

INFLUENCE OF TORREFACTION AND HYDROTHERMAL CARBONISATION ON FUEL AND ASH PROPERTIES

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In this work, torrefied as well as hydrothermal carbonised biomass have been examined. To evaluate the torrefaction process, grindability, ash melting behaviour and fuel as well as ash composition of untreated and torrefied woods were analysed. For that purpose populus, alder, spruce and birch have been used. Significant differences in heating values and particle size distributions could be observed. For spruce and birch a mean increase in the heating value of 15 % has been observed. For poplar and alder the heating value slightly increased by 7-9 %. The increase in heating value can be mainly explained with the decrease in oxygen and hydrogen containing compounds. The median values of the ground fractions for the torrefied woody biomass were within the range from 80 to 95 μm , whereas the non-torrefied woody biomass showed median values ranging from 180 to 230 μm . Main components of the ash of all analysed wooden biomass are potassium oxide, silicon oxide and calcium oxide. Torrefied biomass shows a broader melting range and a more pronounced melting peak. Analysis of ash melting, ash characteristic numbers and FactSage simulations of the untreated and torrefied wood, show a lower melting range at lower melting temperatures referring to the untreated biomass. The H/C and the O/C ratio of the HTC coals show similar results as lignite. Except for the hydrothermal carbonised green waste, the HTC-coals of spent grains and compost show a high melting range in the field of the torrefied woods.

Keywords: torrefaction, ashes, calorific value, biochar

1 INTRODUCTION

One of the current challenges of the German energy network is to reduce its dependence on fossil fuels and to achieve a sustainable environmental scenario. The bioenergy in Germany reached 7.5 % or rather 985 PJ in the year 2014 [1]. A new study of the current year shows that the potential of unused biogenic waste and residual products in Germany amounts to 448 PJ, with the major proportion of residual forest wood (48 %) and straw (31 %). A small part is built by liquid manure and dung (16 %), scrap wood (3 %) and urban waste (0.6 %) [2]. In the scenarios for achieving the objectives of the energy concept, the federal government of Germany expects that the primary energy consumption will be reduced by 50 % in 2050, so that the bioenergy could provide more than a quarter of the remaining demand (1.915 PJ) [1]. In that scenario the main apportionment is divided as follows: already used residual and waste materials (28 %), until now not used residual and waste materials (23 %), energy crops (7 %), additional required biomass (25 %) and other.

However, the full use of the indigenous energy potential of biogenic residues and wastes would not be sufficient to cover the needed amounts of bioenergy according to the scenarios of the energy concept of the federal government. It requires extensive information and education to open up the untapped potential of biogenic residues and waste.

One possible approach is to use pre-treatment processes, such as torrefaction or hydrothermal carbonisation. As fuels, all agricultural residual materials, straw, energy plants, short-rotation plantations and grass cut or landscape conservation material are of interest.

Compared to coal, biomass has a relatively high moisture content, a hydrophilic behaviour, low energy density and is difficult to store [3, 4]. In addition some types of

biomass are difficult to grind due to their wet and fibrous character. This is a problem when biomass is to be used as fine particles in pulverized or dust firing systems to produce heat or electricity, such as cofiring with coal.

Torrefaction has been proposed as a process for upgrading biomass by thermal treatment that occurs in an inert atmosphere at moderate temperatures in the range of 200-300 °C [3-6]. It is similar to a mild pyrolysis and therefore takes place in absence of oxygen. Typical residence times are a few minutes to about one hour. During the refinement process the fuel runs through the following steps depending on the operating temperature: drying, depolymerisation, decomposition and carbonation. Hemicellulose, cellulose and lignin are all subject to these steps, although at different temperatures. Hemicellulose represents the least thermally stable structure. During the torrefaction process, the moisture content and low weight organic volatile components are removed, producing a brown, brittle and hydrophobic solid product with an increased energy density [7].

In contrast to the torrefaction process where rather dry woody fuels are used, for the hydrothermal carbonization (HTC) biomass types with a high moisture content are of main interest [8].

To perform the procedure of HTC, the addition of water is required. Beside water also a catalyst, such as citric acid or iron salts, is added [8]. The catalyst lowers the activation energy needed in the process and thus speeds up the conversion process. In a pressure vessel, the mixture is then heated up to a temperature between 170-250 °C, so that the exothermic conversion process can begin. Typical pressures are in the range of 10-20 bars and must correspond at least to the saturation pressure in order to prevent an evaporation of the water. Typical residence times are a few hours to a day. Two product streams are created that are isolated by

filtration: 1) an insoluble, char product and 2) water soluble products [9, 10].

2 METHODS / MEASUREMENT TECHNIQUES

2.1 Evaluation Method

The untreated and torrefied wood was wood delivered in form of wood chips whereat the moisture content of the untreated wood amounted to 23-26 wt.-%, that of the torrefied wood to about 2-4.5 wt.-%.

To study the ash melting behaviour, the following measurement techniques are used: Ash compositions were investigated and determined by X-ray fluorescence (XRF) analysis as well as atomic emission spectroscopy (ICP-OES). Thus, the elemental composition of the ash was determined both qualitatively and quantitatively. To determine the mineral phases, a powder diffractometer (XRD) was used. With the ash melting microscope (AMM), the characteristic melting temperatures were determined. Due to the rather vague significance of the ash melting microscope, the ashes were measured additionally by Simultaneous Thermal Analysis (STA). The results obtained experimentally were then qualitatively compared and evaluated with equilibrium calculations.

The calculation of the mass and energy yield is shown in equation (1) and (2):

$$Y_{mass}(\%) = \left(\frac{m_{product}}{m_{feed}} \right)_{wf} \quad (1)$$

$$Y_{energy}(\%) = Y_{mass} \left(\frac{HHV_{product}}{HHV_{feed}} \right)_{wf} \quad (2)$$

The water-free mass of the feed was determined by thermogravimetric analysis after heating up to 110 °C and waiting for 30 min. The mass of the product represents the remaining mass after the torrefaction process (300 °C, 30 min; e.g. 2.7).

2.2 Ash Treatment

The methods used for the ashing or incineration heat-up and holding periods are for biomass the same or even higher as DIN EN 14775. For the coals (HTC and Lignite) the norm of DIN EN 51719 is used. A holding period of 13 h was chosen to ensure a full conversion of larger sample volumes during incineration.

2.3 XRF Measurements

For ash analysis, the instrument of Shimadzu EDX-800 HS was used. The examination requirement for fuel ashes by means of compressed tablets according to DIN 14775 for the determination of ash composition was used in this case. The pellet contains 100 mg of the test ash and 20 mg of a binder, in this case wax. The mixing ratio should always be 10:2. After successfully weighing the material mixture, it has to be mixed for 3 minutes in an agate mortar to homogenize and then filled in a pressed mold.

2.4 ICP - OES Measurements

With the help of a suitable flux (lithium metaborate), the biomass according to DIN 51729 is manufactured according to DIN EN 14775 - 11. The sample was mixed with lithium metaborate LiBO₂ and melted at 1050 °C for

about 15 min. After cooling, the melt is dissolved by hydrochloric acid (HCl). Only clear fusion solutions should be used for the investigation of the ICP - OES.

2.5 XRD Measurements

Powder X-ray measurements were performed at room temperature using the diffractometer X'Pert (Philips) in a Bragg-Brentano geometry with the Cu-K α radiation. The phase identification was carried out using the software HighscorePlus2.2.2 (Panalytical) and PowderCell 2.4 [W. Kraus & G. Nolze, *Federal Institute for Materials Research and Testing, Berlin, Germany*] in a combination with the Inorganic Crystal Structure Database (Karlsruhe, Germany). Semi-quantitative analysis of the detected phases was performed with the software Powdercell.

2.6 AMM Measurements

The melting microscope used is by the company Hesse Instruments. Due to the fact that the investigation of the ash melting behaviour by ASM is an optical measuring method, according to DIN CEN / TS 51730 - 1 convention we need to define factors to determine the characteristic temperatures for biomass more precisely. For the tests, a cylindrical specimen was prepared. The measurement was repeated at high deviations to the determined values i.e. > 30 °C. All experiments were carried out under atmospheric conditions.

2.7 STA Measurements

Coupling a thermo balance type STA PT1600 by the company Linseis with a DSC sample holder creates the TG - DSC instrument (STA) with which it is possible to draw conclusions on both chemical decomposition reactions as well as on the ash melting behaviour. In this simultaneous measurement technique we detect the change in mass due to temperature dependence and in addition to this we can detect simultaneously the endothermic and exothermic heat flows. For evaluation the software TA Evaluation V 2.0.0 by Linseis was used. The Al₂O₃ crucible had the following dimensions: outer diameter 7 mm, height 4 mm and wall thickness 0.5 mm. The STA samples to be investigated were prepared in accordance with DIN 51006. For better comparability of the results always the same initial weight (about 15.75 mg) was used, with a specially designed plunger that compresses the ash in the crucible and spread evenly. All experiments regarding the ash analysis were carried out under oxidizing conditions. Here, the reaction chamber of the instrument was flushed with 100 nml / min with a heating rate of 10 K/min. The investigated temperature ranges from 20 to 1500 °C.

The simulations of the torrefaction process were investigated at the same heating rate as the ash analysis (10 K/min) but with a nitrogen atmosphere. Before heating up, the reaction chamber was purged (about 30 min) with nitrogen to ensure an oxygen-free atmosphere. The temperature was held at 110 °C for 30 min to evaporate the water. Afterwards it was continuously heated up to 300 °C for 30 min.

2.6 Heating value

The heating value was determined with a bomb calorimeter from Paar Instrument Company (DIN 51900). The weight of one sample pan was 1 g and the adiabatic bomb calorimeter contained 2 l tap water. The pan with the sample is placed inside the bomb and the ignition

wire is fixed to the electrodes. Then the bomb is closed and filled with oxygen until a gauge pressure of 30 bar is reached. Afterwards the bomb is placed inside the water tank and closed tightly. With a constant heat capacity of the system, the heating value of the sample can be calculated from the temperature change inside the system.

2.8 FactSage Modeling

The calculation program FactSage was used for the simulation of equilibrium calculations. The calculation method is based on the Gibbs energy minimization, with less than 0.01 wt.% phases neglected. As a basis for the calculations both the organic and the inorganic constituents of the fuels are used in the form of pure elements. The organic constituents were determined according to DIN 51721 up to DIN 51727 on the basis of elemental analysis (MACRO-Company for elemental analysis systems GmbH). The inorganic components were determined by XRF. Here, the fuels were ashed at 550 °C. The air ratios required for the experiments were taken into account and implemented into FactSage. The databases used were FT-oxide, FT-Salt and FACT-PS. The expected mixed crystals were estimated by appropriate phase diagrams. As a result, the composition of the gas, solid and liquid phase of individual fuels was generated. Furthermore, the phase fractions (solid - liquid) are determined as a function of temperature and air speed.

3 TORREFACTION RESULTS

3.1 Fuel Characteristics

The torrefied wood was provided by a company, where both the torrefied and the appropriate untreated wood were delivered. The process temperature was 300 °C with a residence time of 30 min. To evaluate the torrefaction process, grindability, melting behaviour and fuel composition as well as ash composition of untreated and torrefied biomass were examined. For that purpose populus, alder, spruce and birch were used. For better comparability between untreated and torrefied biomass, the same sieve was used during the grinding process.

The fuels were ground with a cross hammer mill SK 100 from the company Retsch GmbH. Comparing the modal value as well as the median value of the particle sizes of torrefied and untreated biomass, significantly lower values for the torrefied material can be observed. Although the grinding was performed with the same sieve (mesh size=250 µm), the modal particle size for torr. birch, for instance, is reduced by almost 70 % (not shown in **Table I**), and its median particle size (d50) by almost 60 % (e.g. **Table I**). The median values of the ground fractions for the torrefied biomass were within the range from 80 to 100 µm, whereas the non-torrefied biomass showed median values ranging from 180 to 230 µm. This means that with torr. biomass a much finer particle fraction can be reached at the same energy input. For the non-torrefied biomass, continuous grinding was not feasible, because the moisture of the untreated and fibrous wood caused agglutination on the sieve.

Table I: Data of the proximate and particle size analysis of the torrefied und raw biomass (wf)

Fuel	Median value [µm]	Fixed C [%]	HHV [MJ/kg]	Volatiles content [%]	Ash content [%]
Alder	200.6	15.65	19.11	84	0.77
Torr. alder	100	22.13	21.05	76	1.65
Spruce	180	15.14	18.83	84	0.74
Torr. spruce	82	27.21	23.29	71	1.66
Birch	225	14.45	19.25	85	0.39
Torr. birch	90	27.23	22.60	72	1.53
Populus	195	15.03	17.41	84	0.41
Torr. populus	100	20.41	20.85	78	1.51

For the untreated biomass, the results of the higher heating values only slightly differ. Torrefaction, however, causes a partly significant increase of the heating value (according to DIN 51900 - 1). For spruce and birch an average increase of about 15 %, for populus and alder of about 7-9 % is observed. The increase of the heating value after the torrefaction process can be explained by the reduction of oxygen, hydrogen and moisture within the fuel. Thereby the decrease in oxygen is the highest. Further outcomes of torrefaction are the reduction of volatiles (according to DIN EN 15148) and the increase of ash content (according to DIN EN 14775 at 550 °C).

A comparison of the analytical data (e.g. **Table I**) with the literature clearly shows that the ash content of the samples in this study are unexpectedly high. Due to the evaporation of water and the volatilization of oxygen and hydrogen compounds the inorganic content of the fuel is concentrated during the heating process of the torrefaction. This mass loss is mainly dependent on the fuel, the process temperature and the residence time. Typical mass losses are in the range of 10-35 mass .-%. To follow along with this increased ash content the torrefaction was analysed by TGA (see below **Figure 1**).

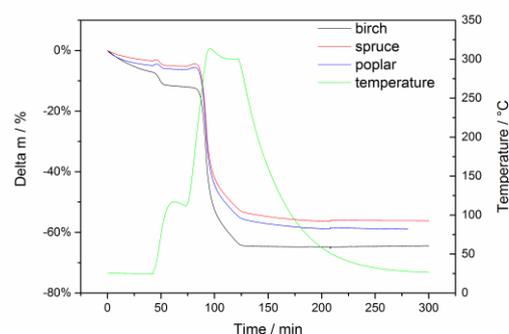


Figure 1: Experimental data of the investigated woods using thermogravimetric measurements (TGA)

Here, the process parameters of the delivered torrefied biomass have been set. To evaluate the mass yield due to the torrefaction process the mass loss after the waiting period of 30 min at 110 °C and after 30 min at 300 °C was used.

If it is assumed that the inorganic part of the fuel after the torrefaction has remained constant, the higher ash content of the torrefied biomass can be explained by the release of oxygen and hydrogen compounds.

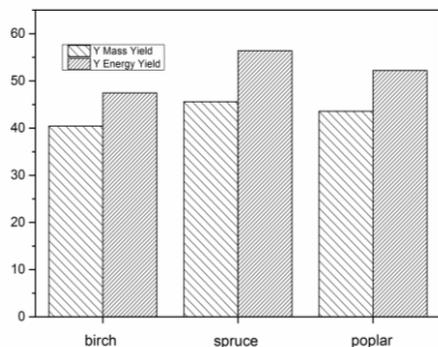


Figure 2: Energy and mass yield (wf) due to the torrefaction process

With increasing temperatures and residence times during the torrefaction process, a decrease in the mass yield is expected. Lu et al. [11] and further investigations show [12–14] the same trend. In this study, due to the high mass yield of 40-45 % a minor energy yield of 47-56 % results.

3.2 Ash melting behaviour

The ash composition of the investigated fuels is shown in **Figure 3**. With respect to the torrefied fuels an increase of all components can be seen due to the concentration of the ash content. The main components of the ashes are in all cases CaO, K₂O and SiO₂.

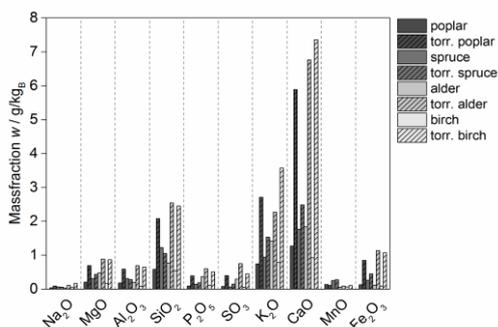


Figure 3: Ash composition of the untreated and torrefied woods

Looking at the characteristic melting temperatures, which were determined by the ash melting microscope (AMM) from Hesse Instruments, a trend can be observed (see **Figure 4**): Torrefaction causes a decrease of the shrinkage temperature ($T_{Shrinkage}$) whereas flow temperature (T_{Flow}) and hemisphere temperature increase.

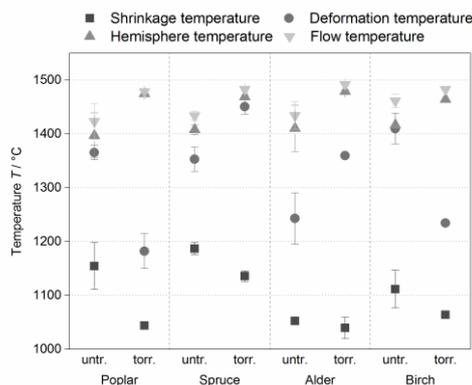


Figure 4: Comparison of the characteristic ash melting temperatures, ashed according to DIN EN 14775 / TS 51730-1

In **Figure 5** and **Figure 6** the results of the Factsage simulations and the data of the ash melting microscope are contrasted. The temperature range of the shrinkage process is determined by Evic et al. with 15 to 30 % of the liquid phase, that of T_{Flow} at 75 % of the liquid phase, depending on the biomass type [15]. Wieland et al. [16] determined the shrinkage temperature for a bituminous coal at 10 % and that of T_{Flow} at 70 % of the liquid phase. Since there is no standard specification yet, in that study the dotted lines are in according to the literature. Here, not one temperature but a temperature range for the shrinkage process from 15 to 30 % of the liquid phase is determined.

The results of the FactSage simulations are in good agreement with the ash microscope data. On the one hand, in contrast to the torrefied spruce, a minor distinct melting range for the untreated spruce, showed in a sharp increase of the curve, is detected. On the other hand, the shrinkage temperature is found in the range of 15-30 % of the liquid phase. In all cases the flow temperature of the untreated and torrefied biomass is found in the range of 75-90 % of the liquid phase.

The discrepancy between the ash melting behaviour relating to the results of the STA, the AMM and FactSage is based on the different ash composition of the untreated and torrefied biomass fuels. Especially the content of potassium of the raw biomass is 20 to 40 % higher in contrast to the untreated biomass. Potassium can build in presence with silicates low-melting compounds. It is assumed that the compounds of potassium silicates are responsible for the slight and minor melting range of the raw biomass.

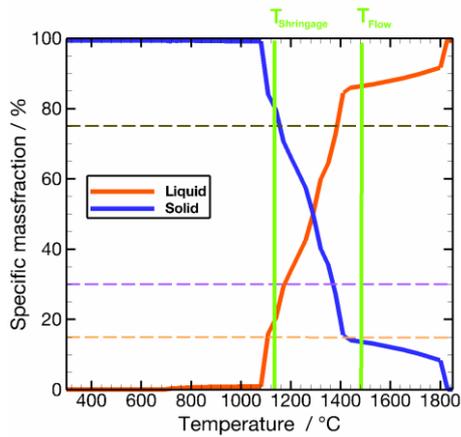


Figure 5: Comparison of the ash melting behaviour of torrefied spruce with FactSage and AMM data

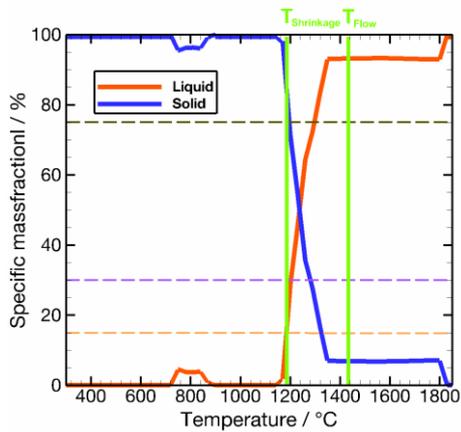


Figure 6: Comparison of the ash melting behaviour of untreated spruce with FactSage and AMM data

In order to identify melting phases, the biomass was analysed by simultaneous thermal analysis (STA) (e.g. Fehler! Verweisquelle konnte nicht gefunden werden. and Fehler! Verweisquelle konnte nicht gefunden werden.). For that purpose, the samples were ashed at different temperatures (550 °C, 650 °C; 750 °C; 815 °C, 900 °C) in the laboratory and heated up to 1550 °C in an oxidizing atmosphere with a heating rate of 10 K/min. The evaluation of the results shows that there are no significant differences caused by the torrefaction process during the entire heating-up period. Rather the heat flow signal as well as the mass loss as a function of the temperature can be divided into three characteristic zones. In the first zone (approx. 400 °C) decomposition reactions of alkali hydroxides (CaOH, MgOH) are assumed to take place. Between 550 °C and 950 °C the highest mass loss is detected. Release of CO₂ as well as decomposition of carbonates (CaCO₃, MgCO₃) into metal oxides (CaO, MgO) is likely to happen in this temperature range. Furthermore the release of potassium is observed. It is assumed that at temperatures higher than 400 - 800 °C potassium in the gas phase mainly exists as KCl and K₂SO₄. The third zone stretches across a temperature range from 1100 °C to 1500 °C and is identified by a characteristic melting peak. Comparing the melting peaks of untreated with the ones of torrefied

woods, a less distinct melting peak for the untreated biomass can be observed. A characteristic example for all investigated fuels is shown in **Figure 7** and **Figure 8**.

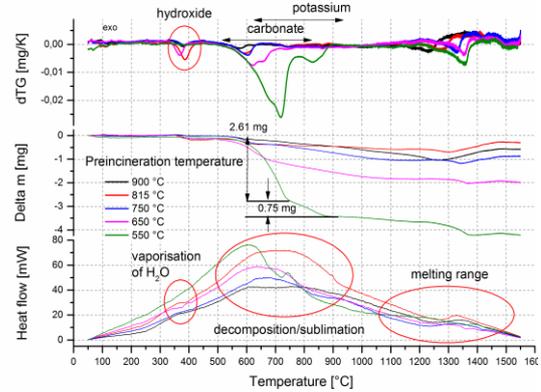


Figure 7: Analytical results of the STA experiments (untreated birch)

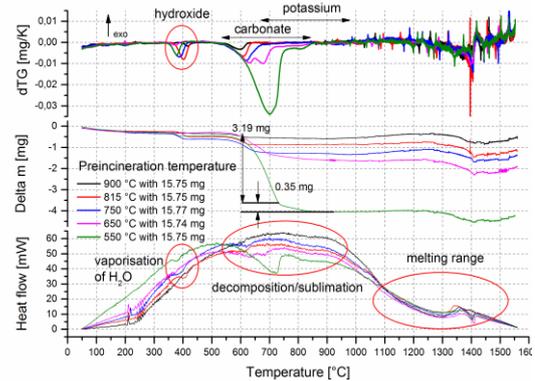


Figure 8: Analytical results of the STA experiments (torrefied birch)

4 HTC RESULTS

The product of hydrothermal carbonisation has properties similar to lignite. For this reason, the most important fuel properties of the three investigated HTC coals are compared in **TABLE II** with a typical brown coal from Germany. The hydrothermal carbonised fuels were delivered; The spent grains were produced at 230 °C and 27 bar, the compost as well as green waste at 210 °C and 20 bar with a residence time of 3h.

Table II: Data of the proximate and particle size analysis of HTC coals and lignite (wf)

Fuel	Median value [µm]	Fixed C [%]	HHV [MJ/kg]	Volatiles content [%]	Ash content [%]
HTC					
Spent grains	45	24.22	29.47	70.89	3.44
Compost /leaves	60.93	41.12	25.81	49.68	4.74
Green waste	40.12	33.48	24.53	60.35	4.80
Lignite					
TBK Lausitz	80	41.97	24.84	53.1	5.95

The composition of the HTC coals depends strongly on the primary feedstock. Noticeable in **Table II** is the high HHV and volatiles content of the HTC-spent grains. Except for the ash content, the proximate analysis of compost and lignite are in a good agreement. The data of the hydrothermal carbonised green waste lies between the other HTC coals.

Looking at **Figure 9** a large difference in the ash composition can be seen. The main components of the compost are CaO, NaO, SO₃ and MgO. A large proportion of the spent grains ash represents SiO₂, CaO as well as Fe₂O₃. Lignite mainly consists of SiO₂, SO₃, CaO and Fe₂O₃. The ash of green waste is dominated by SiO₂ and CaO.

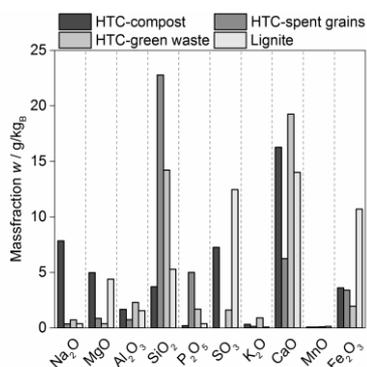


Figure 9: Ash composition of the HTC coals and lignite

In **Figure 10** the results of the ash melting microscope are shown. Remarkable is the missing hemisphere and flow temperature of the spent grains. Due to the high content of SiO₂ and CaO, which are responsible for high melting compounds, a complete fusion of the sample was not feasible. Except the shrinkage temperature, the characteristic temperatures for lignite as well as compost are similar. These fuels are melting at high temperatures because of the increased CaO content.

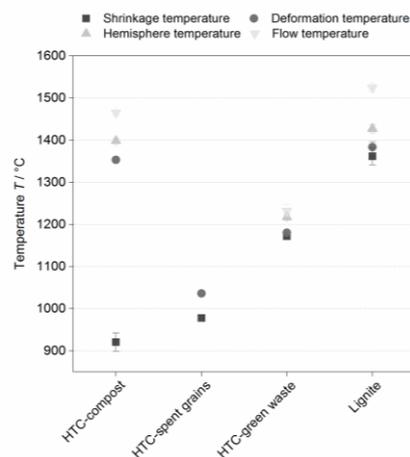


Figure 10: Comparison of the characteristic ash melting temperatures ashed according to DIN EN 51719

5 CONCLUSIONS

With the same sieve screen the median values of the ground fractions for the torrefied woods were more than halved in contrast to the untreated biomass. For the non-torrefied biomass, continuous grinding was not possible, because the moisture of the untreated and fibrous wood caused agglutination on the sieve.

Torrefaction partly caused an increase in the heating value up to 15 %. The increase in heating value can be mainly explained by the decrease in oxygen-containing compounds. In **Figure 11** an expected trend can be seen. The coalification increases with the torrefaction up to the hydrothermal carbonisation.

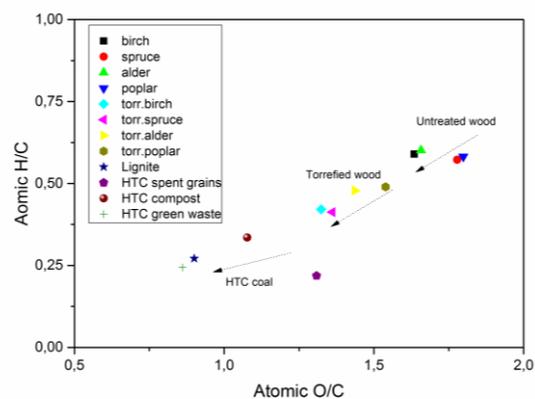


Figure 11: H/C and O/C ratios of the investigated fuels

The ash melting behaviour of the torrefied woods are characterised by a broader and higher melting range in contrast to the untreated wood. It is assumed that the higher potassium content of the untreated woods in presence of SiO₂ leads to potassium silicates with a lower melting range. Also, the high melting range of carbonised compost and spent grains indicate a rather low risk of slagging. Further investigations, especially with respect to experiments at the plant, are necessary to give better prediction of the combustion behaviour.

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