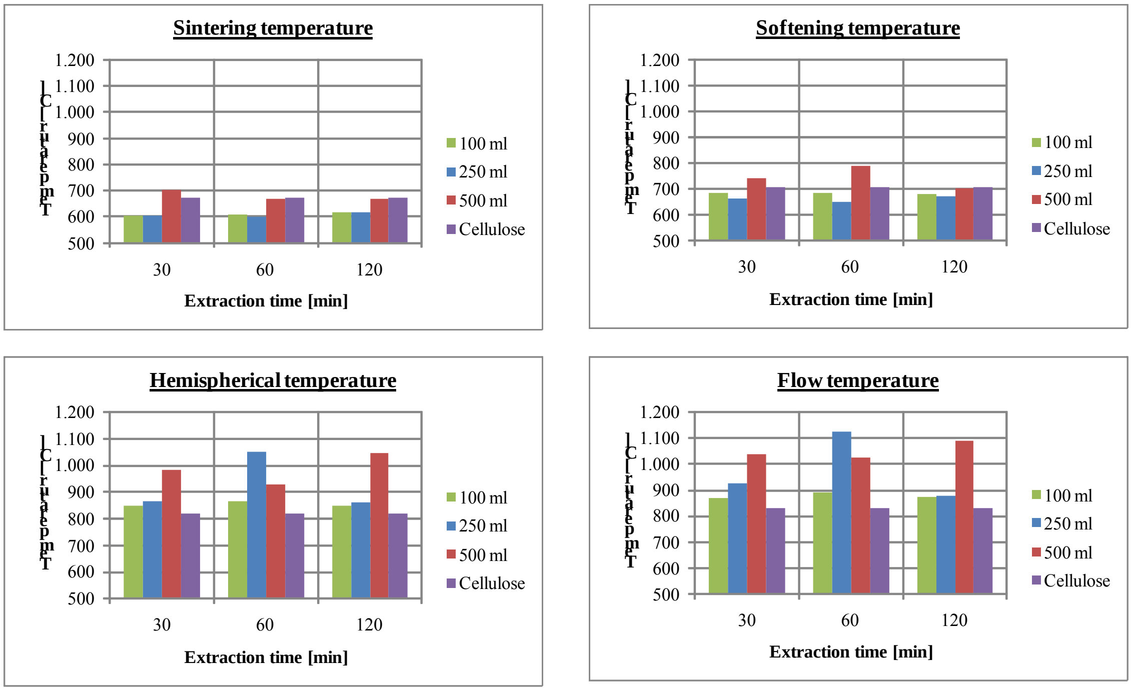

Sintering temperature

Softening temperature

Hemispherical temperature

Flow temperature

Figure 6: Impact of the extraction agent water on the ash melting behavior


Sintering temperature

Softening temperature

Hemispherical temperature

Flow temperature

Figure 7: Impact of the extraction agent acetic acid on the ash melting behavior

As Figure 6 shows, no improvement of the ash melting behavior can be achieved by extraction with water. Noticeable is, however, that both the sintering and the softening temperature of the extraction residue are partially lower than that of the pure cellulose. A positive effect on the ash melting behavior has, however, the extraction with acetic acid. Although no significant increase of sintering and softening temperature can be determined a significant increase in the hemispherical and flow temperature is reached. In Figure 8, the ash content of the fuel treated with acetic acid is shown as a function of extraction agent volume and duration. It is apparent that the ash content of up to 0.4 wt.% (at 500 ml acetic acid) to 1.2 wt.% was (at 100 ml) was reduced. The extraction time, however, has no significant effect on the ash content.

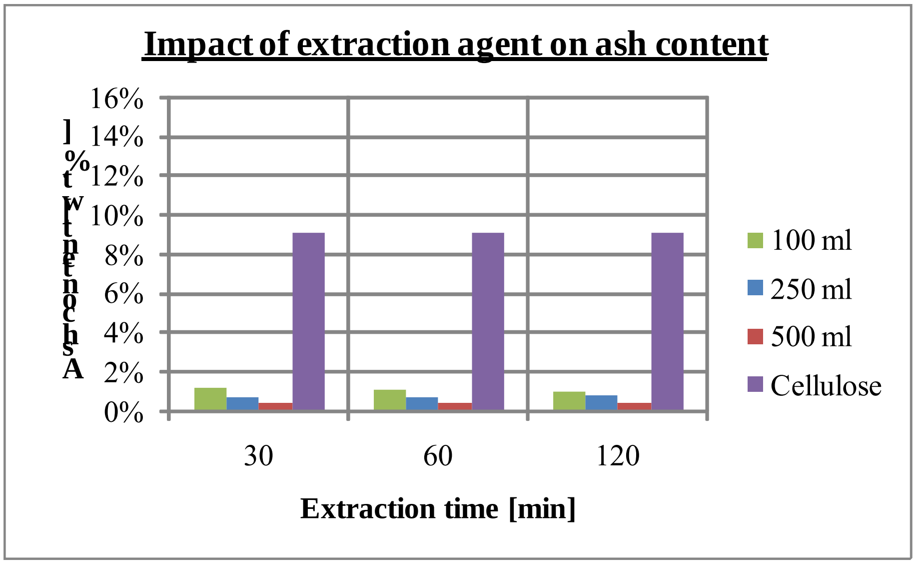


Figure 8: Impact of the extraction agent acetic acid on the ash content

With the aid of the ion chromatography the concentration of the dissolved sodium was measured. The resulting degree of extraction of sodium was calculated to 30 % for water and 98 % for acetic acid.

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

The aim of the thermal treatment is to release sodium out of the source material and using the remaining char for the pellet production. For carrying out the pyrolysis in laboratory scale, a modified laboratory furnace with a retort was used (Figure 9). Therefore, the source material was filled in the retort and set with a temperature controller to the pyrolysis temperature (400 °C; 600 °C). During pyrolysis the retort was continuously purged with nitrogen. After the experiments, a trace analysis of the pyrolysis residue was performed and the ash melting behavior in the melting microscope determined. The analysis results are summarized in Table 4.

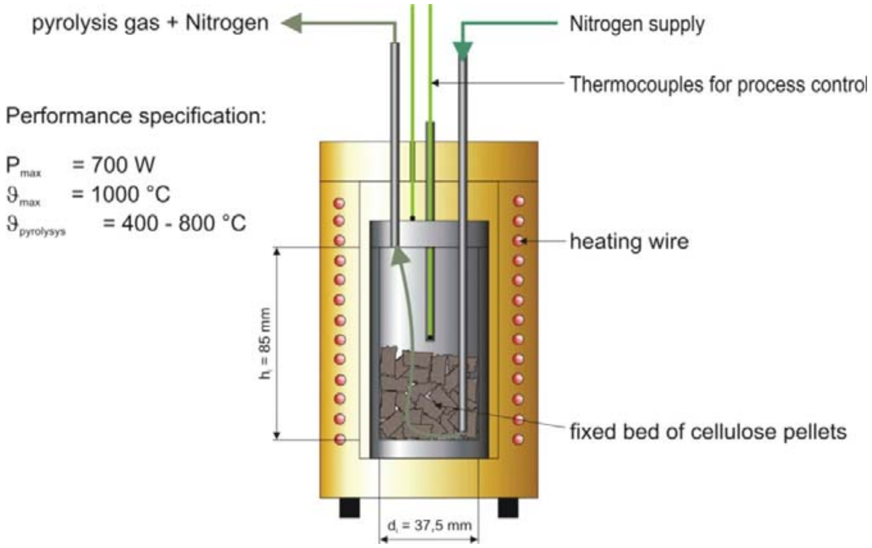


Figure 9: Design and function of laboratory pyrolysis facility.

Table 4: Trace analysis of pyrolysis char

Element	**Symbol**	**Unit**	**400 °C**	**600 °C**	**Cellulose**
Aluminium	Al	mg/kg (d.b.)	148.87	93.64	231.3
Sodium	Na		29092.51	28081.05	38510.0
Potassium	K		26.71	12.52	38.2
Calcium	Ca		413.10	351.19	444.1
Magnesium	Mg		83.44	54.09	123.5
Iron	Fe		28.62	28.61	98.0
Silicon	Si		191.72	59.40	253.6
Softening temperature	ϑ_{ST}	°C	833	831	847

The trace analysis of cellulose char compared to the unmodified source material shows that through pyrolysis a small reduction of the ash-forming constituents could be achieved. Taken into account the influence of pyrolysis temperature, as expected, a higher element release at 600 °C can be determined. If the ash melting behavior is considered, it appears that in consequence of the low sodium release an increase of the softening temperature cannot be achieved.

5 Summary

To enable the use of biogenous residues in established wood pellet heating boilers fuel modification methods can be considered. To improve the ash melting behavior of cellulose residues of the diaper production four modification methods were examined in laboratory scale. The advantages and disadvantages of each modification method are compared to the case of cellulose residues in Table 5.

Table 5: Comparison of advantages and disadvantages of fuel modification methods

Method	**Advantages**	**Disadvantages**
Addition of biomass to the source material	--	- No improvement of the ash melting behavior
Addition of additives to the source material	- Significant improvement of the ash fusion temperature above 1200 °C from 2 wt .% $Ca(OH)_2$, $CaCO_3$	- Increase in the ash content of 3 wt .% additive to about 10 wt.%
Extraction/Leaching of the source material	- Significant improvement of the ash melting behavior for extraction with 500 ml of acetic acid to max. 1100 ° C - Reduction of the ash content to 0.4 wt .%	- High equipment costs for the large-scale realization
Thermal pretreatment of the source material (e.g. pyrolysis of the source material)	--	- additional expenditure of energy for the thermal treatment necessary - no improvement in the ash melting behavior

In summary, it should be noted that the addition of additives and the leaching of fuel lead to an improvement of the ash melting behavior. In further examinations must be verified if the lab scale results will be confirmed during real combustion conditions. For this purpose further combustion experiments will be carried out in pilot plants such as batch reactor [9] and a domestic pellet boiler. Therefore it must be verified how the modification methods lead to an influence in the combustion behavior.

6 Acknowledgments

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