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Production of Solid Sustainable Energy Carriers from Biomass by Means of Torrefaction

Deliverable No. D8.5

Report on test methods and properties of torrefied biomass

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1 Summary

The main focus of the deliverable D8.5 Report on test methods and properties of torrefied biomass is the development and evaluation of new methods and parameter to describe torrefied biomass in a better way. Within the WP8 eight new methods were developed including water absorption, grindability, degree of torrefaction, particle size and size distribution, flowability properties, NIR spectroscopy, leaching behavior and TGA method and will be discussed in the first part of D8.5

In the second part in D8.5 is an evaluation of different fuel properties of various torrefied materials. The change in carbon content, calorific value, dependent on different raw material and/or torrefaction time and temperature will be examined in detail.

2 Report on test methods

Torrefied material shows a significant different behavior concerning fuel properties. For a better description different new analysis methods were developed. Those methods should give a better overall description of torrefied biomass for the end-user as well as the producers. Hence, this could also lead to possible new standards for torrefied materials, which could increase the quality of torrefied biomass.

2.1 Hydrophobicity – water absorption

2.1.1 Introduction and objectives

Hydrophobic behavior or the water absorption capacity of torrefied biomass differs from regular “white” biomass/pellets. For this reason the hydrophobicity behavior of torrefied material was investigated and various tests concerning the water absorption capacity were conducted. The designed method was evaluated with the Round Robin II which was organized in the SECTOR project (D8.4 “Round robin II – Validation of new test methods”).

The test trails included the behavior of torrefied material with water - directly, relative humidity and also a combination with the mechanical durability. Especially the mechanical durability change of torrefied pellets after the water treatment was investigated. The mechanical durability was linked to the water absorption because it is the most influenced parameter during transport and has the highest effect on feeding systems of e.g. combustion plants. The effect of water exposure on durability and pellet quality could also affect the storage decision.

2.1.2 Method development and analyses

Following sections deals with the methods development of the different water absorption methods. Basically two different approaches were made: exposure test at different relative humidity and immersion test of torrefied material in water.

2.1.2.1 Exposure tests

To determine the effect of high air humidity on torrefied pellets the following method was developed. Torrefied pellets were stored for some days in a surrounding with very high air humidity. This condition was reached by different saturated salts solutions in a closed surrounding at ambient temperature (22° C). This equilibrium method with different saturated salt solutions is described by Greenspan (1977). Two different exposure tests over a saturated NaCl (rel. humidity 75 %) and with a saturated K_2SO_4 (rel. humidity 95 %) solution were realized.

Exposure tests with NaCl and K_2SO_4

A container is filled with 350 ml water (water height about 1 to 2 cm) and 90 g NaCl / 70 g K_2SO_4. Into the container a tray with 100 g sample (Figure 1) was placed. The sample tray should not be in touch with the solution. For a better contact of the sample and atmosphere holes were drilled in the bottom of the sample tray. After placing the sample tray in the container, it is sealed with a lid. The moisture content (according EN 14774) of the original sample was determined for comparison.

Figure 1: Experimental setup for NaCl (right) / K_2SO_4 (left) exposure tests

Every 24 hours (exclusive weekends), the sample is reweighed and the water absorption due to higher humidity is determined. To survey the relative humidity and the temperature inside the experimental setup a data logger was used.

Long term test

Also one long term exposure test was conducted. The experimental setup is the same as the exposure test with K_2SO_4 but with a total sample volume of 1.5 kg. The test duration was nearly twice as long as for the other exposure tests. In the beginning and in the end of the test the mechanical durability of the sample was determined according to EN 15210 (double determination).

2.1.2.2 Immersion tests

The second method was developed for the determination of the water absorption ability of torrefied material especially pellets. Additionally the loss of mechanical durability was determined. The following method was part of the SECTOR Round Robin II – Torrefied pellets. All in-house tests were also done with the following method description. Especially for the SECTOR RR II was also a "short version" of the method developed: to ensure a high number of participants the method was also offered without the mechanical durability test.

Method description

In order to determine the absolute absorbed water, the moisture content (EN14774-2) of the original sample (WC_{or}) must be known. As a reference data the original mechanical durability ($D_{U\ or}$) (EN15210-1, double determination-mean value) needs to be determined as well.

For the determination of the water absorption, 650g (for double determination 2x 650 g) pellets are required. The pellets are sieved with the 3.15 mm round hole sieve.

From the sieved material 600 g are weighed in into the soaking pan (m_{wi}). This is filled up with sufficient water, which means 2-3x of the pellets volume. The water level should be at least 2 cm higher than the pellets. In order to avoid entrapped air and clumping of pellets repeated gentle stirring may be needed. After one hour the test portion is separated from the water by using a sieve appropriate for liquid/solid separation and let the sample drip free of water for 30 minutes.

After the dripping time the wet pellets are weighed out (m_{wa}) and weighed in to drying trays (e.g. aluminium trays) and dried to constant mass (max. 24 hours) at 105°C. From the obtained data the absolute water absorption (WA) can be calculated according to equation 1.

The dried pellets are left at ambient atmosphere in order to stabilize for at least 24 hours. Afterwards the moisture content (EN14774-2) and the mechanical durability ($D_{u\ at}$) (EN15210-1, single determination) is tested. The loss of mechanical durability ($D_{U\ loss}$) is determined according equation 2

Equation 1: Determination of the absolute absorbed water:

$$WA = \frac{(m_{wa} - m_{wi})}{m_{wi}} * 100 + WC_{or}$$

WA … Water absorption [%]
m_{wa} … mass of the pellets after dropping time [g]
m_{wi} … mass of the initial weight of the pellets [g]
WC_{or}…original moisture content [%]

Equation 2: Determination of the loss of mechanical durability:

$$D_{U_{loss}} = \frac{(D_{U_{or}} - D_{U_{at}})}{D_{U_{or}}} * 100$$

$D_{U\ loss}$ … Loss of mechanical durability [%]
$D_{U\ or}$ … mechanical durability of original sample [%]
$D_{u\ at}$ … mechanical durability after stabilisation at ambient atmosphere [%]

2.1.3 Results and experiences

In this chapter the results of the different water absorption tests are discussed. The detailed results concerning for the water absorption test of the Round Robin II can be found in the D8.4 “Round robin report 2 – Validation of new test methods”.

2.1.3.1 Exposure tests

Exposure test with NaCl

In Figure 2 the moisture content of different samples at various torrefaction temperatures is displayed. The moisture content of the original samples varies between 2-9.5 w-%$_{ar}$. Over a period of app. 9 days the moisture content was controlled and results in a continuous increase. At the end of the experiment the moisture contents of the different samples are between 8.2 to 10.8 w-%$_{ar}$.

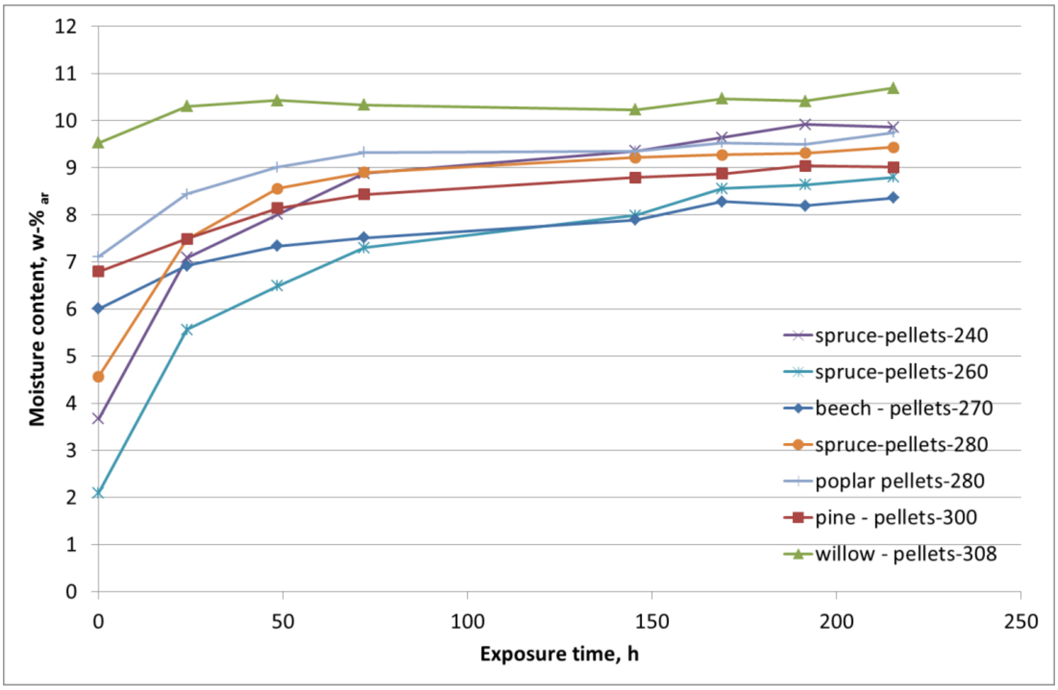

Figure 2: Exposure test with NaCl (rel. humididty 75 %) of different torrefied materials (pellets)

Exposure test with K_2SO_4

The results of the exposure test with K_2SO_4 are shown in Figure 3. The original moisture contents are between 2-9.5 w-%$_{ar.}$ The exposure time was 7 days and after these 7 days the moisture content increased to 9.8-10.8 w-%$_{ar}$.

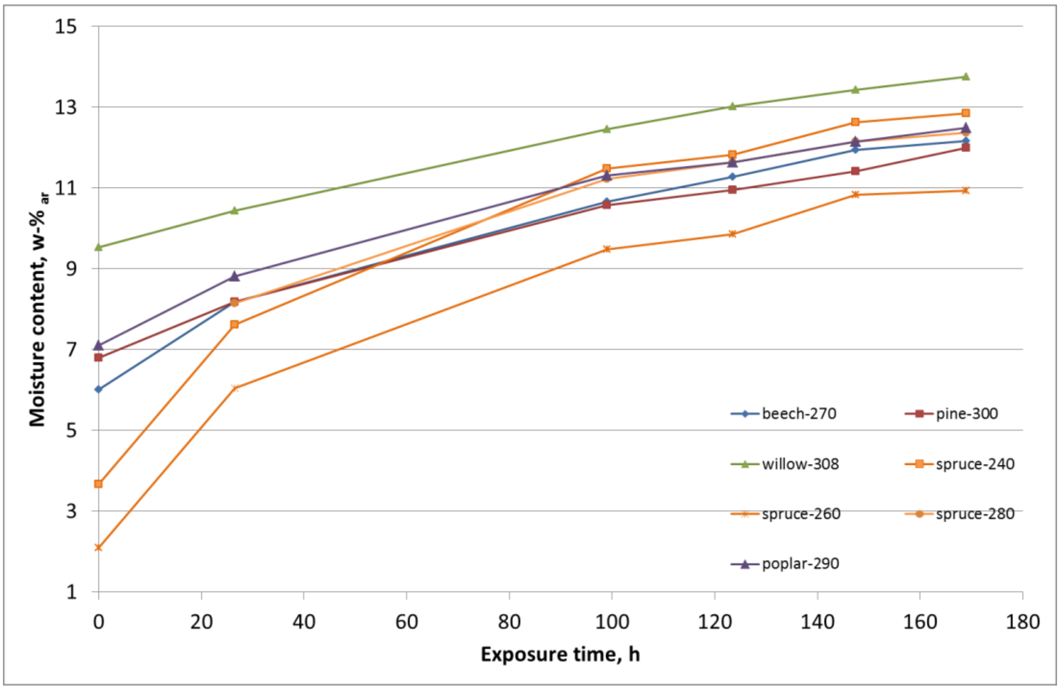

Figure 3: Exposure test with K_2SO_4 (rel. humidity 95 %) of different torrefied materials (pellets)

In Figure 4 (K_2SO_4) and in Figure 5 (NaCl) the corrected moisture content (with the original moisture content) is displayed. Especially for the spruce samples the influence concerning the water uptake in correspondence to the torrefaction temperature can be seen. The lowest torrefaction temperature (spruce 240 °C) shows one of the highest water uptakes. On the other side the torrefaction temperatures of app. 300° C results in a lower water uptake at the same exposure time. For both experiments willow shows the lowest water uptake.

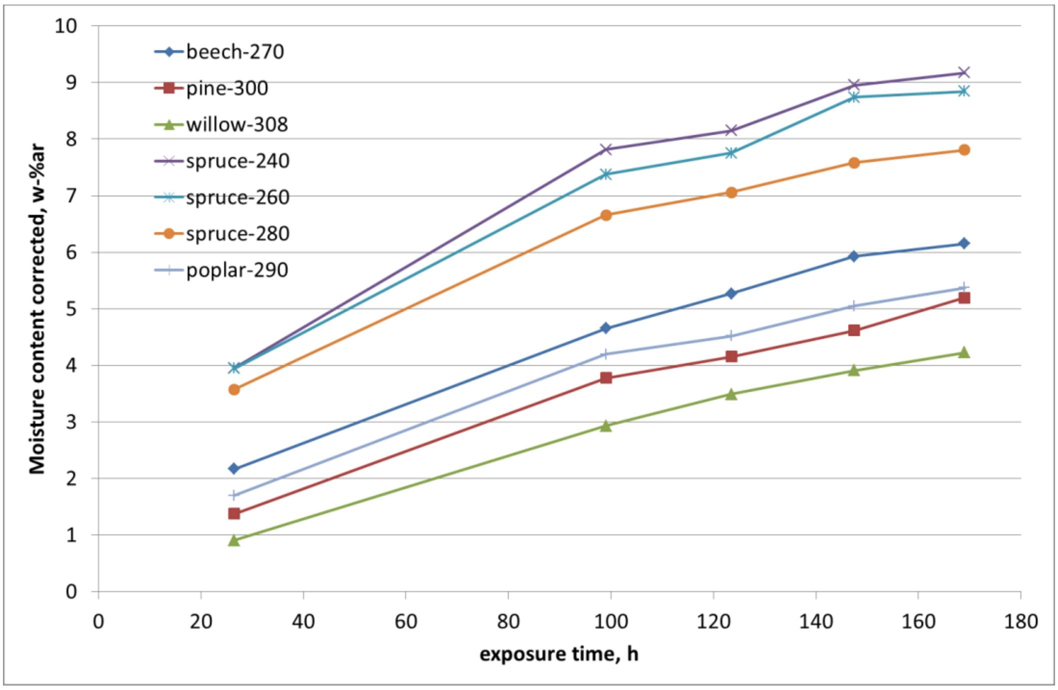

Figure 4: Corrected moisture content - exposure test with K_2SO_4 (rel. humidity 95%) of different torrefied materials (pellets)

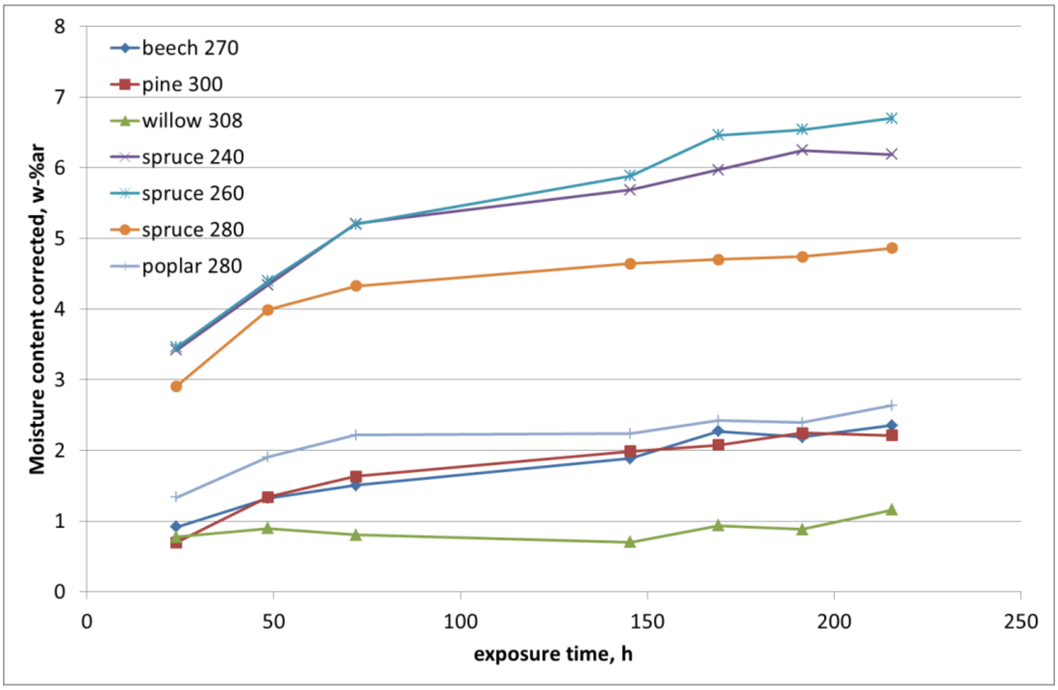

Figure 5: Corrected moisture content - exposure test with NaCl (rel. humidity 75 %) of different torrefied materials (pellets)

Long term exposure test

The long term exposure test was conducted with the K_2SO_4 setting for 14 days (Figure 6). At the beginning and after 14 days the mechanical durability was tested. The loss in mechanical durability (app. 6 %) can be clearly seen. Over time the water uptake process slows down and reaches an equilibrium. The water uptake of the sample beech is 7 w-% or a moisture content of 13.2 w-%$_{ar}$.

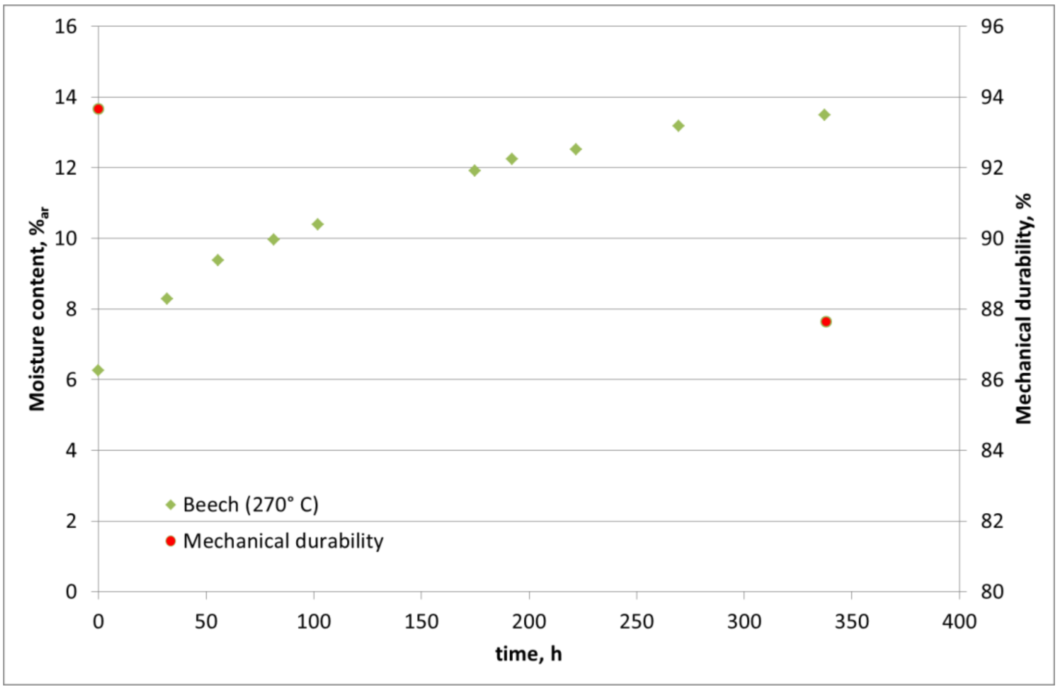

Figure 6: Long time exposure test K_2SO_4 (rel. humidity 95 %) with mechanical durability at beginning and end of storage time

2.1.3.2 Immersion tests

For the immersion tests various pre-experiments were conducted. Those experiments included a different immersion time (Figure 7), different samples from different producers and also different torrefaction temperature (Figure 8). Furthermore the Round Robin II results will be discussed briefly.

In Figure 7 different immersion times (1h and 2 h) were tested and the result is that the difference between 1 and 2 hours is small. Therefore 1 hour immersion time was chosen, which was optimized to 30 min immersion time for RR II and the following tests. The loss in mechanical durability is visible but is not linked to the water uptake.

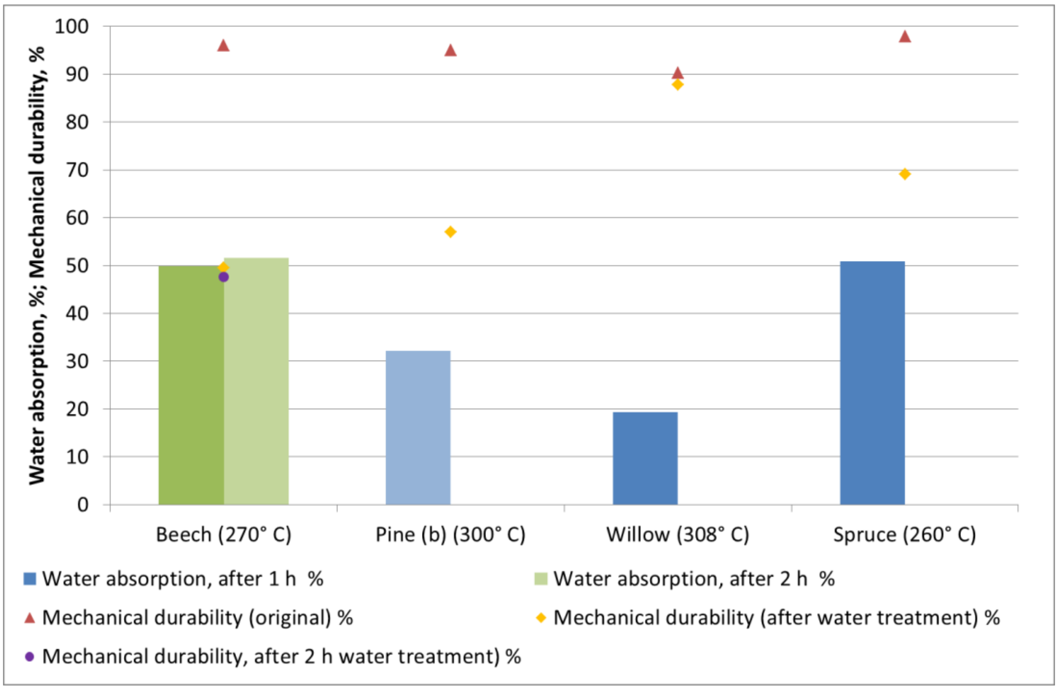

Figure 7: Immersion pre-tests with different immersion times, samples and torrefaction temperatures with mechanical durability test at before and after immersion

For comparison also “white” pellets were analyzed as well and the result is obvious (Figure 8). The water absorption is app. 200 % and after the water experiment the pellets were dissolved and no mechanical durability experiment could be conducted. The samples with higher torrefaction temperature (willow, pine and forest residues) show the lowest water uptake (25-40 %).

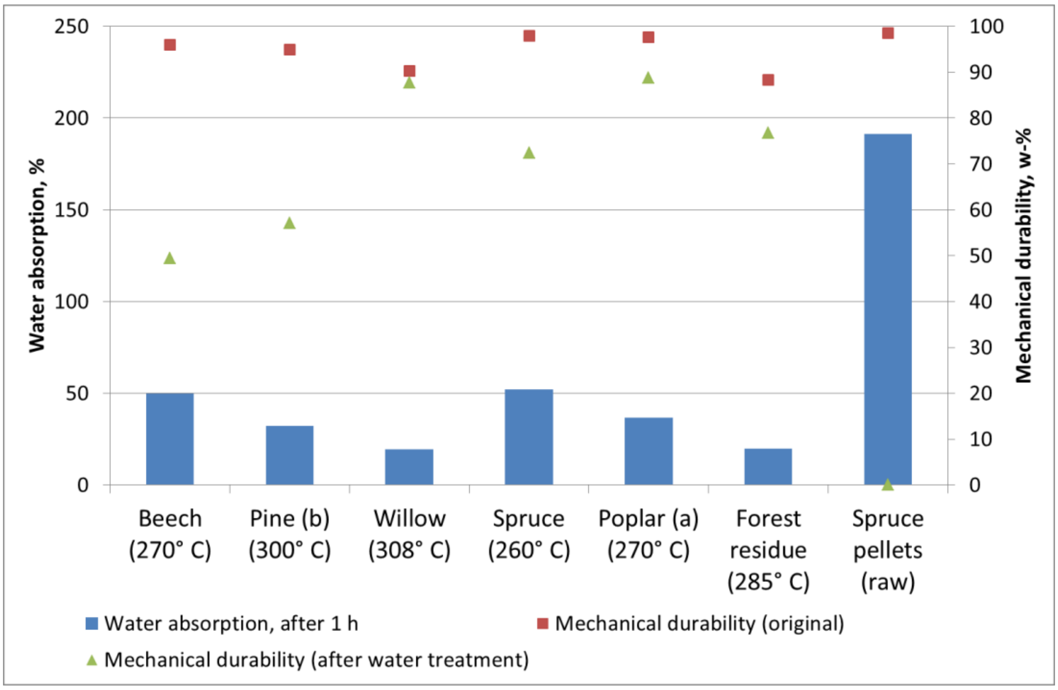

Figure 8: Immersion test of torrefied samples and spruce pellets ("white pellets") with mechanical durability before and after water treatment of 1 h

Round Robin II results

A total of 23 testing laboratories participated in the test method “water absorption”. The participation was open for everybody who is able to perform the selected test according to the given standards and method descriptions.

For the water absorption test conducted within the Round Robin II the result is very promising (Figure 9 and Figure 10). The described test procedure was used in the RR II and can be found in detail in D8.4 “Round Robin report 2 – Validation of new test methods”.

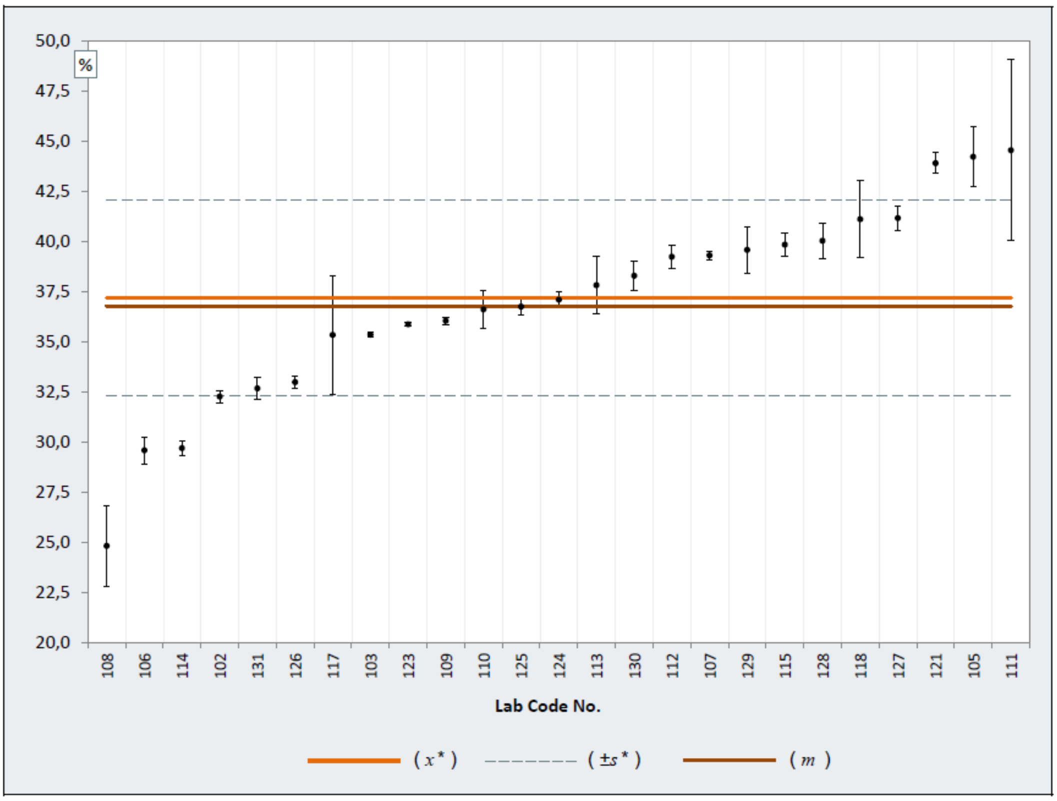

Figure 9: Results of round robin 2 – water absorption / immersion test

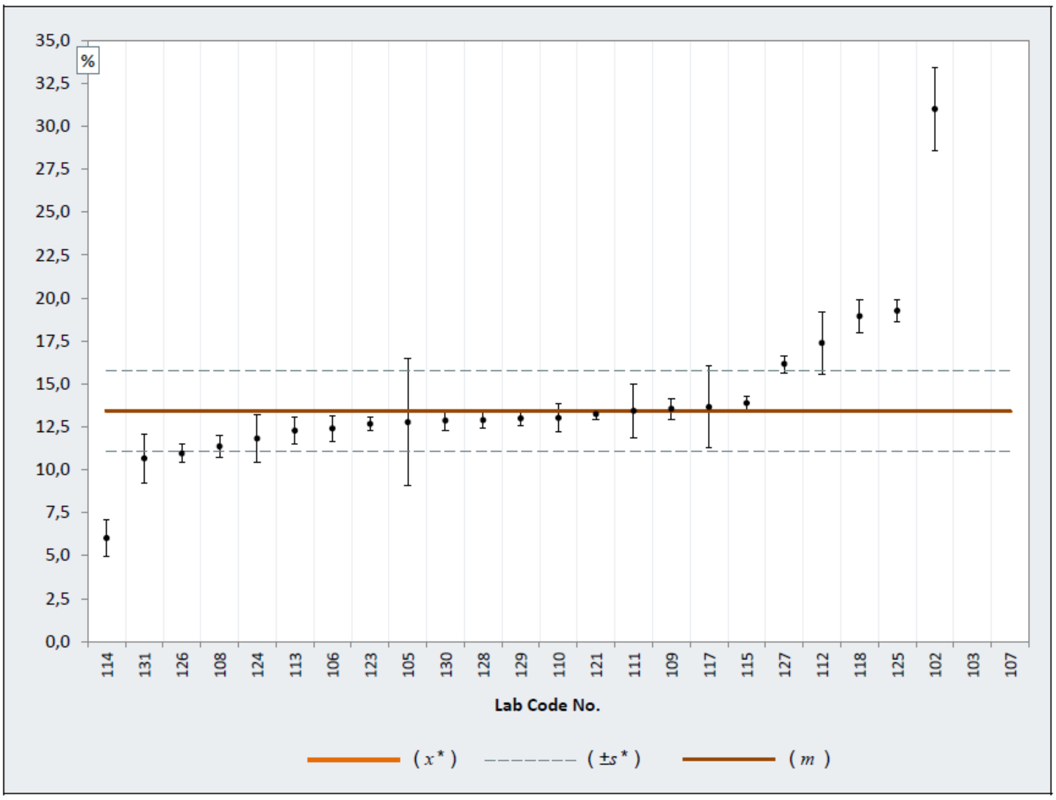

Figure 10: Results of round robin 2 - water absorption / loss of mechanical durability

Additional to the results from the RRII a different number of samples were analyzed according to the RR II procedure (Figure 11). The chosen samples were pine 300° C (lower water uptake – high loss of mechanical durability), willow (lowest water uptake – lowest loss of mechanical durability), pine 285° C (medium water uptake – medium loss of mechanical durability) straw 270° C (lower water uptake – high loss of mechanical durability) and straw 260° C (highest water uptake – highest loss of mechanical durability).

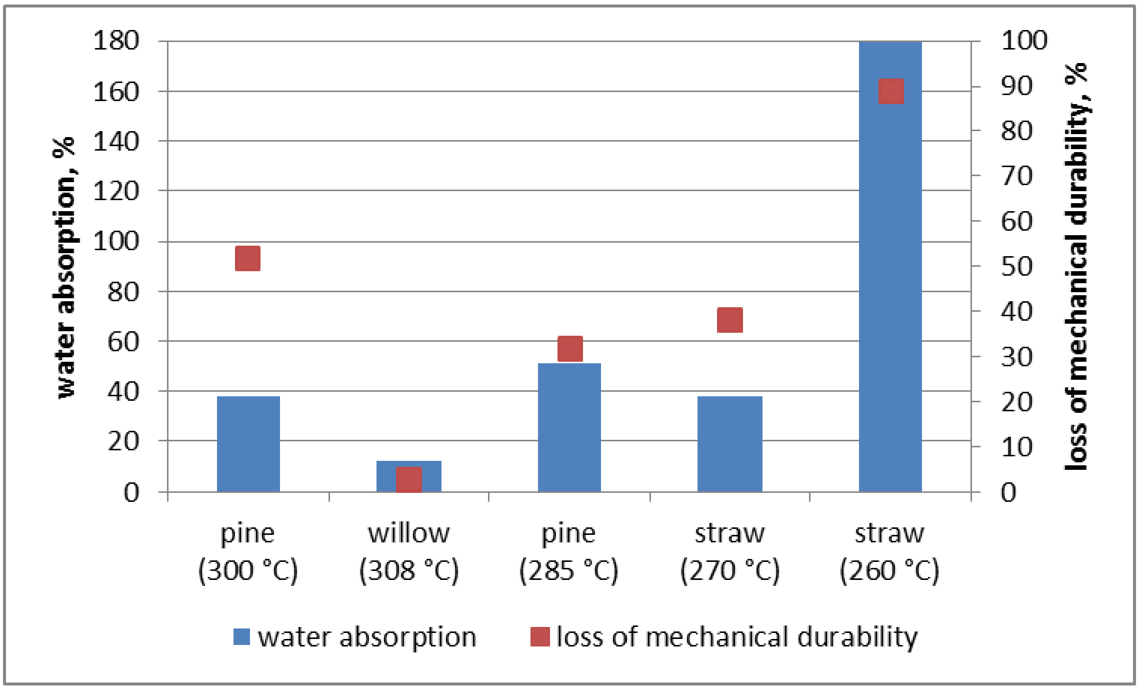

Figure 11: Different samples analysed according method description: water absorption

2.1.4 Summary and Conclusions

Different methods and different samples were tested to describe the water behavior of torrefied material better.

The exposure tests were developed to be able to use an "easy" not complicated test setting at different relative humidity's. Within these tests the wood type as well as the torrefaction temperature shows an influence. Lower torrefaction temperatures means higher water absorption. Long term experiment showed a loss of mechanical durability with increasing moisture content. The method development for the water absorption of torrefied material included immersion time, influence of torrefaction temperatures as well as the link with mechanical durability. The "simple" water absorption is an interesting parameter but the connection with the mechanical durability is especially important because of significance for e.g. storage, transport, grindability.

Overall it can be stated that the water absorption and also the linked loss of mechanical durability are more dependent on the pellet quality than on the sample type (e.g. wood type) or the torrefaction temperature. A shiny even pellet surface absorbs less water than an already brittle pellet. The water absorption method could also lead to a classification of the product torrefied pellets. This classification could have various categories such as e.g. ≤

20 %; ≤ 40 %, ≤ 60 % and > 60 % and should be tested and evaluated in cooperation with the end-users to determine which loss of mechanical durability is crucial.

For the further development of the new methods, this round robin test was very important and useful. Especially the performance data of the “Water absorption” were for the first test promising. With some modifications in the method description and more detailed information in some fields (e.g. water temperature, sieve holes diameter), the method can be used in practice. Especially the remarks from some participants were very useful and give new approach for on-going and future development.

2.1.5 References

Deliverable 8.4 “Round robin report 2 – Validation of new test methods”

EN 15210-1 2010-02: Solid biofuels - Determination of mechanical durability of pellets and briquettes - Part 1: Pellets

EN 14774-2 2009-12: Solid biofuels. Determination of moisture content. Oven dry method. Total moisture. Simplified method

L. Greenspan, “Humidity fixed points of binary saturated aqueous solutions,” *Journal of research of the national Bureau of Standards, A. Physics and Chemistry A*, vol. 81, pp. 89–96, 1977.

2.2 Grindability

2.2.1 Introduction and objectives

A method was to be developed to standardize the measurement of the grinding energy required during the milling process of torrefied biomass pellets. This is especially important for a seamless application of torrefied pellets in e.g. a co-combustion plant as it will require an adjustment of the mills.

The here presented method is a laboratory method requiring a small (yet representative) amount of pellets to be ground in a cutting mill while the power consumption is recorded. Subsequently the specific grinding energy will be calculated from the power consumption values. During its development the method was tested in the laboratories of the DBFZ on seven different torrefied pellet samples. In order to better understand the relation of this method to existing methods for pellet characterization values were compared to mechanical durability, hardness and modified Hardgrove Index (HGI). Finally, a verification of the method was achieved by conducting a round-robin test with 11 participating laboratories.

2.2.2 Method development and analyses

The developed method is described in the following sections:

Equipment

The cutting mill (with a collecting vessel) should have a capacity of around 60 l/h and a circumferential speed of approximately 20 m/s. The collecting vessel should have a capacity of minimum 5 l. A Fritsch “Pulverisette 19” (revolution speed of 3000 rpm, rotor with V-cutting edges and fixed knives, 1 mm sieve with trapezoidal perforation) was used during the method development at the DBFZ.

The power measuring device should have a measuring range from 1 W to 4 kW and the measuring period should be set to 1 s. A Fluke PQ clamp meter 345 was used at the DBFZ.

The metering unit is used for dosing the pellets with a uniform mass flow. The metering unit should be equipped with a frequency converter to adjust the dosing to the respective sizes of the pellets. For the analysis a mass flow of 10 g/s is required. The least possible stress has to be applied for the metering unit, which reduces the pre-comminution effect by e.g. abrasion. A Gericke GLD 87 feeder was used at the DBFZ achieving a pellet mass flow (PMF) of 7 g/s with the given pellet samples (see also Table 2).

A laboratory scale (measuring range: up to 5000 g with a display of 0.1 g), a stopwatch and a collecting vessel (container volume of about 10 litres) are used for the determination of the dose rate and the grinding process.

Preparation Procedure

The mill used for assessing grindability has to be firmly attached on the fixed base, checked for operability and the presence of any impurities. The mill is fitted with a 1 mm sieve with trapezoidal perforation.

The fines of the pellets used for the test have to be screened with a 3.15 mm round-hole sieve (according EN 15149-1). Afterwards, a sample of 2.5 kg (with moisture as received) of the test material is poured into the feed hopper of the metering unit.

Before starting the fine grinding it is necessary to adjust the throughput of the metering unit. Therefore the screened pellets are placed into the feed hopper and a collecting vessel is placed in front of the metering device. Subsequently, the metering unit is turned on at a selected frequency and the pellets are fed into the collecting vessel for one minute. After turning off the metering unit, the delivered volume is weighed and the throughput is calculated. This process is repeated until the PMF is adjusted to 10 g/s.

The power measuring device has to be installed directly at the power supply line ahead the mill. It has to be guaranteed that neither the power of the metering unit nor any other forces are captured. The measured values have to be stored in the shortest possible interval (best: one value per second).

Measuring process

Initially, the idle power consumption of the cutting mill has to be recorded before starting the fine grinding of the torrefied pellet sample. Thus, the mill equipped only with a sieve and the power measuring device is turned on and the idle power is measured over a period of at least 120 s.

Afterwards, the metering unit is turned on and thus, the grinding process is started. The starting time of the metering unit needs to be recorded to analyse the particular parts of the power measuring after the procedure.

If no more material is fed into the mill, the milling process is completed and the metering has to be stopped. Again this particular time has to be recorded. The mill has to be run continuously for at least another 120 s to obtain further data for measuring the idle power after the load. Afterwards the cutting mill is stopped and subsequently the power measuring device is also switched-off.

The milled material, which is collected in the collecting vessel, has to be weighed.

The determination is repeated two times and the results of the calculated specific grinding energy are averaged.

Interpretation and calculation

To determine the applied grinding energy for milling torrefied pellets, the stored output values have to be divided into three sections. The three sections are called as follows (see also Figure 12):

- idle power before grinding P_{I1}
- total active power P_{total}
- idle power after grinding P_{I2}

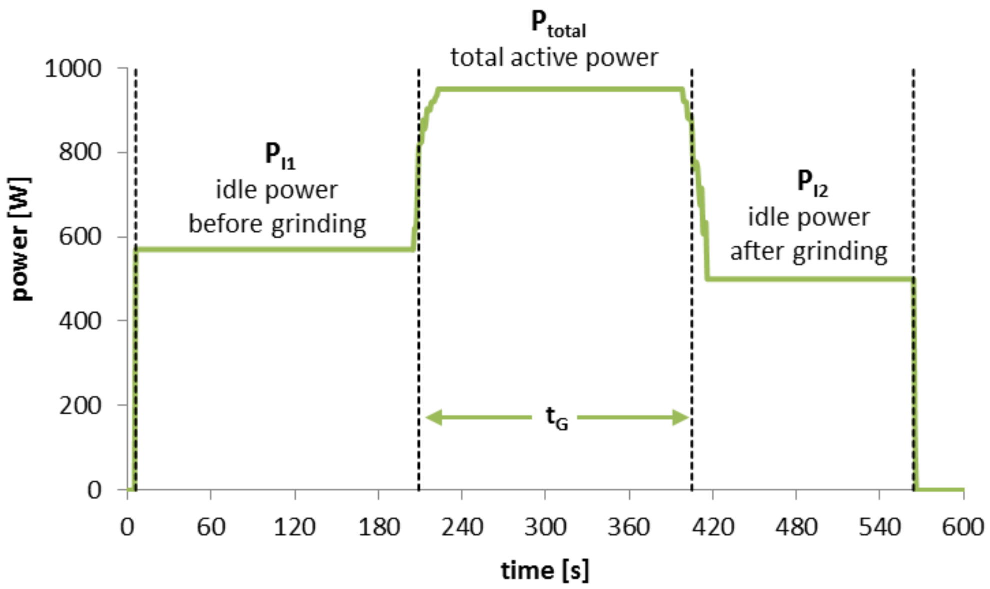

Figure 12: Typical power measurement curve during grinding of torrefied biomass. The relevant sections for calculating the specific grinding energy are shown.

The idle power $\boldsymbol{P_{I1}}$ and $\boldsymbol{P_{I2}}$ (unit: W) are averaged and lead to the total idle power $\boldsymbol{P_I}$:

$$P_I = \frac{\overline{P_{I1}} + \overline{P_{I2}}}{2}$$

During the grinding process the average total active power $\boldsymbol{P_{total}}$ is recorded, which is the sum of the energy applied for the grinding $\boldsymbol{P_G}$ and the idle power of the mill $\boldsymbol{P_I}$. Thus, $\boldsymbol{P_G}$ can be determined by subtracting $\boldsymbol{P_I}$ from $\boldsymbol{P_{total}}$.

$$P_G = P_{total} - P_I$$

With this result the energy consumption during the grinding process $\boldsymbol{E_G}$ (unit: Wh) is determined:

$$E_G = P_G \cdot t_G$$

The time during which $\boldsymbol{P_{total}}$ is observed is defined as $\boldsymbol{t_G}$ (unit: h).

This yields to the mass specific grinding energy $\boldsymbol{E_m}$ (unit: Wh/kg), which is specified with one decimal point:

$$E_m = \frac{E_G}{m_G}$$

Testing and validation of the method at the DBFZ

Five types of torrefied pellets from wood, one from straw and one from forest residue were used for the initial development and testing of the method. Their specific grinding energy was measured according to the method described above and additionally they were tested for mechanical durability, hardness and modified HGI (Table 1).

The pellet hardness was measured using the KAHL Pellet Hardness Tester by first randomly selecting 20 pellets to determine their average length (L_{avg}). Based on the L_{avg} another 20 pellets in the range of L_{avg} ± 2 mm were selected individually placed on the anvil of the Kahl hardness tester.

The modified Hardgrove Index HGI was first introduced by Bridgman et al. (2010) adapting the original HGI, described in ISO 5074 (1994), so that the volumetric differences between coal and biomass are accounted for. Hence, instead of using a defined mass the modified HGI requires a defined volume (50 cm³) of the substrate to be ground.

Table 1: The seven torrefied biomass pellets, their torrefaction conditions and their mechanical durability, hardness and modified HGI.

biomass	$Temp_{torr}$ [°C]	$Degree_{torr}$ [%] (reduction in volatile content)	Mechanical Durability [%]	Hardness [N]	Modified HGI
Willow	308	6	87.7	105	34
Pine	300	8	90.3	132	36
Poplar	280	8	94.5	199	28
Beech	270	6	95.7	236	21
Spruce	260	6	97.6	486	25
Forest residue	308	9	89.3	98	55
Straw	270	7	97.9	273	23

2.2.3 Results and experiences

Testing and validation of the method at the DBFZ

The specific grinding energy could be successfully measured according to the described method and with the instruments available at the DBFZ. Both the residue materials straw and forest residue were the most extreme with straw requiring the highest and forest residue requiring the lowest energy for grinding (see

Figure 13). The five wood samples were all in the range of 4-7 Wh/kg and this range was probably largely due to the torrefaction temperature and the degree of torrefaction.

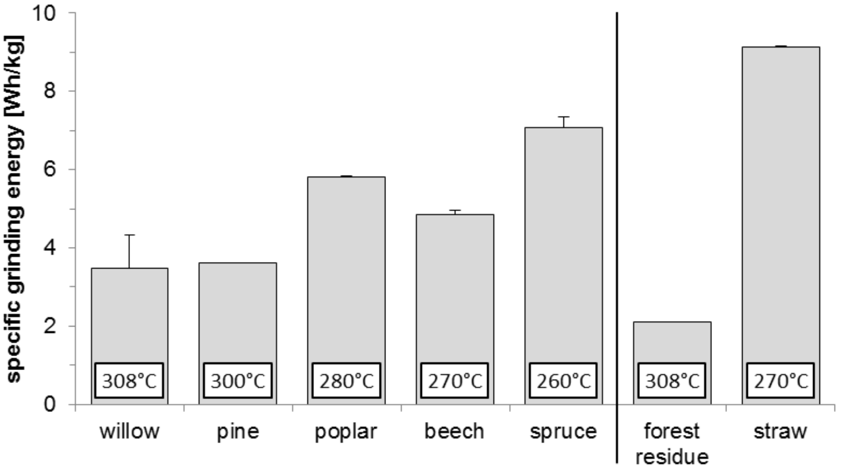

Figure 13: The seven torrefied biomass pellets and their respective specific grinding energy.

The specific grinding energy was found to be in a positive linear relation to the durability of the pellets (R^2 = 0.79) and also affected to a certain degree by the pellet hardness (R^2 = 0.52). A weak linear correlation of the specific grinding energy with the HGI was observed indicating that the parameters are complementary (see Figure 14). In all three cases the values for straw seemed to be the furthest away from the other values which is not surprising as straw has a very different fiber composition (cellulose, hemicellulose, lignin) than woody biomass.

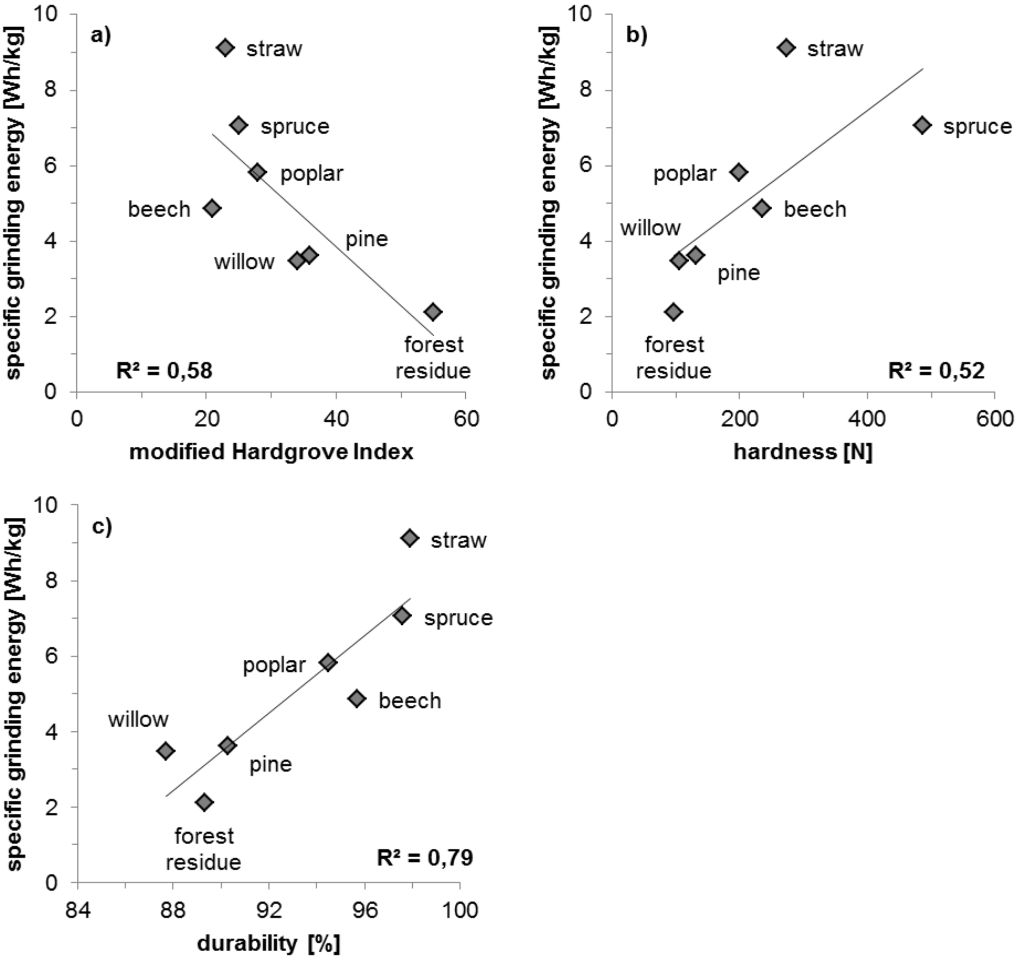

Figure 14: Correlation of specific grinding energy with (a) modified Hardgrove Index, (b) hardness and (c) durability. Correlation coefficient R^2 is indicated for each figure.

Looking just at the torrefied wood pellets, both durability and hardness increased in the following order willow < pine < poplar < beech < spruce. In case of specific grinding energy this pattern is slightly different with beech having a lower grinding energy than poplar.

The final product after applying the in 2.2.2 described grindability method was presented in a particle size distribution curve which shows very similar results for all five torrefied wood pellets (Figure 15). Again straw and forest residue have the most extreme curves with 94 % off all the forest residue particles being below 0.7mm while the same was true for only 84 % of all straw particles. When comparing the particle size distribution with those gained from grinding in a ball mill appropriate for the HGI method slightly different curves can be observed (Figure 3b). The particle size distribution curves when using the cutting mill all have a rather linear increase in sample mass between 0 and 600µm whereas the particle size distribution from the ball mill has a non-linear increase which was also observed in a study by Bridgeman et al. (2010) comparing torrefied biomass and standardized coal.

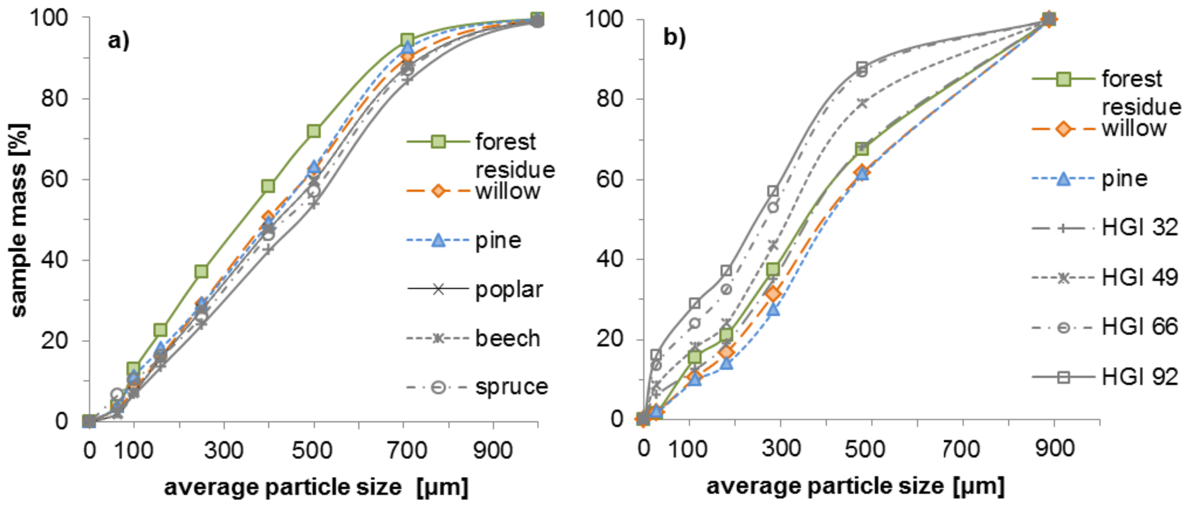

Figure 15: Particle size distribution obtained when a) applying the standardized grindability method to the respective torrefied biomass pellets using a cutting mill (sieve mesh size Ø = 1 mm) and b) grinding a selection of three torrefied biomass pellets and standardized coals in a ball mill according to the HGI method (sieve mesh size Ø = 0.9 mm).

Round-Robin Test

All of the 11 laboratories that participated in the round-robin test were able to perform the procedure with at least one repetition while 5 of labs did two repetitions. The equipment of the labs was different (Table 2) and especially adjusting the feeding rate was a problem in many cases (note: when the Round-Robin test was initiated a feeding rate of 15-20 g/s was still thought to be desirable).

Table 2: Equipment used by the laboratories during the round robin test and realized pellet mass flow (PMF).

Lab	Cutting Mill	Metering Unit	PMF [g/s]
1	Retsch SM100	manual	2.7
2	Retsch SM2000	Vibratory feeder (Retsch DR100)	8.4 - 8.8
3	Fritsch Pulverisette 19	Vibratory feeder	4.6 - 4.9
4	Retsch SM300	Vibratory feeder (Retsch DR100)	n.a.
5	Fritsch Pulverisette 19	n.a.	n.a.
6	Retsch SM300	Vibratory feeder (Retsch DR100)	19.3
7	Retsch SM2000	manual	n.a.
8	Fritsch Pulverisette 19	n.a.	3.7
9	Fritsch Pulverisette 19	Metering screw	7.0 - 7.7
10	Fritsch Pulverisette 19	manual	2.0
11	Fritsch Pulverisette 19	manual	2.0

n.a. = information not available

In total there were 27 values obtained for specific grinding energy ranging from 5 to 30 Wh/kg (Figure 16). This rather large variation is mainly due to the different feeding technologies and the respective feeding rates.

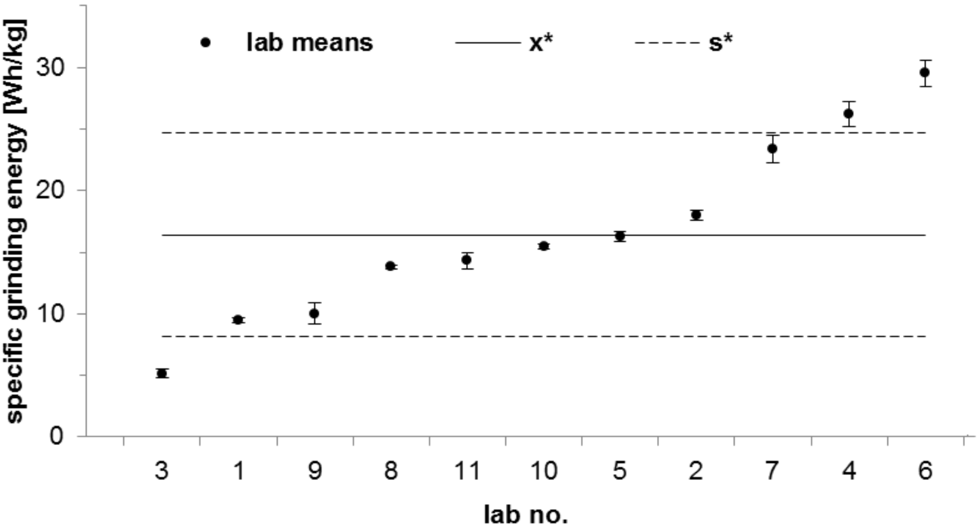

Figure 16: Evaluation of Round Robin Test with robust average (*x) and robust standard deviation (*s**) of the entire data set as well as lab mean values and the respective standard deviations.**

However, almost half of the obtained values (13 out of 27) were between 13.1 and 19.7 Wh/kg which is within ± 20 % deviation from the robust mean value of 16.4. A quarter of the values (7) were between 14.8 and 18.0 Wh/kg which is within ± 10 % deviation from the robust mean value.

The individual performance of the laboratories was rated with the z-score (a common performance variable), in this case calculated from the robust standard deviation *s* and the robust average *x*. The results were very promising with nearly two thirds of the laboratories (8 out of 11) having a 'very good' performance while the remaining three were rated 'satisfactory'.

2.2.4 Summary and Conclusions

In this subtask of WP 8.1 a novel grindability method for torrefied pellets could be developed after several initial tests at the DBFZ laboratories. The main parameter that this new method will yield is the specific grinding energy (Wh/kg). To better understand the nature of this parameter it was compared to other methods such as mechanical durability, hardness and modified HGI. While no close link could be found to the modified HGI and hardness the specific grinding energy was closely related to the durability of the torrefied pellets. The two pellets batches made from residue materials (straw and forest residue) were both at the far end of the spectrum for almost all investigated parameters indicating their individual grinding characteristics compared to regular torrefied wood pellets.

The validation of the method by a round-robin test with 11 participating laboratories was successful and helped identify some shortcomings of the method. Thus, in the future the pellet mass flow will be set to 10 g/s and either a vibratory feeder or a feeder with metering screw should be used.

Current discussions in the ISO technical committee on solid biofuels (ISO TC 238) regarding a unified test method for grindability of thermally treated biomass fuels indicated a slight favor towards establishing a method using a hammer mill. Thus, the focus of future research should be on evaluating the reproducibility of results gained by using different types of hammer mills on the same torrefied material.

2.3 Degree of torrefaction

2.3.1 Introduction and objectives

Torrefaction covers a wide range, from soft thermal treatment to a process ending close to charcoal. Because of this wide range, the properties and parameters of the material change. For a forecast of the process, it is very important to find a way to describe the state of the torrefaction process.

Within SECTOR project two possible definitions, or rather methods, were analyzed. On the one hand the loss of volatile matter, based on the change of the volatile matter content during the torrefaction. On the other hand the anhydrous weight loss, based on the weight loss of the material during the torrefaction process. Those two approaches were evaluated and compared.

2.3.2 Method development and analyses

There are different possibilities to describe the progress of the torrefaction. Within the SECTOR project the focus was on two methods:

Loss of volatile matter

The loss of volatile matter is defined as the percentage loss of volatile matter from the volatile matter content of the raw material.

$$LVM = \left(1 - \frac{VM_{tor}}{VM_{raw}}\right) * 100$$

LVM	loss of volatile matter
VM_{tor}	volatile matter content of the torrefied material
VM_{raw}	volatile matter content of the raw material

The analysis of the volatile content of the raw material as well as of the torrefied material was included in the material characterization in WP3 and therefore only some additional measurements were required.

Anhydrous weight loss

The anhydrous weight loss is defined as the water free weight loss during the torrefaction in percent.

$$AWL = \left(1 - \frac{w_{tor}}{w_{raw}}\right) * 100$$

AWL	anhydrous weight loss
w_{tor}	weight of the torrefied material
w_{raw}	weight of the raw material

The anhydrous weight loss is measured by the producers during production and was reported in WP4 as well.

2.3.3 Results and experiences

The following diagram (Figure 17) shows the change of the loss of volatile matter and the anhydrous weight loss on different “torrefaction levels”. Also plotted in Figure 17 are the change of net calorific value, hydrogen content and carbon content. The samples considered were spruce at the torrefaction temperature 240°C, 260°C and 280°C of the same producers.

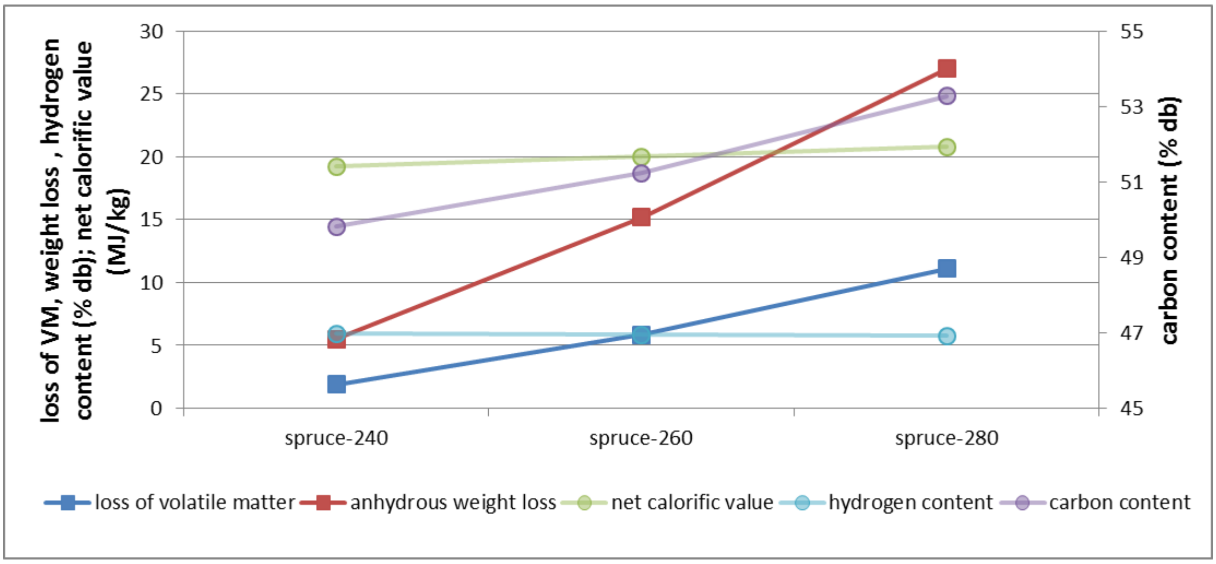

Figure 17: Anhydrous weight loss and volatile matter loss at “different torrefaction” levels of sample spruce (with change of carbon content, hydrogen content and net calorific value)

In Figure 18 the considered sample was straw at the torrefcation temperatures 250°C, 260°C and 270°C.

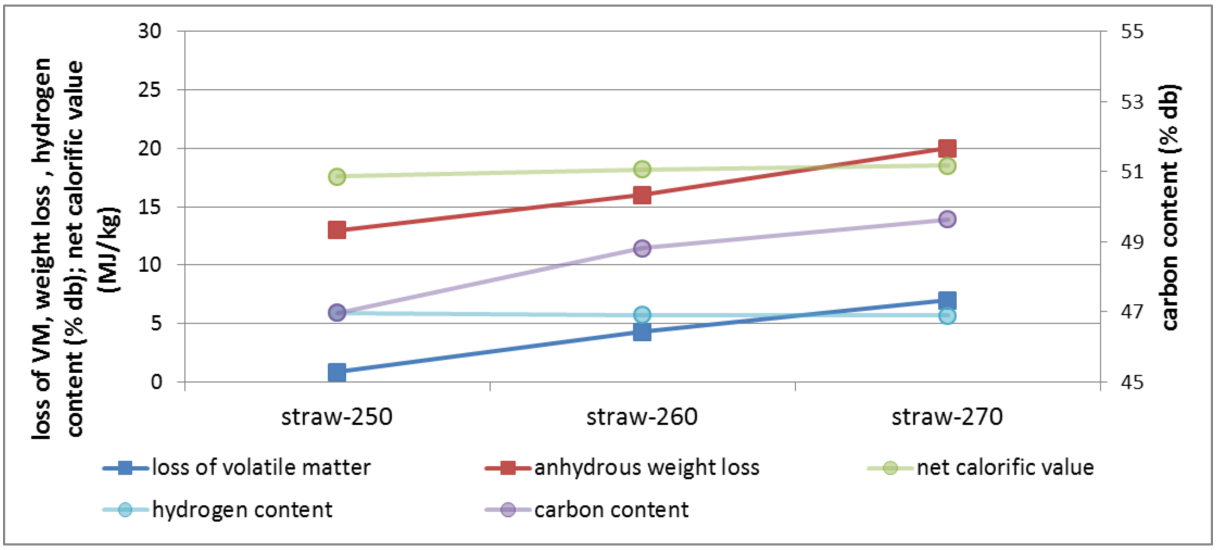

Figure 18: Anhydrous weight loss and volatile matter loss at “different torrefaction” levels of sample straw (with change of carbon content, hydrogen content and net calorific value)

In Figure 17 and Figure 18 the behavior of both, the loss of volatile matter and the anhydrous weight loss is very similar independent of the material. The anhydrous weight loss starts on a higher level and increases more with higher torrefaction temperature. The behavior of the other parameters is as expected: the net calorific value and the carbon content slowly increase and the hydrogen content slightly decline. This behavior is typical for a torrefaction process with an increasing torrefaction temperature. Both, the loss of volatile matter and the anhydrous weight loss describe the degree of torrefaction in a very good way.

In Figure 19 the anhydrous weight loss and the loss of volatile matter of the sample pine at different torrefaction temperatures from different producers are shown. Also displayed in Figure 19 are the change of net calorific value, hydrogen content and carbon content.

It can be clearly seen that different producers show different results for the anhydrous weight loss and the loss of volatile matter. The sample pine 280 from producer B shows lowest change and also at higher torrefaction temperature (pine 300 producer B) the weight and volatile matter loss should be theoretically the highest. This could be explained by the different torrefaction technologies used within the SECTOR project. Hence, every producer uses a different reactor and also different raw material. Another explanation could be the possible different torrefaction time due to the different reactors and production methods.

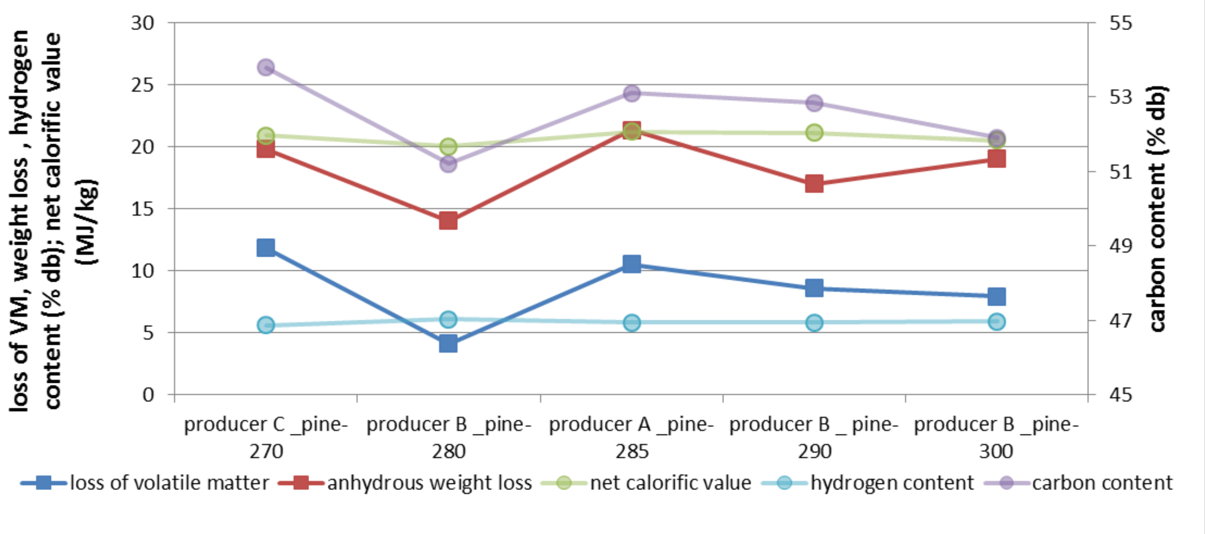

Figure 19: Anhydrous weight loss and volatile matter loss at "different torrefaction" levels of different producers (with change of carbon content, hydrogen content and net calorific value)

Both methods give a good possibility for an easy and quick determination of the progress of the torrefaction. But several parameters influence the torrefaction process, like torrefaction temperature, residence time, used raw material and the torrefaction technique. Also without the declaration of these parameters a rough estimate is possible with the degree of torrefaction.

2.3.4 Summary and Conclusions

The determination of the volatile matter (EN 15148) is quick and easy method and can be done in every laboratory with a muffle furnace. For producers it could be a problem that they only in rare cases have a fully equipped laboratory. The big advantage is that only the raw material and the torrefied material is needed and the loss of volatile matter can be determined. Hence, the raw material is not always available and therefore can be also a disadvantage for the determination. Another disadvantage of the volatile matter approach is that the results have a very narrow bandwidth, so the expressiveness is less significant. For producers it could be a problem that they only in rare cases have a fully equipped laboratory and are not able to determine the loss of volatile matter easily.

Nearly all producers within the SECTOR project use anhydrous weight loss definition to describe the progress of the torrefaction, hence the degree of torrefaction. About 2/3 of the production costs involve the feedstock costs; the anhydrous weight loss provides a straightforward prediction of the production cost associated with torrefaction under certain operating conditions. To determine the anhydrous weight loss no extra analyses are necessary, it can be calculated from the data of the torrefaction process itself. This is also the main problem of the method. Only the producer can determine the anhydrous weight loss. All data, concerning the anhydrous weight loss, used in this section are data which are provided by the SECTOR-producers. For the end-user the degree of torrefaction based on anhydrous weight loss is not verifiable, which is the downside of this approach.

General

In this section the advantages and disadvantages and also the discussion process of the two methods are presented:

- Both have the big handicap that for the determination the raw material is needed.
- Both methods are actually a “backward” method because the raw material is usually not available for laboratories or the end-user, therefore both methods are not perfect for an evaluation.
- The producers prefer the definition over the weight loss – due to the importance at the production and the prediction for the production costs based on the feedstock costs.
- For lab analysis the approach based on the volatile matter content is reasonable. The determination of the volatile matter is a standard method and every laboratory which does routine volatile matter analysis is able to check presented value. If the raw material is not available a rough check is possible by the use of literature data for the volatile matter of the raw material.
- With the raw material and the torrefied material laboratories can check the declaration of the producers if the loss of volatile matter is used. With the anhydrous weight loss a check is not possible.

There was a discussion within the SECTOR project about the degree of torrefaction, which resulted in the decision of the SMB board to use the anhydrous weight loss as degree of torrefaction, but also the loss of volatile matter can be used as further parameter.

In general the gained information of the degree of torrefaction (volatile matter or anhydrous weight loss) is not relevant for a better description of torrefied material in general especially concerning the end-users. It can be considered as additional parameter. For the end-users e.g. the calorific value, carbon content or the energy density are of greater interest.

2.3.5 References

EN 15148 2010-04:Solid biofuels - Determination of the content of volatile matter

2.4 Particle sizes and size distribution

2.4.1 Introduction and objectives

Particle size distribution and share of fine particles (below 3.15 mm) of non-torrefied pellets can be measured by horizontal screening according to EN 15149-1. Moreover, particle length can be measured according to prEn ISO 17829. Both standard methods apply for torrefied pellets as well and no further method development was deemed necessary. However, measurement of particle diameter and maximal particle length according to prEn ISO 17829 requires measurements of a high share of individual particles using a caliper. Thus, this method suffers from high labor consumption. Therefore the question was raised whether the determination can be facilitated by novel image analysis methods allowing for the measurement of large sample sizes within a short period of time.

Instruments for the determination of size and shape criteria by image analysis are continuously being developed and several technical solutions are applied. Additionally, there can be a wide scope of output parameters as provided by an image analysis device (e.g.: Feret-diameter, Maximum Length, Martin Diameter, Maximum Chord, Particle Shape Factor, Sphericity, Roughness, etc.).

As a consequence, it is not found reasonable to create a standard method for the functioning of a measuring device or for the applicable principle itself. Rather it was deemed more useful to ensure that the image analysis method would provide meaningful results by defining a procedure for testing and calibrating the instrument in order to evaluate the reliability of the created results as relevant for biofuels. Moreover, a selection of simple key parameters was made in order to identify whether the image analysis instrument is able to determine certain particle dimensions at a sufficient accuracy. This draft standard calibration method (see Annex A) was also presented to the ISO TC238 working groups. Due to an overload of work items, however, the approach could not yet be discussed in detail.

2.4.2 Method development and analyses

For the SECTOR project, pellet diameter and pellet length of torrefied pellets were measured with the standard method according to prEn ISO 17829 and also in parallel using an image analysis device which was calibrated according to the above mentioned draft standard (Annex A).

Samples of torrefied pellets were measured according to prEn ISO 17829 using a calliper (Figure 20). In addition, the same samples were analyzed using a continuously measuring image analysis device (Haver-CPA 4, Haver & Boecker GmbH, Germany) allowing for highly detailed information on the size and shape of the bulk material (Figure 20, Figure 21).

Figure 20: Size classification of pellets by calliper (left) or by image analysis (right)

For image analysis, pellets were spread horizontally by means of a vibrating feed canal and a conveyor belt. After separation, each individual pellet passed a light source opposite of a digital CCD line camera. The camera records 4096 pixels over a width of 400 mm, thus the resolution per pixel is 98 µm. From the retention time within the camera's scope and the recordings for the varying horizontal expansion, the size of each particle's two-dimensional silhouette is recorded and calculated by a computer (Figure 21, Figure 22).

The image analysis determines particle size usually as “maximum particle length” (in mm, i.e. arrow “4” in Figure 22), i.e. the maximal distance between two pixels of the particle circumference. In contrast, horizontal screening (EN 15149-1) assesses particle size rather as particle width i.e. as the “minimal Feret Diameter” (in mm, see arrow “6” in Figure 22).

The minimal Feret Diameter determines the minimal distance of two parallel tangents of the particle circumference. Therefore, in case of cylindrical particles such as pellets, the minimal Feret Diameter gives the actual particle diameter. In contrast, pellet length is better described by the “Standard length” (in mm, i.e. arrow 7 in Figure 22) than using “maximum particle length” (arrow 4) as minimal Feret Diameter and Standard length are aligned in 90°.

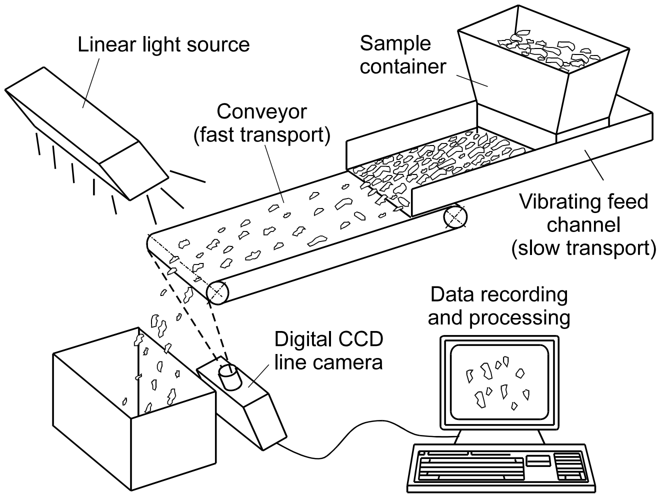

Figure 21: Continuous measuring image analysis device

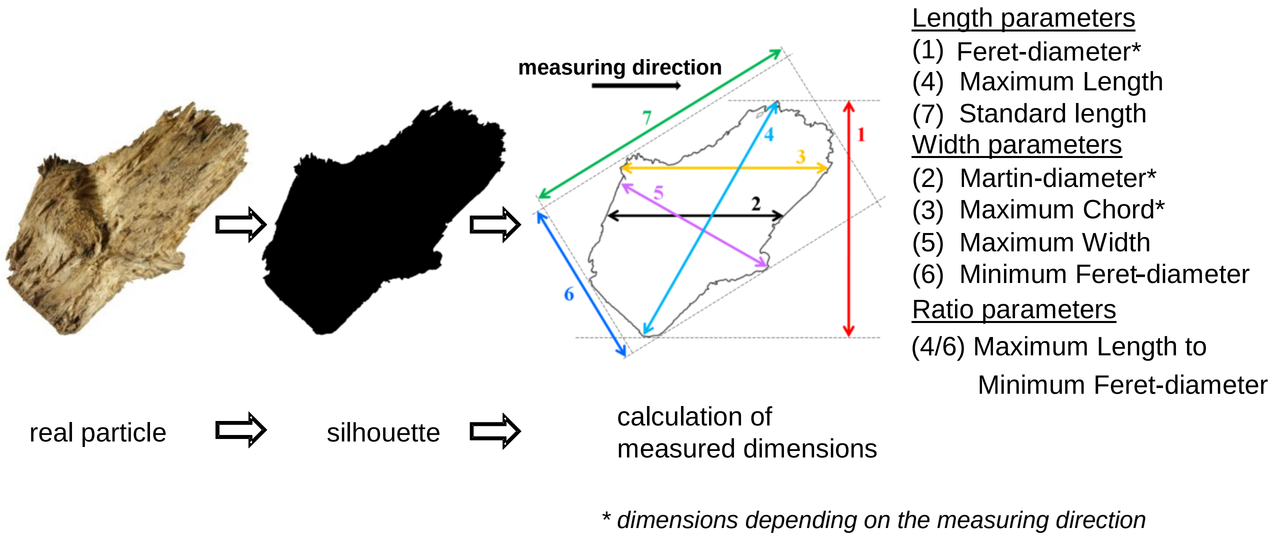

Figure 22: Measuring principle of the continuous measuring image analysis device

2.4.3 Results and experiences

Trials with torrefied pellets have proven that the continuously operating image analysis method is useful to assess the size and particularly the share of oversized pellets in a sample and it provides comparable results (Figure 23). In average the image analysis provides a 3.7 % higher pellet length compared to calliper measurements, and the measured diameter is about 15 % higher. But an evaluation about which of the two values is more trustful is not easy. There is always a risk of handling the calliper with too high forces, this would lead to pressing the pellet (e.g. into any cavities) and would thus reduce the dimensions measured. On the other hand the image analysis is known to have a tendency of rather measuring higher dimensions; this could happen when due overloading or improper separation particles could overlap when traveling through the camera window. Thus, the slight deviations observed here can easily be explained be physical uncertainties which are applicable for both methods.

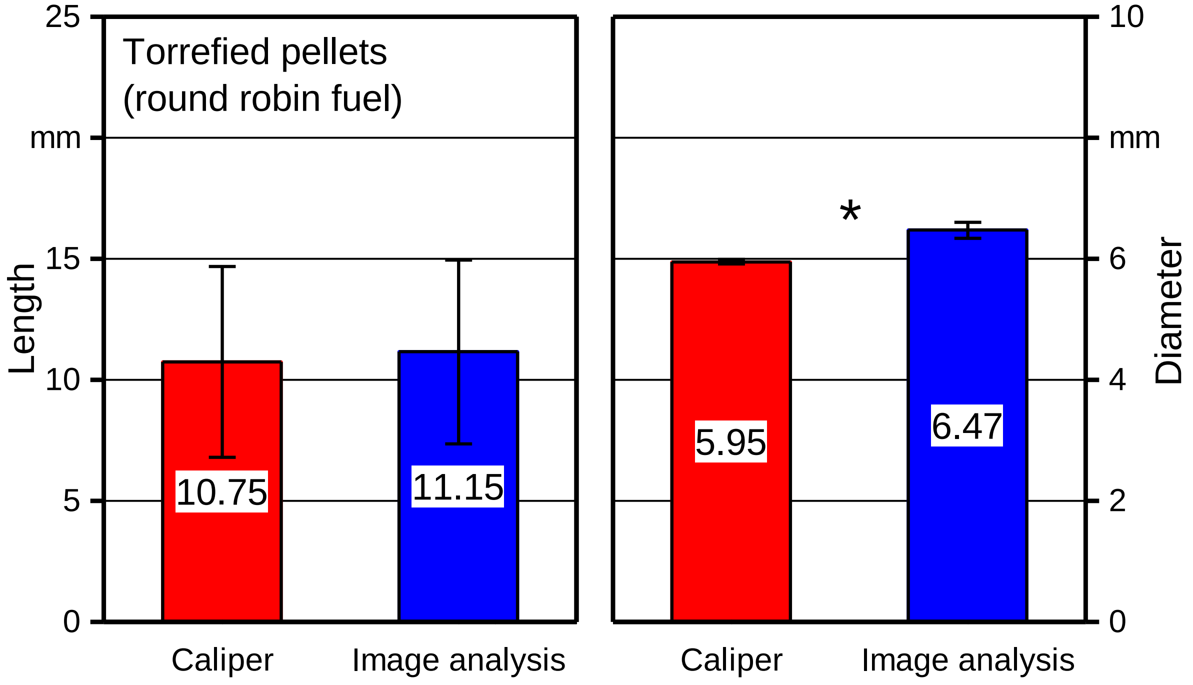

Figure 23: Example of length (right) and diameter (left) results for method comparison using image analysis (Haver-CPA 4 Conveyor) versus calliper(hand)-measurement. Indicated error bars display the absolute amplitude of all measured values.

The trials using a *Haver-CPA 4 Conveyor* (by Haver&Boecker) also showed that image analysis can be much less time consuming than the drafted ISO method using calliper measurement by hand. Consequently it needs to be noted that the image analysis allows a much larger sample to be processed, thus achieving a higher representativity by each measurement. Therefore the results cannot easily be influenced by too scarce sample masses used in the determination.

2.4.4 Summary and Conclusions

On an everyday testing routine the use of image analysis for determining pellet lengths or diameters (and particle size distribution) is highly recommendable, if such quality criteria shall be established for the fuel. But it is also obvious that the extremely complex method and instrument used for image analysis cannot simply be described as a standard. However, instead of standardising the instrument itself it is much more useful to define a standard for its calibration and to leave it to equipment industry on how the measurement by image analysis will actually be realised technically. This would ensure a high confidence in the reported results.

Thus, a respective draft standard procedure for calibrating such an image analysis apparatus was therefore developed by TFZ within the scope of the SECTOR project. It defines a required set of standard calibration pieces and their application in an instrumental check of the image analysis. These definitions are based on a comprehensive research using various materials to identify the proper forms and shapes for the standard sample pieces.

The full draft of the developed standard for calibrating such an image analysis device is given in Annex A.

2.5 Flowability properties for both pellets and powder

2.5.1 Introduction and objectives

Flowability of a bulk fuel can be determined by several parameters. In the SECTOR project they are described by two parameters, the bridging properties and the angle of repose.

Bridging is the phenomenon where particles form a stable arch above an opening. All particles, regardless of the size, could potentially form an arch and in the case of biofuels this is particularly a problem for internal transport systems of heating plants and infeed mechanism of boilers. Several parameters influence the bridging tendency: They are fuel related parameters including e.g. mean particle size, proportion of long particles and moisture content. Or they are handling related parameters including e.g. friction against surfaces and angle of repose. For measurement purposed it is therefore unavoidable, that bridging needs to be determined by applying measurements in a repeatable environment. Such environment can be achieved by using a specially built and clearly defined bridging apparatus. The applicability of such a method was tested in the SECTOR project. The goal was to introduce a method which allows to compare torrefied pellets with any other solid biofuel material under repeatable conditions.

The angle of repose of a biomass material can influence the bridging, but it can also be seen as a material property for itself which can also describe the flowability of biomass. It was here the objective to test the applicability of an adapted method for non-biomass bulk material and to compare the results with those from other biomass fuels.

2.5.2 Method development and analyses

Measuring bridging tendency

Bridging was determined in an apparatus based on a Swedish design which had initially been modified and optimized by TFZ during a previous research project ("BioNorm 2"). It uses a movable floor with expandable opening (Figure 24) where the opening width (OW) at the moment when the bridge fully collapses is recorded as an indicator for the bridging properties of the tested fuel.

A sample is subjected to bridging by placing it over an expandable slot opening facilitating the building of a bridge. The opening width of the slot is taken as a measure for the bridge building properties of the sample (Figure 24).

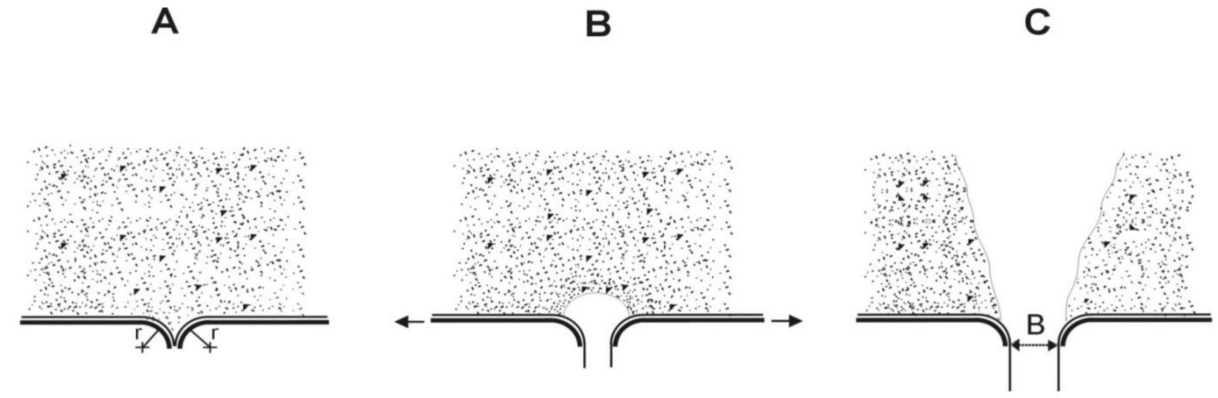

Figure 24: Operation principle of the bridging tester

For the test a box with a bottom area of 1.1 ± 2.0 m (± 0.01 m) and a minimum height of 0.75 m (± 0.01 m) was used. The sides of the box were made of oriented strand board (OSB); the bottom was made of two flexible mats with rubber surfaces.

The expandable slot divides the middle of the box’s bottom. The slot is formed by round edges. These round edges form a quarter of a circular arc with an effective radius of 125 mm. When the bottom is fully closed, the two mats meet in the centre of the box' length without forming any slot. The mats are fully even and horizontal to the ground, except at the round edges (see drawing in Figure 24). The slot is capable of being gradually expanded while the edges are parallel and the bottom is prevented from becoming inclined during any phase of the opening procedure. The expansion was executed in a way, which ensured that the mats remained in place, except at the rounded edges, where they were sliding over a plate which forms the rounded edges (Figure 24). This design avoids that any friction between the bottom and the fuel sample in the box can occur when the slot is being expanded.

The apparatus used to perform the trials according to the above described principle is shown in Figure 25. The opening movement of the two bottom halves was performed synchronically, thus ensuring that the slot was widening without changing its position. The maximum possible opening width was 1.5 m. The edges of the slot remained parallel during the opening procedure, however, a tolerance of 10 mm was acceptable. The opening speed was 180 mm /minute (± 50 mm / minute).

The container was positioned firmly at a height of 1.5 m, which ensured that all sample material could freely fall through the slot without causing any blockages. A metric rule was used to measure the opening width between the rollers to the nearest centimeter (Figure 25).

Figure 25: Apparatus for bridging tests: Top left: complete box with opening floor driven by crank handle. Top right: filling of the box with sample material. Bottom left: beginning of floor opening with measuring rule showing the dimension of gap while material starts to fall through. Bottom right: fully collapsed bridge (view from top)

The minimum volume of the test portion used was 1.5 m³ loose volume. The container was filled by pouring the sample material from a height of maximum 500 mm above the rim of the container without applying any compaction to the sample. Loading was done using a wheel-loader. A shovel was used to level out the sample so that the sample is evenly spread in the container.

By starting the slot opening procedure a slot opening under the sample is generated. The sample material forms a bridge, which overstretches the slot (Figure 24). As soon as the bridge collapsed, the slot opening motion was stopped and the slot width was measured at both sides of the container and reported as average to the nearest centimetre. The reading was conducted at the minimum horizontal distance between the slot edges as indicated in Figure 24 by the letter "B".

The remaining sample was unified with the sample material, which has fallen through the slot by emptying the container completely. The container was reloaded with the unified sample and bridging procedure was repeated until 10 repetitions were performed (for non-pelletized materials) or until 5 repetitions were performed (for pelletized materials).

Measuring angle of repose (adopted FEM method)

The method used for the angle of repose was based on the Technical specification FEM 2581 by Fédération Européenne de la Manutention (FEM). It was adopted and adjusted for the trials performed here with pellets. But measurements have also shown that the method could also be suitable for other bulky biomass fuels such as wood chips. However, then the minimum required sample mass may have to be altered.

For the angle of repose a sample volume of minimum 0.7 m³ volume was stored in a big bag. The big bag was elevated with a crane with the discharge outlet pointing to the bottom. The outlet was moved vertically above the centre of two squares that were marked on the floor (outer square: 2.5 m x 2.5 m, the inner square 2 m x 2 m. The center of these two squares was marked with a cross, Figure 26). Then, the ferrule around the discharge outlet of the big bag was fixed manually. The big bag was lifted until the ferrule was located at 1.0 m above the floor. Then the outlet was opened and the fuel percolated onto the floor (Figure 27).

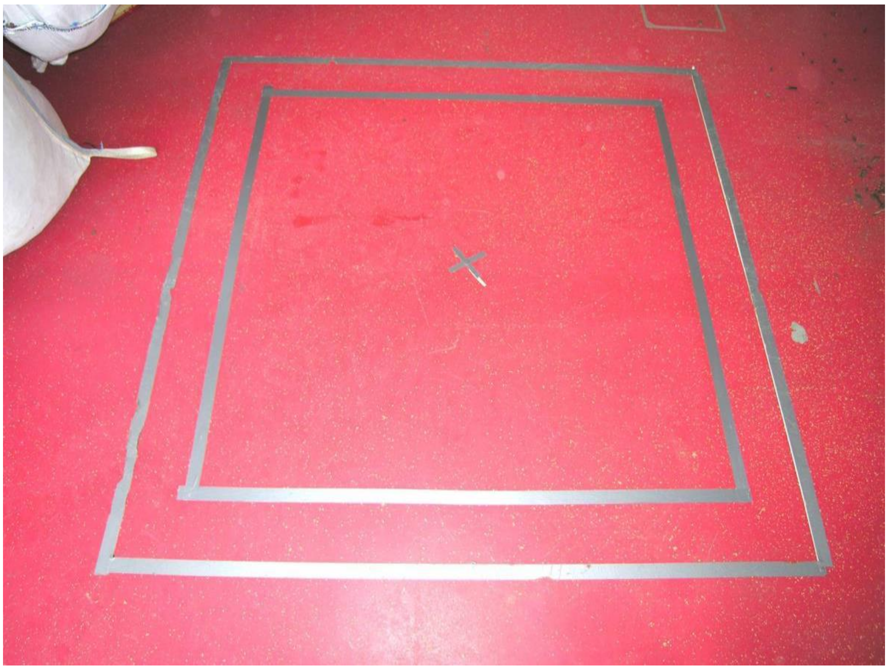

Figure 26: Marked square on the laboratory floor

Figure 27: Position of the filled big bag before opening the lower outlet for unloading

If the fuel was blocked in the outlet of the big bag, a stick was used to dissolve the blockage by stirring within the big bag. This was conducted from above, to guarantee an undisturbed angle of repose. The percolation was interrupted, when about 2/3 of the big bag's content was on the floor. Then the gap between the outlet and the top of the formed cone was reduced to about 10 cm and the last third of the sample volume was discharged onto the cone. This reduction is performed in order to get an even angle of repose (cone). Without reducing the distance, the cone might build a plateau on the top and not a peak.

The height (h) of the cone was measured as mentioned in Figure 28 by using a board and placing a water level on it. Any compaction of the peak was avoided.

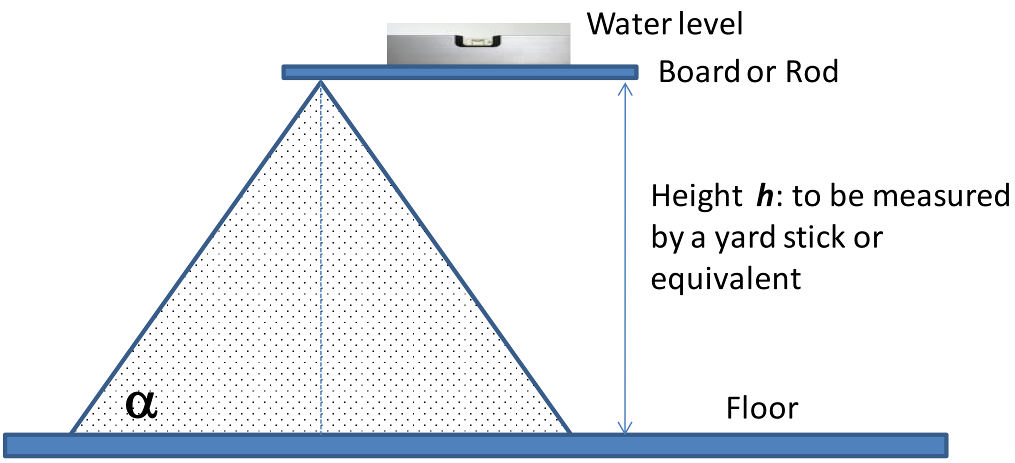

Figure 28: Method to determine the height h for calculating the angle of repose

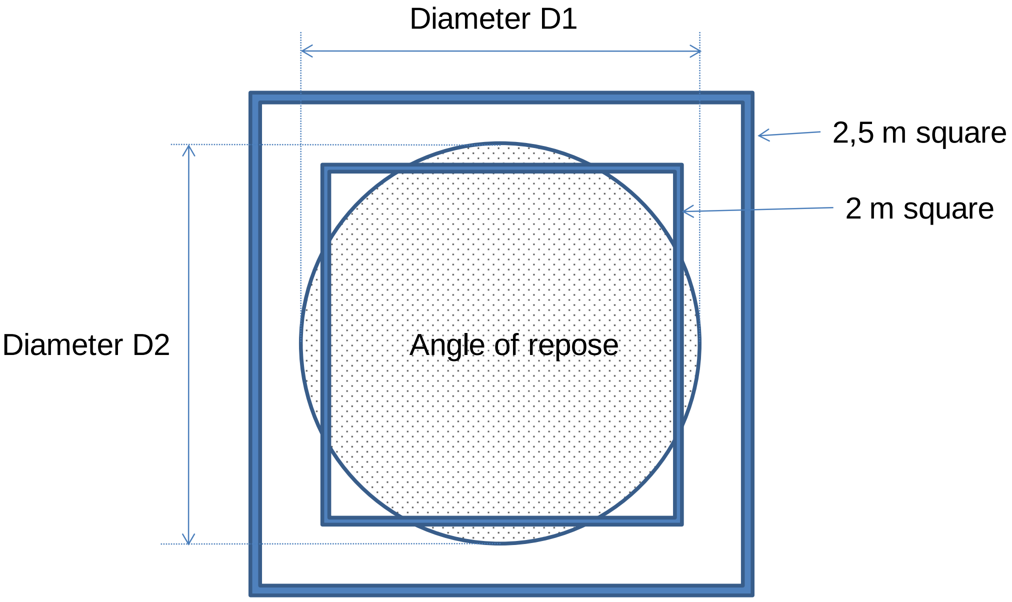

Figure 29: Method to determine the diameters D1 and D2 for calculating the angle of repose

According to Figure 29 two diameters *D1* and *D2* of the sample cone were measured and recorded. The squares shall help to orientate and to be sure, that the two highest diameters will be measured.

The angle of repose α (in °) was calculated using the following equation, where h is the height and D_1 and D_2 are the diameters as recorded (in cm) (see Figure 28 and Figure 29).

$$\alpha = arc\ \tan \frac{4 * h}{D_1 + D_2}$$

For a sample size of n = 3, the mean coefficient of variation of this method is 1.9 % (tested for 9 pellet samples). Thus, a high reliability of the results is given.

2.5.3 Results and experiences

Results of bridging tests

The bridging properties were determined to identify any principally different flowing behavior for torrefied pellets. The measured results are displayed in Figure 30. It shows that torrefied pellets have more or less the same flowing properties as other pelletized wood fuels. Differences are small and are most probably more influenced by the pellet length than by the material type as such. Compared to the bridging properties of wood chips or hog fuel having an opening width which is more than 10 to 20 times wider than that for pellets the observed differences among pellets are negligible. The applicability of the method for torrefied pellets is thus clearly shown in the trials. A draft of the method description (which had mostly been elaborated during the previous EU-project "BioNorm2") is shown in Annex B. It could be developed to become an international standard, if deemed useful.

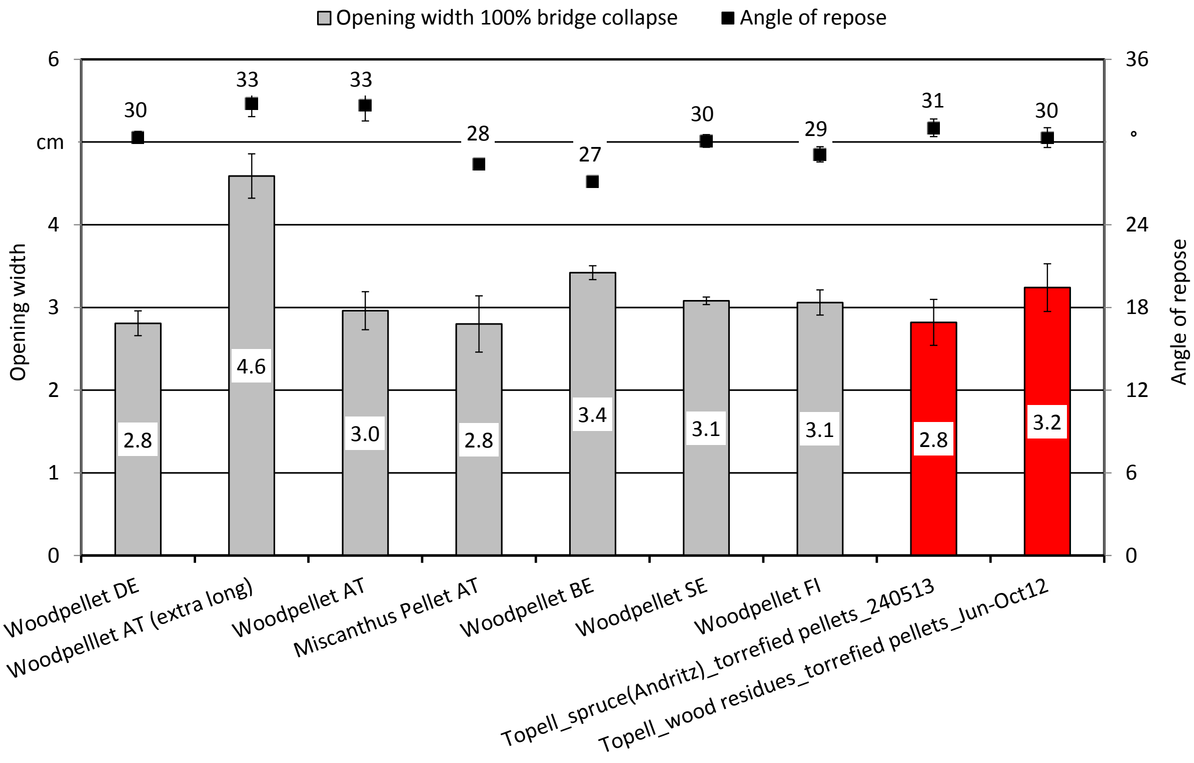

Figure 30: Measured bridging property and angle of repose of two torrefied pellets compared to other biomass pellets (each bridging value represents the mean of 5 repeated measurements per fuel, error bars indicate the standard deviation)

Results for angle of repose

Additionally, the flowability properties can be read from the angle of repose, which is defined as the internal angle between the surface of a pile and the horizontal surface. The angle of repose is also a useful parameter to calculate the volume of a storage pile of a given height. It is largely assumed that the angle of repose (measured by building a pile from the top) is similar to the angle of drain (measured by creating a slope by letting the bulk material escape from a container downwards). This angle of drain was here measured by determining the sample's angle in the bridging tester box (see chapter 2.5.2) after the bridge had collapsed. Tests were performed at TFZ for both methods.

The results of the measurements are given in Table 3. Two different pellet samples were applied in two volumes, 70 and 700 litres. Differences between the two volumes were low when the adopted FEM method was applied. Measurements with an electronic water level (with indication of angle) were less suitable, as deviations were higher.

The angle of drain cannot be interpreted as being compatible with the angle of repose. Obviously here the continuously prevailing wall effects in the box lead to a higher angle (Table 3). It can thus be concluded, that the angle of repose should only be determined using a cone preparation where the sample is dropped onto a clean horizontal ground in a repeatable way (see draft standard method in Annex C). A determination using an electronic water level should in no case be performed due to insufficient accuracy.

Table 3: Measured angles of repose and angle of drain according to different methods

Measured parameter	**Fuel sample used**	
	Topell_wood residues_torrefied pellets_Jun-Oct12	*Topell_spruce (Andritz)_torrefied pellets_240513*
Angle of repose by adopted FEM method 2581 70 l sample	**31,0°** 29.5° - 30.9° (n=3)	**30.3°** 30.5° - 31.7° (n=3)
Angle of repose by adopted FEM method 2581 700 l sample	**31.2°** (n=1)	**29.5°** (n=1)
Angle of repose by measurement with water level (70 l)	**33.1°** 31.9° - 36.1° (n=6)	**33.2°** 31.6° - 34.7° (n=12)
Angle of drain, measured in bridging tester with water level	**36.9°** 34.9° - 40.0° (n=8)	**36.7°** 33.6° - 38.8° (n=3)

It was also shown that angle of repose of the two tested torrefied wood pellets is close to the values as measured for non-torrefied pellets (see Figure 30). Material based differences cannot be expected; therefore the storage design can be based on the experience given for regular wood pellets.

2.5.4 Summary and Conclusions

It can be stated that both methods, the direct determination of bridging tendency and the determination of the angle of repose, as developed for flowability of non-torrefied pellets, are also suitable for torrefied pellets, too. A fully elaborated description of the two methods is given in Annex B and Annex C. If deemed necessary, these methods are ready to become suggested for ISO TC 228 (WG 4) in order to be further elaborated within the ISO standardization for solid biofuels.

It was also shown that angle of drain should not be interpreted as being compatible with the angle of repose. Obviously here the continuously prevailing wall effects in the box lead to a higher angle. Thus the angle of repose should only be determined using a cone preparation where the sample is dropped onto a clean horizontal ground in a repeatable way. A determination using an electronic water level should in no case be performed due to insufficient accuracy.

2.6 NIR spectroscopy

The following report is a short version of the study and serves as deliverable by SLU for SECTOR WP 8. It is supplemented with the full paper published by T.A. Lestander and M. Rudolfsson from SLU and L. Pommer and A. Nordin as open access in the scientific journal Green Chemistry. Both documents will be available through the SECTOR homepage. At http://pubs.rsc.org/en/content/articlepdf/2014/gc/c3gc42479k the full text paper by Lestander et al. 2014 (Green Chem., 16, 4906-4913), is available.

2.6.1 Introduction and objectives

There is a need for efficient on-line techniques to monitor and control process steps in torrefaction e.g. quality parameters like atomic ratios of hydrogen and oxygen in relation to carbon, torrefaction degree and energy content. Most of the structural groups in biomass as well as in torrefied biomass are C-H, C-O, C=O, C=C and O-H. These groups interfere with overtone vibrations in the near infrared (NIR) wavelength region. Collected NIR spectra from such samples therefore contain chemical information, especially of the organic matrix. Because of the nature of NIR spectra having broad and overlapping absorption peaks, but also showing co-variation between wavelengths and sample observations, multivariate calibration techniques are needed to construct robust calibration models. Nowadays, fast and reliable NIR instruments with high repeatability have been developed for harsh industrial environments and they are commercially available. Furthermore, user-friendly software for modelling using multivariate tools are also available as well as on-line computer and instrumental based systems for real time predictions.

The rapidity, time- and cost-effectiveness of the NIR spectroscopic technique as well as its low requirements for sample preparation and negligible use of consumables makes NIR spectroscopy a most interesting candidate also for standardized procedures to reduce the need for wet-based chemical analysis. Such standard methods have already been developed e.g. EN 15948:2012 for the determination of moisture and protein in whole cereal kernels using NIR spectroscopy and ISO 12099:2010 that gives guidelines for the determination of constituents such as moisture, fat, protein, starch, and crude fibre as well as parameters such as digestibility in animal feeding stuffs, cereals and milled cereal products using NIR spectroscopy.

The main objective was to study NIR spectroscopic techniques combined with multivariate calibration modeling and predict an array of properties of torrefied biomass and otherwise carbonized biomass, and thus reduce the need for wet chemical analysis. Another objective was to determine the potential of using NIR spectroscopy as an international standardized technique for the determination of key variables (e.g. H/C and O/C atomic ratios and energy content) of thermos-treated biomass.

2.6.2 Method development and analyses

Samples of Norway spruce *(Picea abies* Karst.) and reed canary grass (*Phalaris arundinacea* L.) were used as biomass models in the thermal treatment like torrefaction and others to obtain different mass yields and carbonization degrees. The changes in chemical composition were analyzed by wet chemical methods for an array of important variables: gross calorific value (GCV), ash content, volatile matter and fixed carbon content, content of carbon (C), hydrogen (H) and oxygen (O) (wt %, dry basis), mass yield expressed as the ratio (in %) of remaining dry mass of the thermo treated sample in relation to its dry mass when untreated. These variables were used as references or y-values, whereas NIR spectra within 950-1650 nm from the same samples were collected and used as x-values in the multivariate calibration modelling based on partial least squares (PLS) regression. Fourier transform infrared (IR) reflectance spectra were also collected in region of 400–5200 cm^{-1} to gain overview of chemical changes of the treated materials. For more details see Lestander et al. 2014.

2.6.3 Results and experiences

The overview of the NIR spectral variation using principal component analysis (PCA) showed a clear curvature for the two first principal components explaining 98.7 % and 1.2 % of the spectral variation in NIR, i.e. almost 100 %, see Figure 31.

The first component was highly correlated to carbon, hydrogen and oxygen content (R^2: 0.918, 0.933 and 0.989 for C, H and O, respectively) increasing in Figure 31 from left to right within the range of 47.1 % to 90.6 % in carbon content.

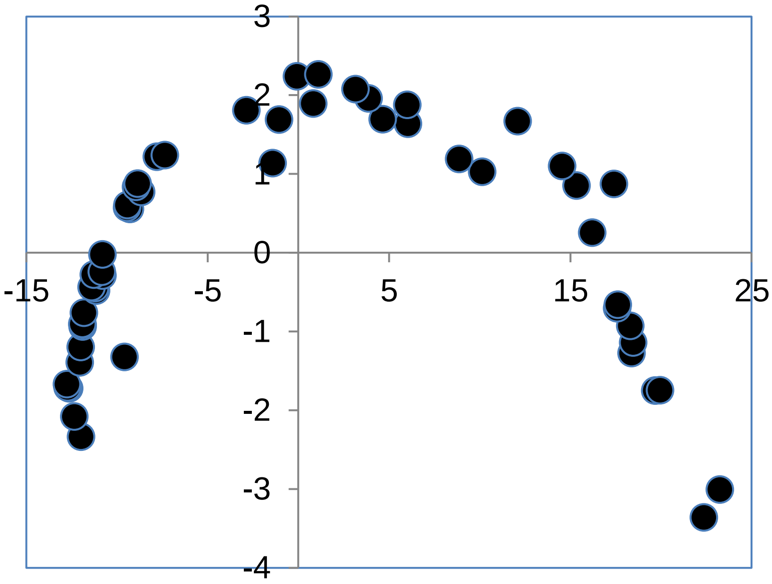

Figure 31: Score plot of PCA components based entirely on NIR spectra (x- and y-axis: first and second principal component, respectively, explaining 98.7 % and 1.2 % of the variation in NIR spectra).

The second component showed a maximum at about 65 % in carbon content. The two samples with the highest score values in the second component were torrefied at 300-310°C for 25 minutes and had a carbon content of about 65 %. Thus, the sign of the slope changed at higher torrefaction degrees (mass yields <55 %) for samples having a carbon contents >65 %. The most noticeable change in the IR-spectra at this level of carbon content was a fast loss of O-H structural groups and a gradual increase in aromaticy of the successively more carbonized biomass, see Lestander et al. 2014.

The results of the multivariate calibration modelling using PLS regression showed excellent prediction accuracies. Such models based on NIR spectra were constructed for gross calorific value, ash, volatile matter and fixed carbon content as well as content of C, H and O and furthermore atomic ratios of H/C and O/C and finally mass yield expressed as the ratio (in %) of remaining dry mass in relation to dry mass when untreated. These models explained 89.0 % to 98.8 % of the variation in reference values. This is very good. One example is the prediction of volatile matter, see Figure 32.

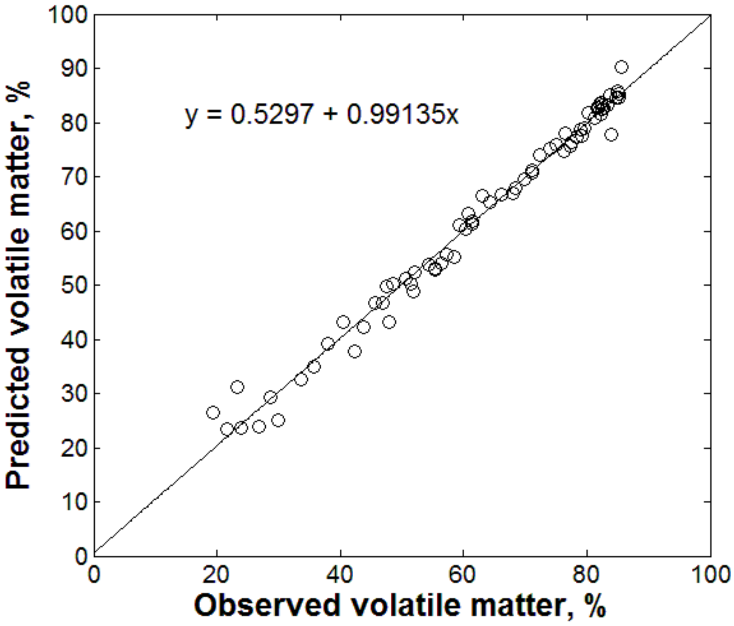

Figure 32: Observed and NIR predicted values of volatile matter in samples of raw and thermo-treated biomass.

More results are presented in Lestander et al. 2014. The model with the lowest and the highest degree of explanation were the ones for ash content and mass yield, respectively. The errors in prediction were small and the overall result was that NIR spectra can be used to construct multivariate calibration models having excellent properties in prediction key variables of torrefied or otherwise thermo-treated biomass, e.g. H/C and O/C atomic ratios and energy content. The application of this technique will improve monitor and control of thermo-treatment processes and reduce the need for wet chemical analysis. Furthermore, the excellent predictions clearly indicate the high potential of using NIR spectroscopy as an international standardized technique for the determination of key variables of carbonized biomass.

2.6.4 Summary and Conclusions

In summary samples of biomass model species (wood and straw) were thermo-treated to different torrefaction and carbonization degrees. The changes in chemical composition were analyzed: gross calorific value; content of ash, volatile matter, fixed carbon, carbon, hydrogen and oxygen; mass yield (%). It was clearly shown that calibration models based on collected NIR spectra from these samples accurately predicted these variables as well as H/C and O/C ratios. Therefore the conclusions were (1) that NIR spectroscopy can be used for predicting a broad range of variables in the ‘green coal’ remaining after torrefaction and other thermal treatments of biomass, and (2) that NIR spectroscopy has high potential utility as a standardized technique for characterizing such treated biomass, and thus, both facilitate process and product control and reducing the need of wet-based chemical analysis as well as the use of consumables.

2.6.5 References

Lestander T. A., Rudolfsson M, Pommer L. Nordin A. NIR provides excellent predictions of properties of biocoal from torrefaction and pyrolysis of biomass. Green Chemistry, 2014, 16 (12), 4906-4913. Open access: http://pubs.rsc.org/en/content/articlepdf/2014/gc/c3gc42479k

2.7 Leaching behavior

2.7.1 Introduction and objectives

Common expectations on torrefied wood pellets handling and storage properties have been high. Expected enhanced durability and hydrophobicity have even suggested open air storage similar to coal. In open air storage areas pellets are exposed to rain. Pellets are not totally hydrophobic and part of the rain is absorbed into pellets, but the rest is running out from fuel storage area. Leachates from biomass outdoor storages can led to solid organic and dissolved organic emissions into watercourse. It is important to assess the quality of run-off waters to ensure that the waters are treated properly. The torrefied biomass pellets are new types of fuels and there is no experience about their long time open air storage and nor the quality of rainwaters from that kind of storage areas.

Elements like Na, K and Cl are easily leachable from conventional biomass and this is likely the same for torrefied materials. Additionally it has been doubted that harmful organic compounds (e.g. PAH) may leach from torrefied material.

The goal of this research was to develop a laboratory leaching test to assess the possible environmental effects of torrefied pellet storage in open area fuel storage areas. Leaching and the quality of leachates depending on process conditions, biomass species and weather resistance of the final product were studied.

2.7.2 Method development and analyses

Leaching properties of five Sector project pellets samples were evaluated and compared to commercial Finnish wood pellets. The same pellet samples were used in small scale logistic testing carried out under the WP6.1 by VTT. The results, e.g. pellet dimensions and mechanical durabilities, are reported in D6.3. Leachates to be researched were produced by using water immersion test developed by VTT. Pellet grades used in tests, leachate production and analysis methods are presented in the following paragraphs.

For evaluation of leachate quality results a questionnaire for SECTOR WP8 partners was sent concerning the statutory criteria or other guidance for rainwaters running out from open air fuel storage areas.

2.7.2.1 Pellet grades used in tests

Five different torrefied pellet grades, which are specified in Table 4, were used in production of leachates. Commercial Finnish wood pellets were used as reference. These same materials were used in small scale logistic tests carried out by VTT in SECTOR WP6. Photos of all used pellet grades are presented in Figure 33.

Table 4: Torrefied SECTOR pellet samples used by VTT in WP8 and WP6.

Producer	Raw material	Sample name told in the shipment
ECN	Spruce	ECN_Spruce-260_torrefied_pellets
ECN	Poplar	ECN_Poplar-270_torrefied_pellets

ECN	Pine	ECN_Pine-270_torrefied_pellets
CENER	Straw	CENER_Straw_270_Pellets_31102013
Topell	Wood residues	Topell Energy-Q4-2013, torrefaction date 1.11.2013

Figure 33: The pellet grades used in the experiments at VTT. Distance between the lines in photos was 10 mm.

2.7.2.2 Analysis methods for leachates

Conductivity, pH, turbidity and evaporation residue of pellet immersion water was determined according to VTT’s internal methods. Determination of suspended solids content was carried out according to the standard EN 872:2005.

Content of dissolved organic carbon (DOC) was determined according to the method EN 1484:1997. Water sample was filtrated with 0.45 µm membrane before analysis. Reactor digestion method 8000 with Hach spectrophotometer was used in determination of chemical oxygen demand (COD).

Nutrients and salts were analysed from pellet immersion water according to the methods listed in the Table 5. Content of polyaromatic hydrocarbons (PAHs) in pellet immersion water was determined according to the method O-5 (liquid chromatography).

Table 5: Methods used in pellet immersion water analyses

Analysis	Method
Total Nitrogen, N	EN ISO 11905-1:1998 (modif.)
NH_4-N	SFS 3032:1976
NO_2-N	A40 D (Aquakem)
NO_3-N	EN ISO 13395:1996 modif.
Total phosphorus, P	A40 B (Aquakem)
Chlorides	EN ISO 10304-1:09 modif.
Sulphates	EN ISO 10304-1:09 modif.
Potassium, K	EN ISO 11885:09 modif.
Calcium, Ca	EN ISO 11885:09 modif.
Magnesium, Mg	EN ISO 11885:09 modif.
Sodium, Na	EN ISO 11885:09 modif.

2.7.2.3 Water immersion test in production of leachates

A 500 g sample of each pellet type was placed in a filtration bag which was then submerged to a water container for the period of 15 minutes (Figure 34). The amount of water in the container was 5 kg i.e. ten times the mass of pellets. After the immersion period, the sample was drained over the water container for another 15 minutes.

Figure 34: A pellet sample submerged to water in a filtration bag during the water immersion test.

Samples for all analyses were taken from the water left in container after the drainage period. The water was carefully mixed before sampling. A sample of tap water was also taken for reference.

2.7.3 Results and experiences

2.7.3.1 Water quality after immersion of pellets

The colour of water was changed to brownish, but only small changes were noticed in water pH after the immersion tests of pellet grades (Figure 35). Most considerable reduction in pH was noticed for reference wood pellets. The pH of the immersion water was 5.4. after the test. With all the torrefied pellet samples the increase or reduction was equal or lower to 0.5. The conductivities of all the immersion waters were between 145 – 200 µS/cm and turbidities 6 – 22 NTU.

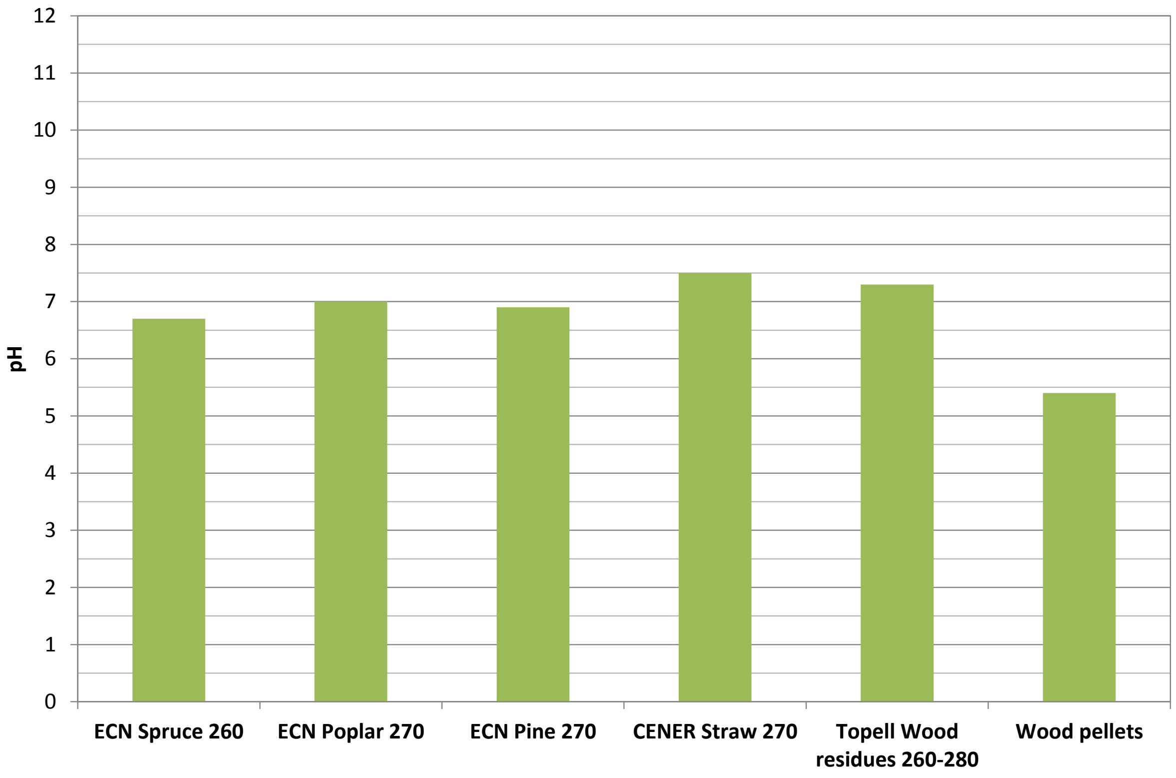

Figure 35: pH of the water sample after the immersion test of pellet sample. The pH of the tap water used in the experiments was 7.

Content of dissolved organic carbon (DOC) in pellet immersion water varied from approximately 30 to 200 mg/l (Figure 36). The lowest values were measured for CENER Straw and Topell wood residue pellets, and the highest value for reference wood pellets. Chemical oxygen demand (COD) was also the highest for Wood pellets and lowest for Wood residues pellets. COD values varied between 110 – 680 mg/l, which are in noticeable level. The highest values are comparable to average COD values in incoming water of a municipal waste water treatment plant in Finland. If the tested torrefied biomass pellets are placed in order of superiority according to the leachate quality, the order is same as in mechanical durability after rain exposure and immersion tests in WP6.1. It can be assumed that leachate quality is dependent on pellets resistance to water.

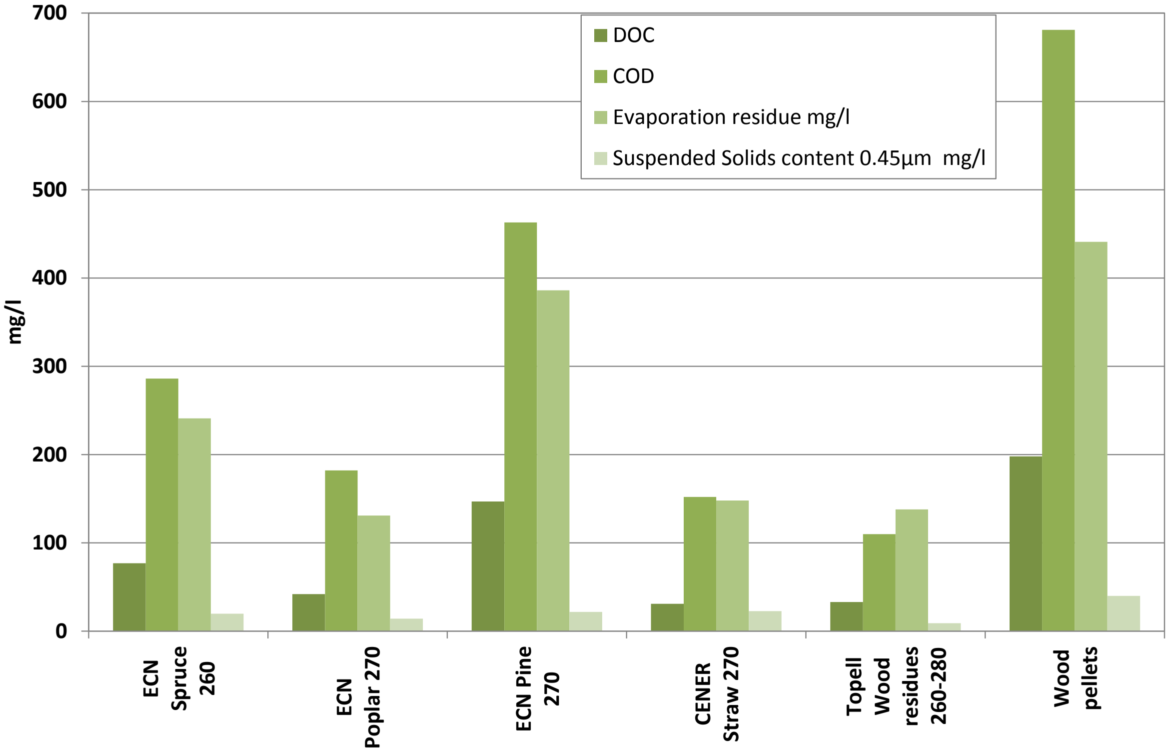

Figure 36: Water quality after immersion tests with different torrefied pellets. Pellet sample was immersed in tap water for 15 minutes.

Remarkable phosphorus contents were analysed from immersion waters (Figure 37). Highest value, approximately 1700 µg/l was determined for reference wood pellets, which are nearly totally disintegrated during the immersion test. Highest phosphorus content for torrefied pellets was determined from immersion water of ECN Pine pellets (appr. 1200 µg/l) and the lowest value for CENER Straw pellets (530 µg/l). Content of other nutrients in immersion waters was low (Figure 38). Potassium concentrations in waters were varying between 8.5 and 25.5 mg/l depending on pellet sample. Most potassium was leached out from torrefied straw pellets, followed by reference Wood pellets and Wood residues pellets. Other nutrients than phosphorus and potassium were hardly noticed after the effect of tap water were taken out of the values.

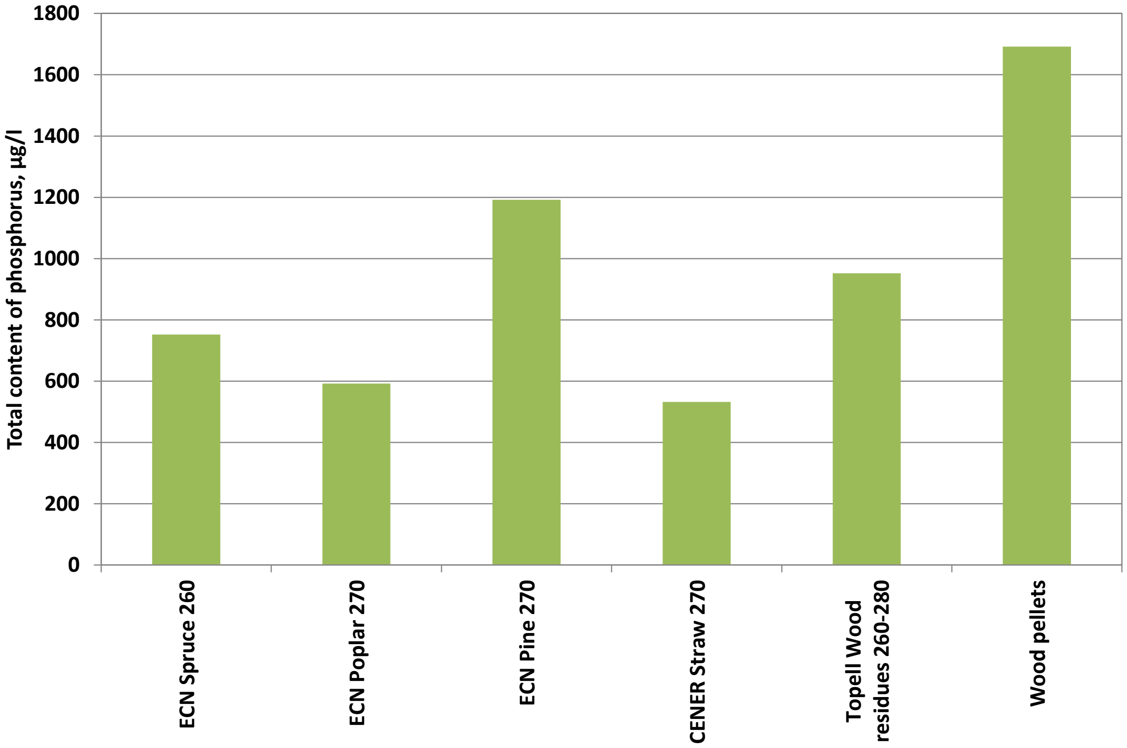

Figure 37: Phosphorus content of water after the immersion test.

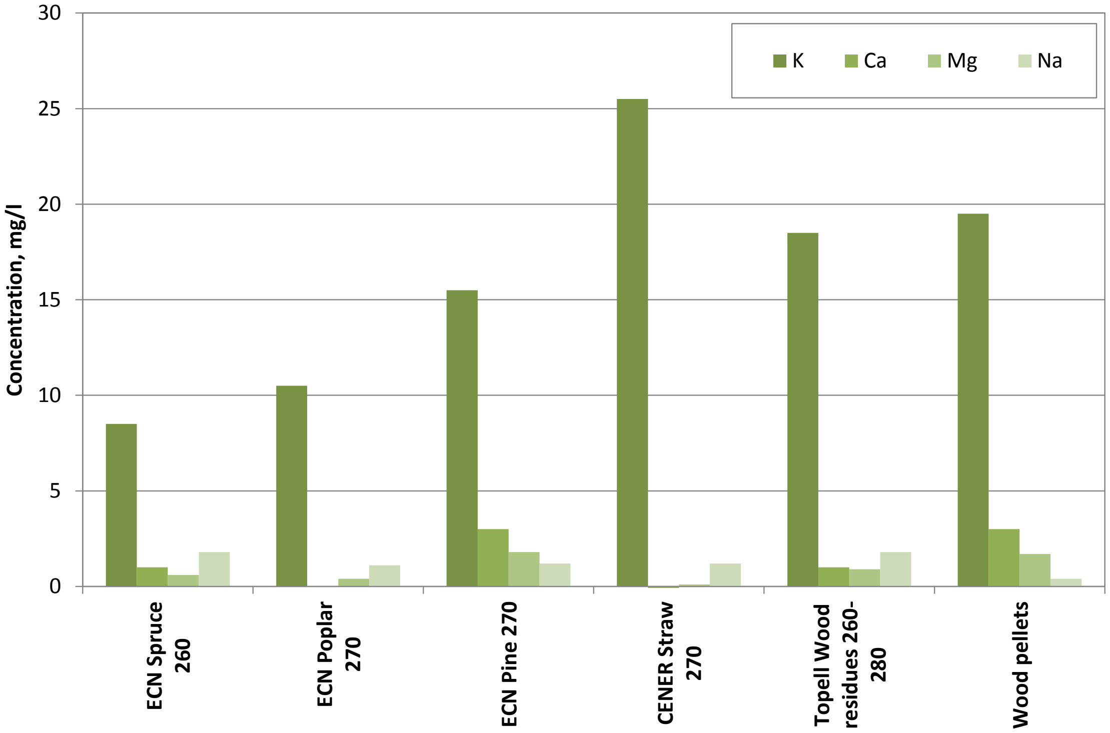

Figure 38: Nutrient concentrations in water samples after pellet immersion tests. The concentrations of these elements in tap water have been taken away from the values.

The polyaromatic hydrocarbons (PAHs) were also analysed from water samples to ensure that no harmful organic substances are leached out from torrefied pellets. The analysis results revealed that there is no concern about leaching of PAH's with the tested pellet samples (Table 6).

Table 6: The content of polyaromatic hydrocarbons in water samples after pellet immersion test. The values are presented as µg/l.

	ECN Spruce 260	ECN Poplar 270	ECN Pine 270	CENER straw 270	Topell Wood residues 260-280	Wood pellets
Napthalene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fluorene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Asenaftene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Asenaftylene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fenantrene	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
Antrasene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fluoranthene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pyrene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bentso(a)antrasene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Krysene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bentso(b)fluoranthene	0.01	0.02	<0.01	<0.01	<0.01	<0.01
Bentso(k)fluoranthene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bentso(a)pyrene	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Dibentso(ah)antrasene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bentso(ghi)perylene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Indeno(1,2,3-cd)pyrene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

CENER straw and Topell wood residue pellets were used to estimate the effect of immersion time on dissolved organic carbon (DOC) and chemical oxygen demand (COD) of immersion water. The quality of immersion waters of torrefied pellets was still better after 45 minutes immersion time if compared to 15 minutes immersion of wood pellets (Figure 39). Nevertheless, the DOC and COD contents in immersion waters increased together with the immersion time.

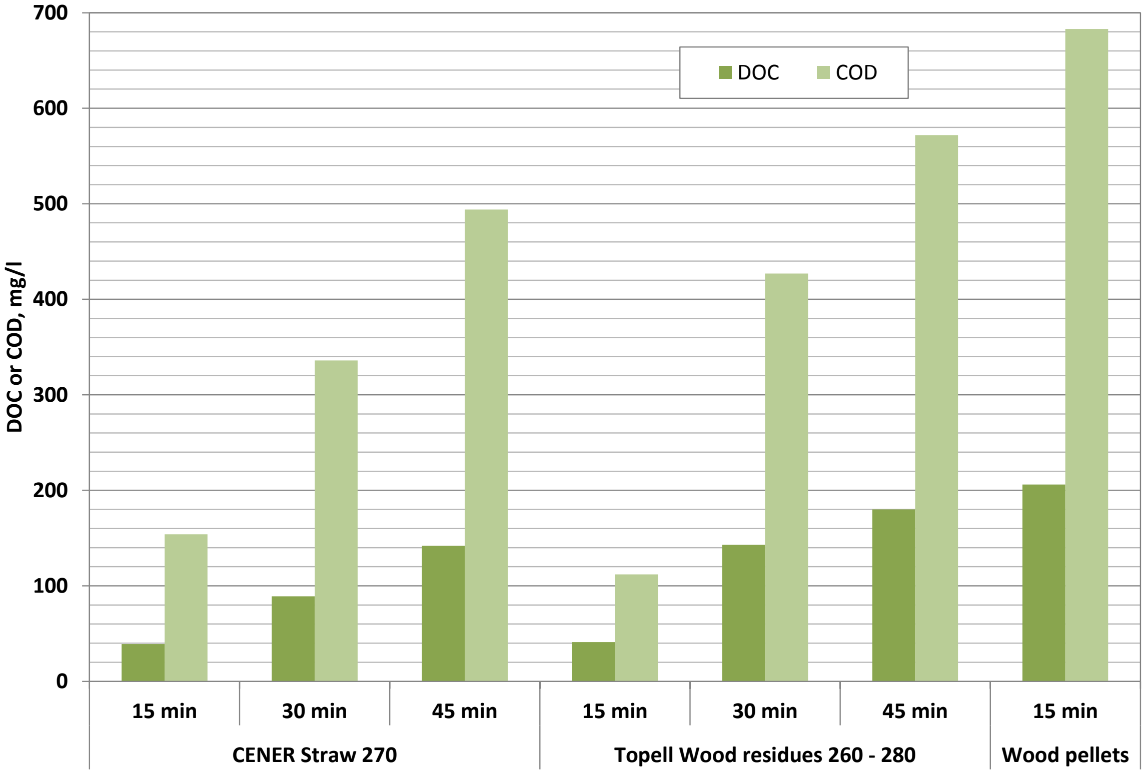

Figure 39: Effect of immersion time on dissolved organic carbon (DOC) content and chemical oxygen demand (COD) of pellet immersion water. Straw and wood residues pellets were made of torrefied material and commercial wood pellets were used as reference.

2.7.3.2 Rainwater quality requirements

The requirements for discharge water quality are needed if a laboratory leaching test is developed to evaluate the leachate quality and the need of rainwater treatment. There is no general, harmonic legislation or guidelines available and therefore applicable information was searched from different sources.

Best available technologies for control of emissions to water in handling and storage of biomass at terminals and at the point of use have been presented by Linberg & Tana 2012:

- Storage areas should be asphalted or sealed with watertight layer to avoid leakages to soil and ground water.
- Sensitive ground water areas should be avoided as handling and storage areas.
- Solids should be removed from leachates and drainage waters.
- Leachates and drainage waters should be routed via a monitoring well and regular water quality control (pH, conductivity, suspended solids, COD/TOC) should be applied.
- Areas with risk of oil spills during handling should be equipped with oil trap wells.

In Finland the rainwaters from open air biomass fuel terminals are usually collected to drains surrounding the storage area and discharged to water way through a settlement basin. It is said in legislation that suspended solids have to be removed from rainwaters of open air fuel storage areas at power plant site (under 50 MW_{fuel}) before discharge to water way (Finnish

Government Decree 750/2013). Requirements for discharge water quality and parameters to be controlled are stated in the environmental permit of the individual fuel storage site. The requirements for water quality usually depend on the water quality of receiving water way. Suspended solids content, pH, conductivity, COD, total nitrogen and total phosphorus are typical parameters to be controlled from water samples.

In Austria the rainwater from fuel storage areas is typically drained in the near surrounding area (Goebl 2014). If the rainwater from storage place is discharged back into river the general waste water emission regulation (BGBI Nr. 186_1996) has to be followed. The regulation includes limit values for overall parameters (e.g. toxicity, solids content, pH), inorganic parameters and organic parameters. The limit values are divided into emissions into rivers and emissions into sewage water system. More important as the guidance is to found an agreement with the responsible agency that determines what has to be done to get the allowance. There are different guidelines in every 9 federal states of Austria.

In the Netherlands the legislation concerning water discharge is basically divided by sources, which means that different laws exist for industry, households and other (Carbo 2014). The requirements for discharge of waste water that has been in contact with non-inert goods during storage and transhipment are applied for open air fuel storage areas (Activiteiten milieubeheer, Artikel 3.4.3. Opslaan en overslaan van goerden). Minimum requirements are stated e.g. for COD, undissolved, heavy metals, PAHs, total nitrogen and phosphorous, but additional requirements may be imposed.

2.7.4 Summary and Conclusions

The goal of this research was to develop a laboratory leaching test to assess the possible environmental effects of torrefied pellet storage in open air fuel storage areas. Leaching properties of five SECTOR project pellet samples were evaluated and compared to commercial Finnish wood pellets. Leachates to be researched were produced by using water immersion test developed by VTT. Statutory criteria and other guidance for rainwaters running out from open air fuel storage areas were searched from different sources to evaluate analysis results of leachates.

15 minutes immersion of pellets increased the COD, DOC and phosphorus content of immersion water remarkably, but leaching of PAHs was not noticed from torrefied pellets researched. Changes in water quality depended on pellet grade and its resistance to water. Lowest quality leachate was collected from the immersion test of reference wood pellets, which were nearly totally disintegrated during the immersion test. It has to be pointed out that wood pellets are not stored in open air storage areas and therefore leachates of wood pellets are not a good reference.

Liquid solid ratio of ten was used in the leachate production tests, which is comparable to standardised waste material leaching test methods. The concentrations of COD, DOC and phosphorus in leachates of torrefied biomass pellets were quite high if compared to for example rainwaters running out from fuel peat production areas. Therefore it can be assumed that the leachates from fuel storage areas should be more dilute. Furthermore it is quite hard to imagine that torrefied pellets are submerged to water in fuel storage area, so the used laboratory leaching test represents a worst case.

The comparison of laboratory leaching test results to circumstances prevailing in open air storage of pellets is difficult. There is no experience about the quality and amount of rainwaters running out from open air storage sites of torrefied biomass pellets. No information is available how much rainwater pellets absorb and how deep into the pile the rain effects. The leaching of pellets probably changes during the storage time also. The worst case situation may be evaluated by a laboratory leaching test, but a connection between the practise and laboratory leaching test should be found. One option to evaluate this could be the sampling of rainwaters from open air fuel storage area and compare the results with laboratory leaching test. That kind of research should be carried out with several torrefied biomass pellet types to get reliable data.

The need for a separate leaching test is not evident. Leaching behaviour testing of torrefied biomass pellets can be performed e.g. together with water absorption test. After immersion of pellets the remaining water is just analysed. According to the legislation and other guidelines the attention should be paid on analyses of suspended solids, pH, conductivity, COD/TOC, DOC and nutrients (e.g. phosphorus and nitrogen). No exact list of parameters can be given because the legislation and guidelines are country specific and can even vary inside a country.

Still another open question is if the torrefied pellets can be stored in open air storage areas. The resistance of torrefied biomass pellets to water is not excellent and therefore not all the investigations performed suggest open air storage. If the pellets are stored under the roof, there is no need for leaching behavior testing.

2.7.5 References

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2.8 TGA method

2.8.1 Introduction and objectives

Thermographimetric analysis (TGA) is a simple, fast and very informative method for determining the torrefaction behavior of biomass. Small samples of 10-20 mg of the ground material are subjected to temperature programs in an inert atmosphere (nitrogen). The mass change as a function of the temperature is recorded and the mass yield, an important a parameter in torrefaction, is determined. The objective was to develop a reliable and informative method for determining one of the important torrefaction parameters as a starting point for large scale torrefaction processes.

2.8.2 Method development and analyses

Because the purpose of performing TGA measurements is to get insight in the torrefaction behavior of biomass when torrefied in full scale torrefaction units the parameters from these full scale treatments have to be implemented in the TGA method. Temperature and torrefaction time can be controlled accurately, but heating rates and particle sizes are to be approximated as good as possible. While varying the TGA parameters the limits of this technique appear. The ultimate method developed is therefore supporting in finding the right torrefaction procedure for each feedstock and every individual torrefaction technique or system.

2.8.3 Results and experiences

The TGA measurements can be used to determine the mass yield at any desired torrefaction time. The heating rate to the torrefaction temperature has been varied to study the effect on the torrefaction behavior. In the following graph the heating rate is increased from 5 to 35°/min and thereby the limits of the TGA equipment are clearly shown (Figure 40). A temperature overshoot is created depending on the heating rate.

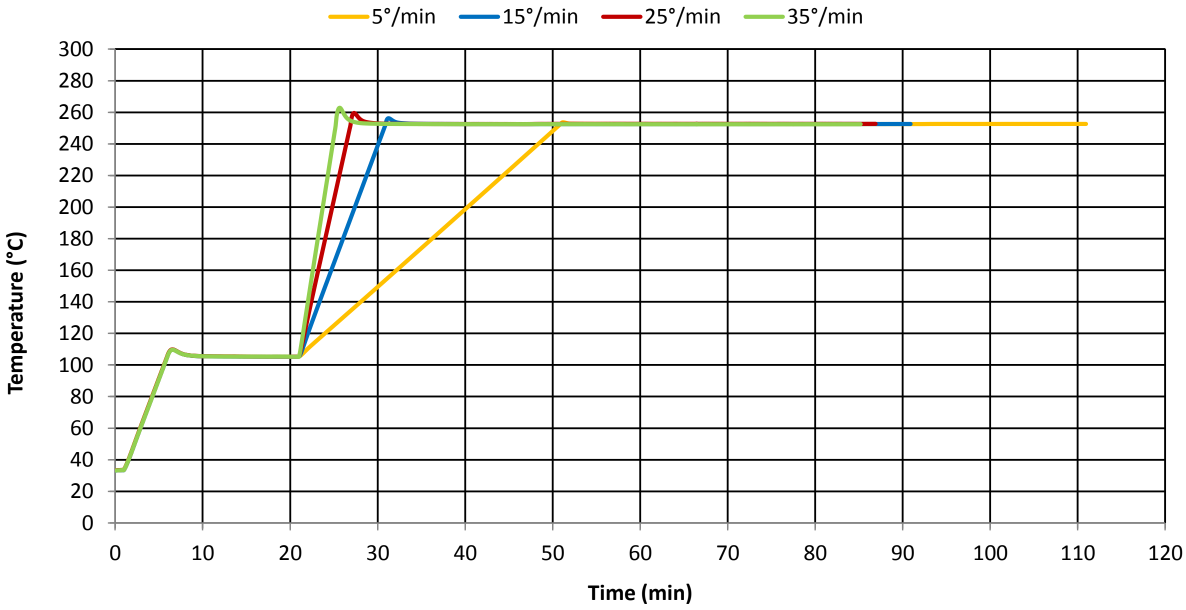

Figure 40: TGA experiments at heating rates from 5°C/min to 35°C/min

Choosing one heating rate the temperature has been varied and typical graphs showing the relative mass versus time are in Figure 41.

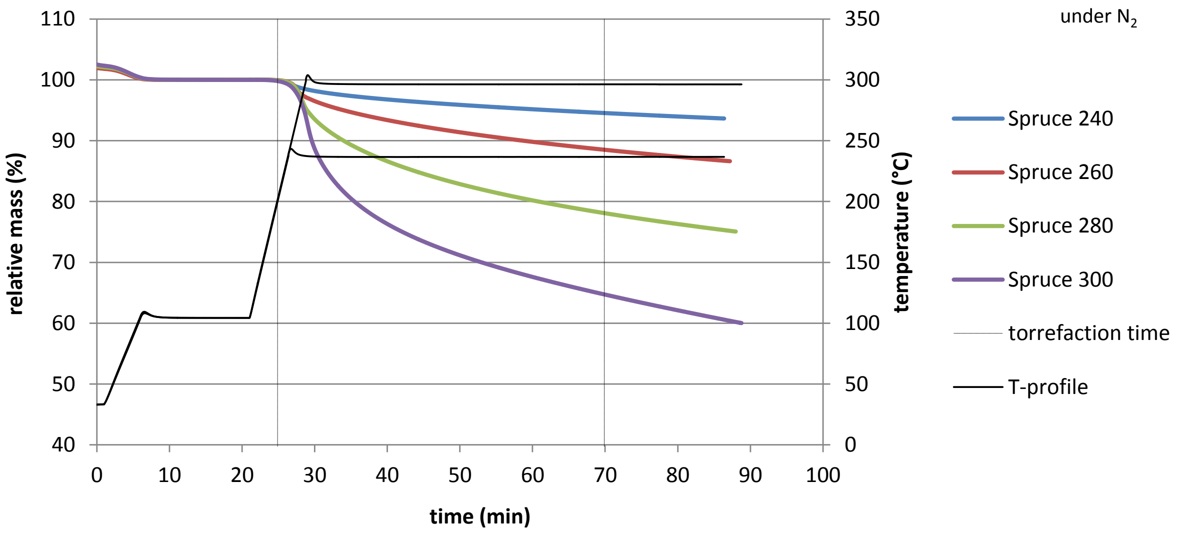

Figure 41: Relative mass loss at temperatures between 240°C - 300°C

These TGA measurements are performed using different torrefaction temperatures, e.g. 240, 260, 280, and 300°C. The sample mass is calculated relative to the moment the sample is heated from drying temperature (105°C) to torrefaction temperature. The torrefaction time (45 minutes in the graph) starts the moment the samples reach 200°C and ends 45 minutes later. The mass yield for each measurement is the relative mass at the end of the torrefaction time. These mass yields at different temperatures are plotted for each material in the next graph (Figure 42).

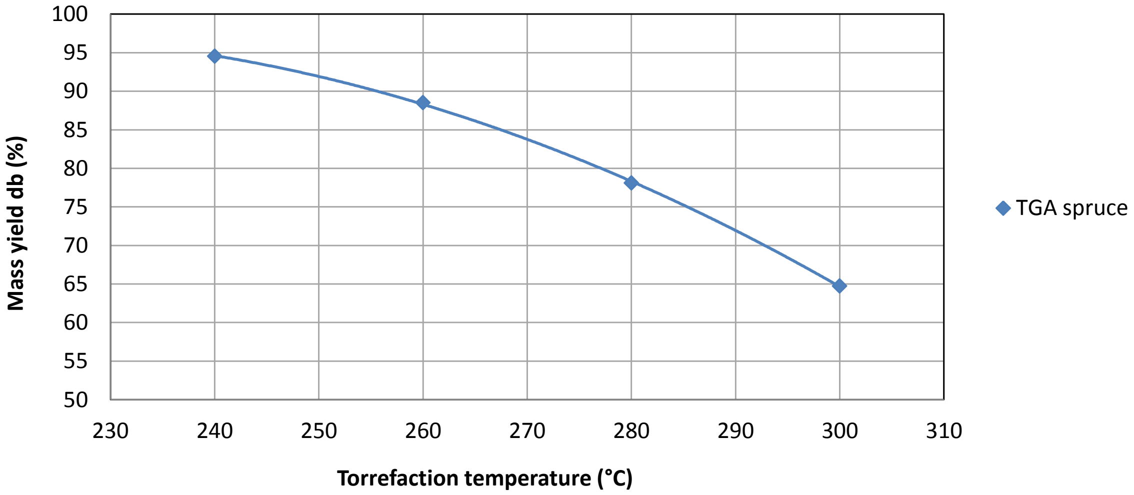

Figure 42: Mass yields at different temperatures

Particle sizes have also been varied and shown that the mass yield increases with the particle size: e.g. 54.7 % MY for <1 mm particles and 50.5 % MY for <0.25 mm particles. Therefore differences in TGA measurements and small (lab)scale torrefaction treatments lead to slightly different results as shown in Figure 43.

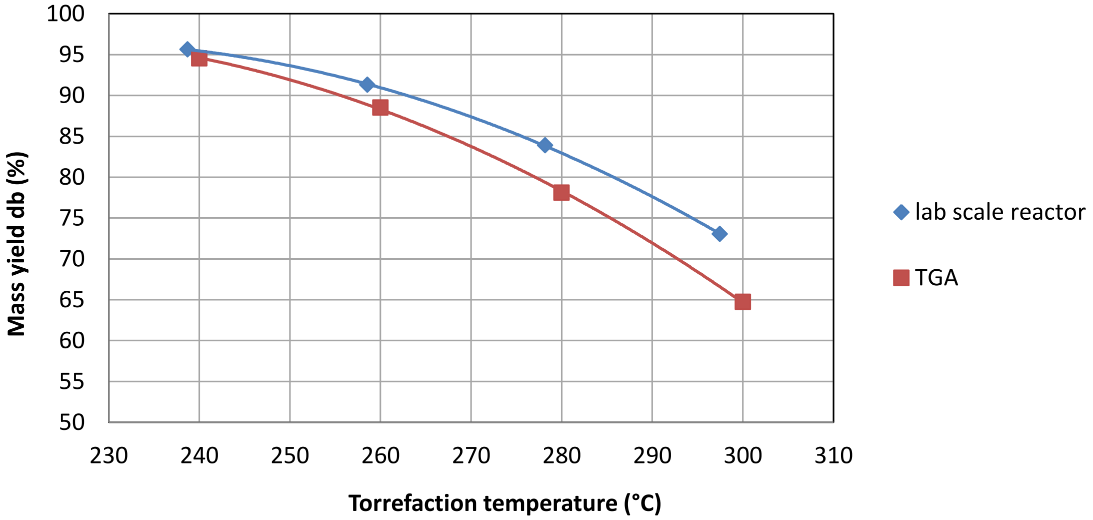

Figure 43: Mass yields at different temperatures of TGA experiments and (lab) scale torrefaction

2.8.4 Summary and Conclusions

Despite the fact that not the exact mass yields from full scale torrefaction treatments can be predicted using the TGA technique it is possible to examine the torrefaction behavior in a quick and reliable way. Therefore the following method has been developed:

- 10-20 mg of the ground material is analysed in a ceramic sample holder under a constant flow of 45 ml/min nitrogen
- Starting temperature is 30°C for 1 minute
- Heating with 15°/min to 105°C, holding time 15 minutes
- Heating to torrefaction temperature with 25°/min, holding time 60 minutes
- Cooling to 30°C.

3 Properties of torrefied biomass

This section of the deliverable D8.5 gives an overview on different properties of torrefied biomass. All discussed analysis parameters were measured within the scope of the SECTOR project in WP3, WP4, WP6 and WP8.

3.1 Introduction

Torrefaction has a great influence on the chemical properties of biomass. The main reason for applying this technology is the improvement of the fuel quality and the operability of biomass at (e.g.) combustion facilities, like an increased calorific value. But torrefaction has also an effect on other fuel characteristics like ash content and carbon content.

This part should give an overview about the transition that torrefaction causes in biomass.

These changes include alterations in the chemical composition of biomass. Due to the degradation of structural substances of biomass (mainly cellulose, hemi-cellulose and lignin) and the removal of organic substances, the carbon content is increased whereby the contents of hydrogen and oxygen are decreased. The concentration of minor elements is also changed, resulting in different ash content and a difference in the release of pollutants (for instance chlorine and sulphur) during e.g. combustion.

3.2 Investigated properties of torrefied biomass

Data selection

Within the SECTOR project various torrefied biomass samples were produced and resulted in 82 samples for analysis. These samples differ in the type of biomass, the reactor used for torrefaction and the torrefaction parameters (time and temperature).

Twenty samples were selected to discuss the influence of torrefaction on different fuel properties. The author picked samples of every biomass type, which are comparable in torrefaction process (e.g. producer/reactor, torrefaction time) and differ at the torrefaction temperature.

For the discussion of the chemical properties the wood chip samples were considered and no densified products. For the mechanical durability the corresponding torrefied pellets were analysed.

In

Table 7 the chosen samples are listed with producer, reported torrefaction date and temperature as well as the SECTOR sample label name.

Table 7: Selected samples for chemical properties evaluation

Material	Producer	Torrefaction temperature (°C)	Torrefaction date	SECTOR sample label
Pine	CENER	-	-	CENER_pine-_white chips_NA
Pine	CENER	280	02.10.2012	CENER_pine-280_torrefied chips_021012
Pine	CENER	290	21.03.2013	CENER_pine-290_torrefied chips_210313
Pine	CENER	300	22.11.2012	CENER_pine-300_torrefied chips_221112
Poplar	CENER	-	-	CENER_poplar-_white chips_NA
Poplar	CENER	280	29.05.2013	CENER_poplar-280_torrefied chips_290513
Poplar	CENER	290	29.05.2013	CENER_poplar-290_torrefied chips_290513
Poplar	CENER	300	28.05.2013	CENER_poplar-300_torrefied chips_280513
Spruce	ECN	-	-	ECN_spruce-_white chips_NA
Spruce	ECN	240	29.10.2012	ECN_spruce-240_torrefied chips_291012
Spruce	ECN	260	24.10.2012	ECN_spruce-260_torrefied chips_241012
Spruce	ECN	280	15.10.2012	ECN_spruce-280_torrefied chips_151012
Bamboo	ECN	-	-	ECN_bamboo-_torrefied chips_NA
Bamboo	ECN	245	24.02.2012	ECN_bamboo-245_torrefied chips_240212
Bamboo	ECN	255	23.02.2012	ECN_bamboo-255_torrefied chips_230212
Bamboo	ECN	265	22.02.2012	ECN_bamboo-265_torrefied chips_220212
Straw	CENER	-	-	CENER_straw-_white chips_NA
Straw	CENER	250	14.02.2013	CENER_straw-250_torrefied chips_140213
Straw	CENER	260	26.06.2013	CENER_straw-260_torrefied chips_260613
Straw	CENER	270	26.06.2013	CENER_straw-270_torrefied chips_260613

The selected samples of pine show a deviation for the sample torrefied at 300°C. The results of this particular sample show the expected trends for the changes in chemical properties at torrefied biomass, but the amount of the changes is unusually low (e.g. net calorific value, carbon content) or high (e.g. volatile matter) and do not fit to the other torrefied pine samples at different torrefaction temperatures. The production dates of the torrefied pine samples differ by several months, so it is possible that there were already differences at the used raw material, which could explain this discrepancy.

Analysis procedures

The applied measurement procedures can be found in Table 8.

Table 8: Applied measurement procedures

Parameter	**Measurement procedure**
Mechanical durability, DU	EN 15210
Moisture content, M_{ar}	EN 14774
Ash content, A	EN 14775
Nitrogen content, N	EN 15104
Calorific value Q	EN 14918
Sulfur- and Chlorine content, S, Cl	EN 15289
Volatile matter, VM	EN 15148
Ash melting behavior	CEN/TS 15370

3.2.1 Net calorific value

One of the main advantages of torrefaction is the improvement of the energy density of biomass. The mass reduction of the biomass is higher than the energy loss, resulting in a higher calorific value.

The net calorific value (Figure 44) shows a significant increase because of torrefaction. Depending on the sort of biomass the net calorific value of the torrefied material increases between approximately 0.6-29 %. The highest increase of net calorific value was measured for bamboo (29 %). Straw showed the least increase with 0.6 %, which could be explained by the lower torrefaction temperatures used. The three different wood types showed an increase of 2.1 to 15.8 %.

This increase is partly based on the increase of carbon content and the decrease of oxygen and hydrogen content.

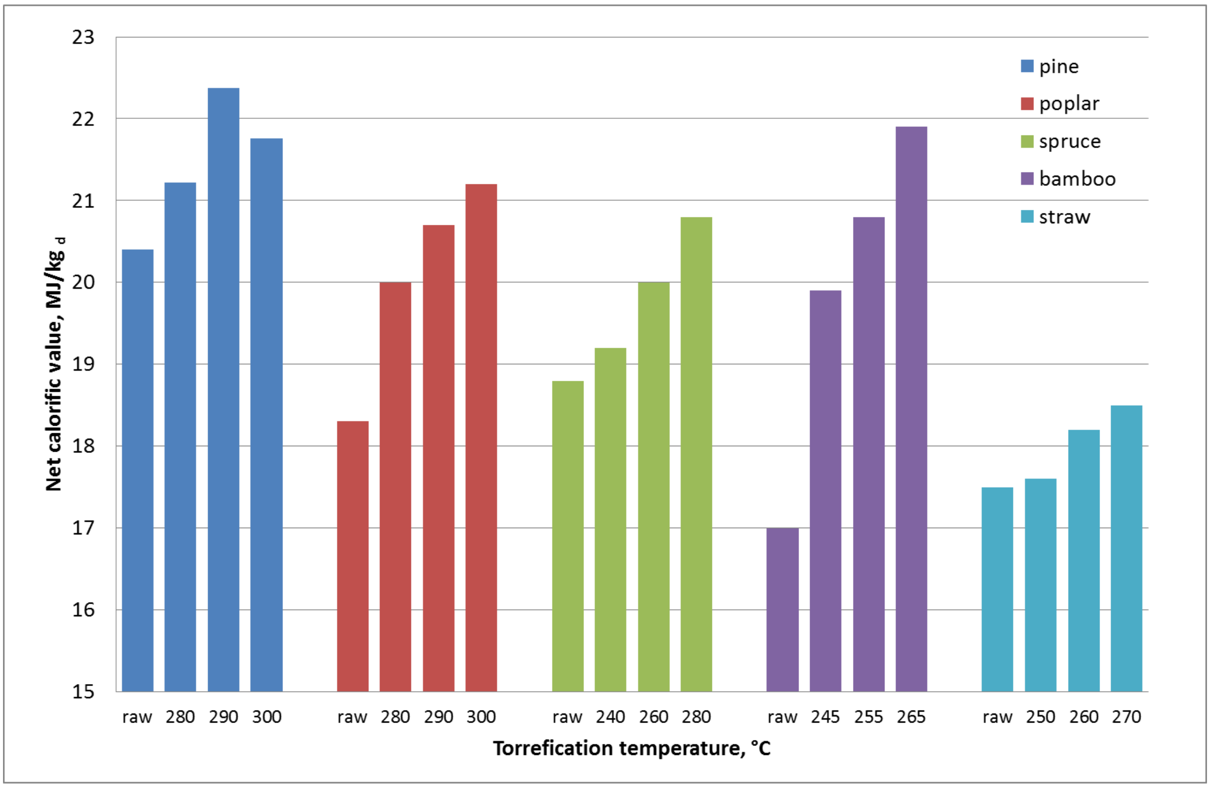

Figure 44: Net calorific value of samples pine, poplar, spruce bamboo and straw at different torrefaction temperatures (240°C-300°C) and the raw material

The amount of increased calorific value correlates with the change in carbon content as presented in Figure 45. It also can be seen the correlation of the different sample types. The pine samples are noted with a separate correlation line because the results clearly range at a different level.

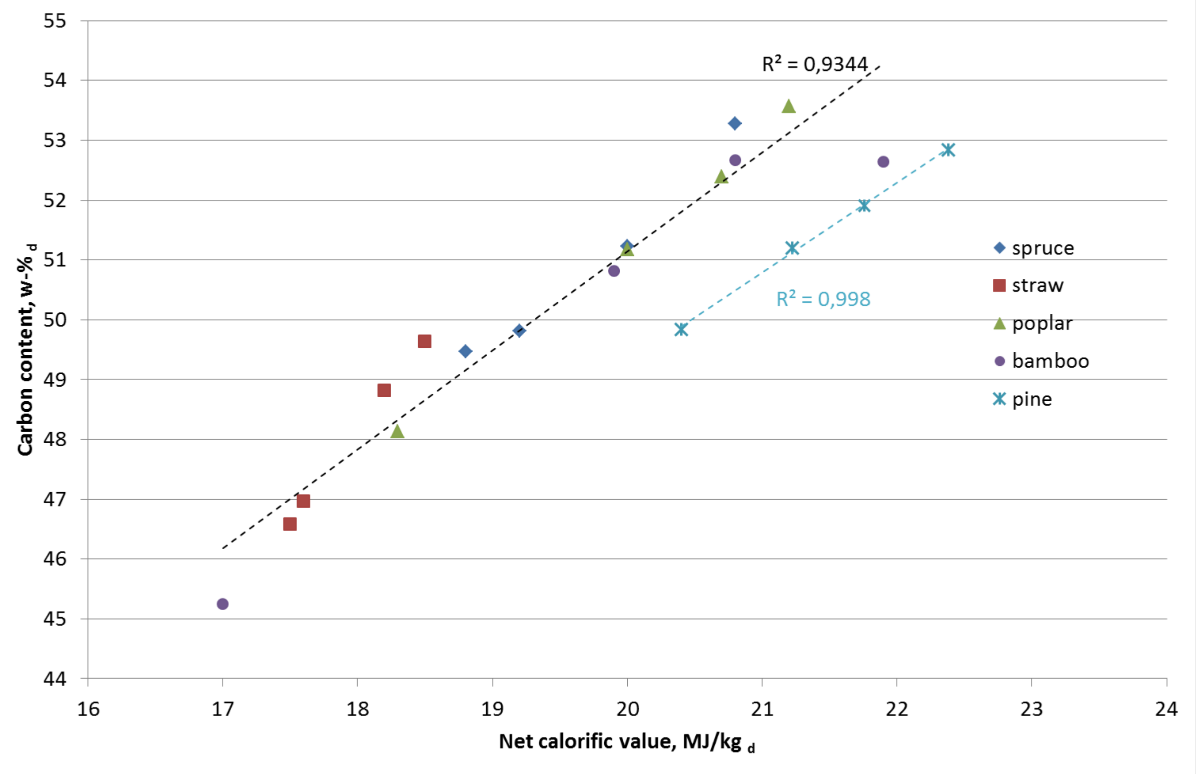

Figure 45: Net calorific value in correlation with carbon content

3.2.2 Elemental analysis

The elemental analysis (hydrogen, nitrogen, carbon and oxygen) of raw biomass and torrefied biomass (Figure 46 - Figure 49) samples show increasing carbon content with rising torrefaction temperature, whereas the content of hydrogen and oxygen decreases.

Contents of carbon, hydrogen and nitrogen were measured using elemental analysis. Oxygen was calculated according to EN ISO 16993.

The decrease in oxygen and hydrogen contents is caused by the loss of oxygen and hydrogen rich volatile compounds during pyrolysis phase of torrefaction.

Although carbon is devolatized in the gaseous and liquid phase as well (mainly as CO, CO_2, CH_4 and aromatic hydrocarbons), the mass loss is higher than the loss in carbon. This leads to an increase of the relative carbon content by 6-16 % depending on the type of biomass.

As an exception the nitrogen content is almost not altered throughout the torrefaction process for some samples like poplar and bamboo. Respectively no correlation of the torrefaction temperature and the nitrogen content can be seen for the samples of pine or spruce.

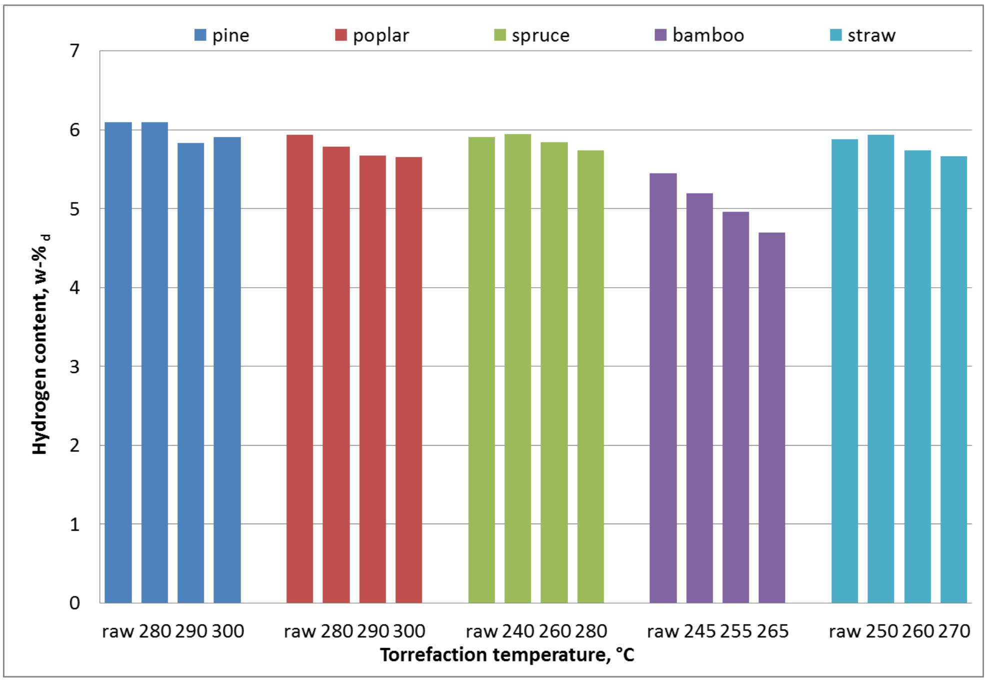

Figure 46: Hydrogen content of samples pine, poplar, spruce bamboo and straw at different torrefaction temperatures (240°C-300°C) and the raw material

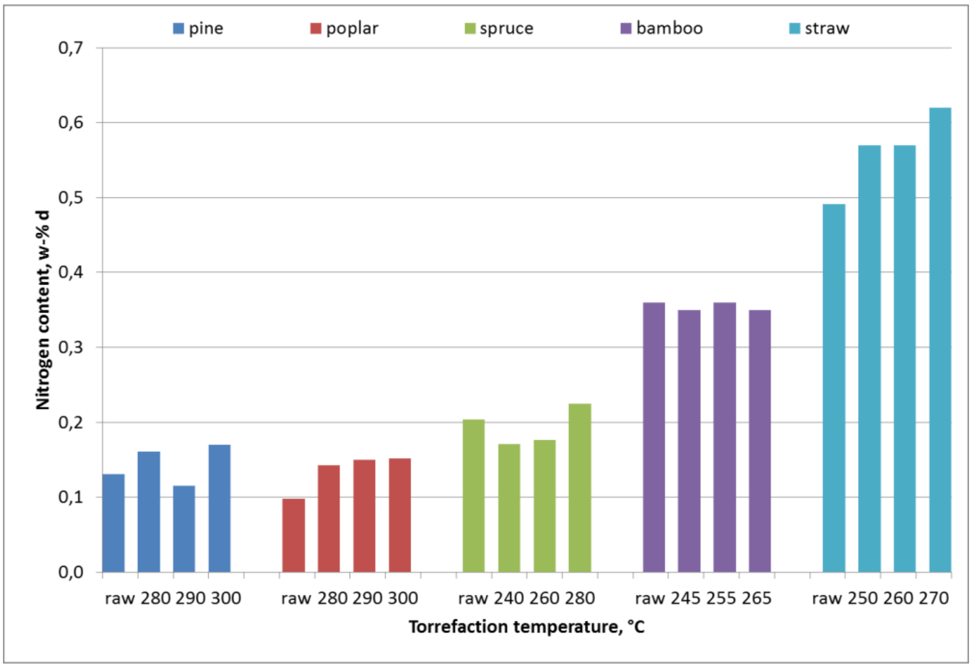

Figure 47: Nitrogen content of samples pine, poplar, spruce bamboo and straw at different torrefaction temperatures (240°C-300°C) and the raw material

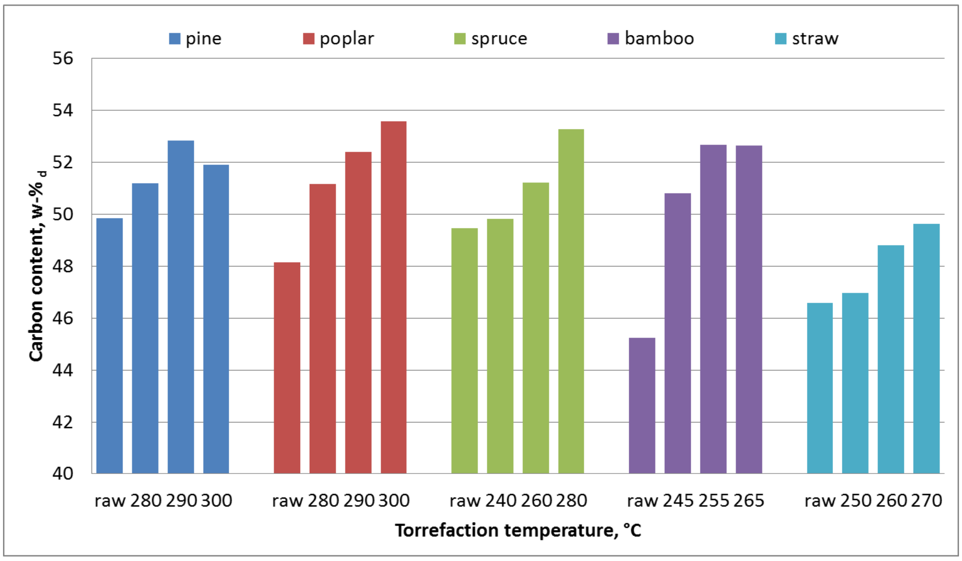

Figure 48: Carbon content of samples pine, poplar, spruce bamboo and straw at different torrefaction temperatures (240°C-300°C) and the raw material

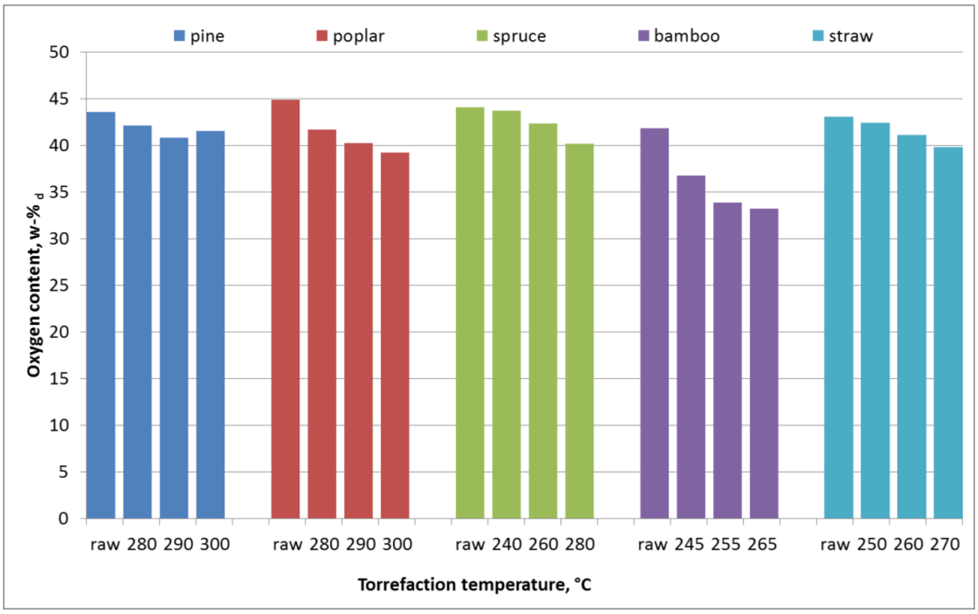

Figure 49: Oxygen content of samples pine, poplar, spruce bamboo and straw at different torrefaction temperatures (240°C-300°C) and the raw material

3.2.3 Volatile matter

A large number of different gases and condensable liquids are expelled during the torrefaction process. These are, depending on the chemical composition of the biomass, mainly CO_2, CO and CH_4 in the gaseous state and H_2O and a variety of organic substances (for instance lipids, alcohols, terpenes, furans, etc.) as condensable liquids.

The loss of volatile matter is increased at a higher torrefaction temperature as well as by extension of the torrefaction time.

For the selected samples the loss of volatile matter is about 7-29 % between the raw material and the torrefied biomass, at the most intense torrefaction parameters (Figure 50).

Concerning the amount of volatile matter reduction, there is no obvious temperature dependency recognizable for the compared biomass types. The chemical composition of the particular biomass has an influence and needs to be considered for determination of the optimal torrefaction parameters.

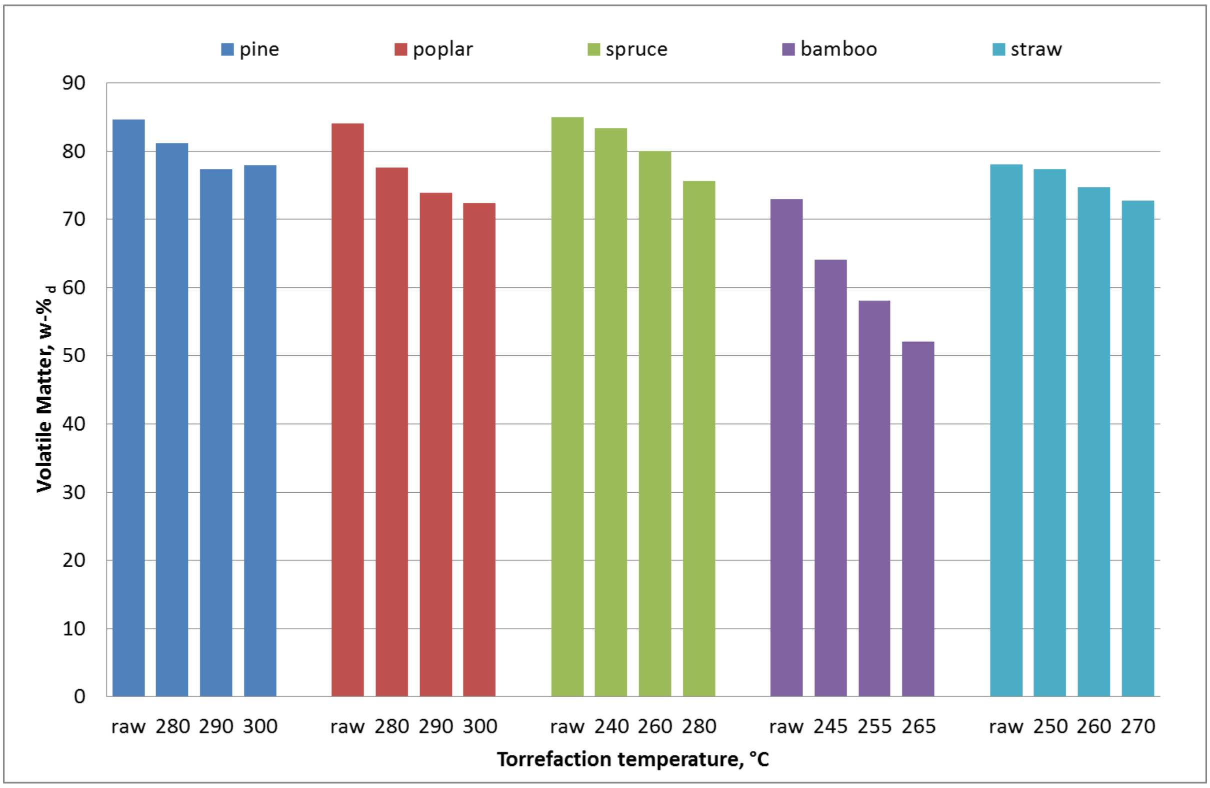

Figure 50: Volatile Matter of samples pine, poplar, spruce bamboo and straw at different torrefaction temperatures (240°C-300°C) and the raw material

3.2.4 Ash content

By comparing the samples of same biomass type but different torrefaction temperaturess an increase in ash content is detectable (Figure 51). Depending on the material it is mostly a slight increase which is measurable for all different biomass typs tested.

This is a consequence of the enrichment of mineral, inorganic compounds due to the released organic matters, respectively the mass loss, during the torrefaction process.

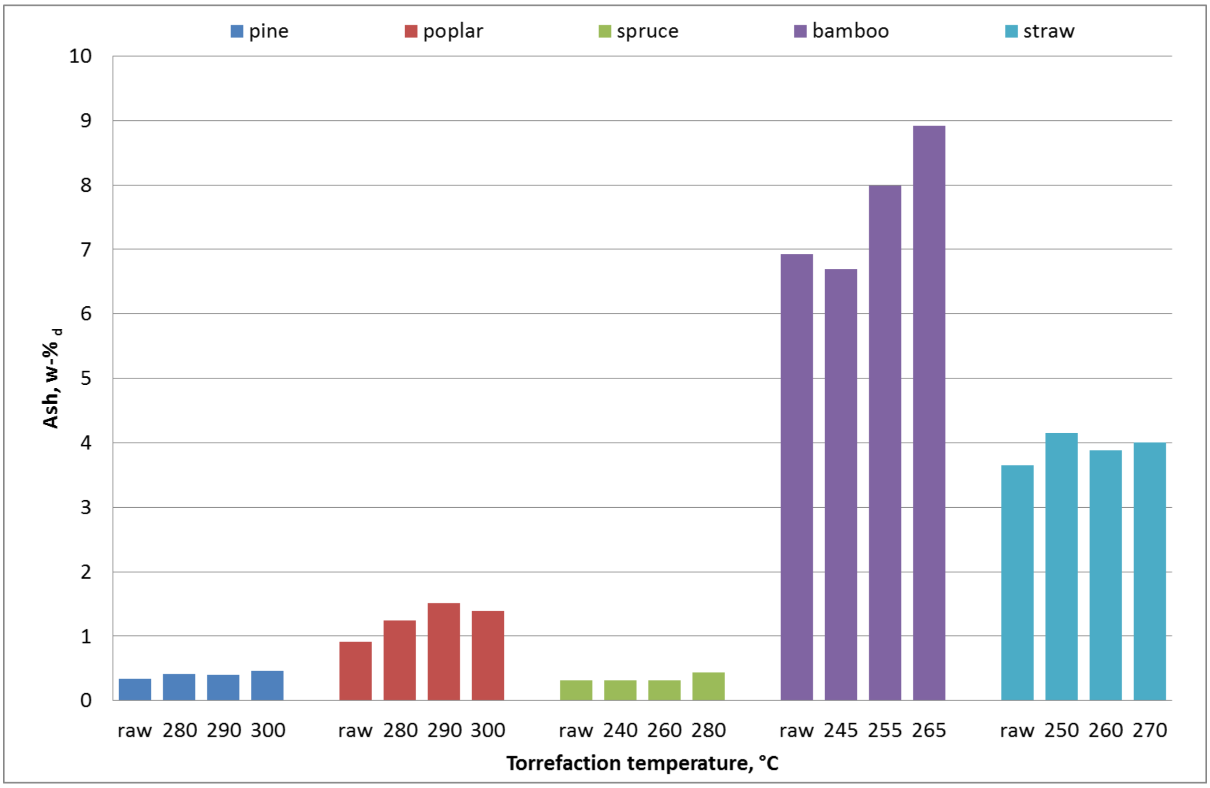

Figure 51: Ash content of samples pine, poplar, spruce bamboo and straw at different torrefaction temperatures (240°C-300°C) and the raw material

3.2.5 Chlorine content and sulphur content

Chlorine and sulphur content are important parameters to be considered in regard of emissions and corrosive effects during the combustion or other thermal conversion methods.

The selected samples do not recognizing any trend or correlation between different torrefaction temperatures and changes in concentration of either chlorine or sulphur (Figure 52 and Figure 53). Some biomass types show an increased content of chlorine and sulphur whereas other types show a decreased content.

The samples in this selection show ambiguous results. The poplar and pine samples show a decrease of sulphur and chlorine content compared to the raw material. In comparison spruce shows an increase of the sulphur and chlorine content. The torrefied straw sample has a higher sulphur and chlorine content compared to the raw material but the amount decreases with increasing torrefaction temperature.

Without further research in the future a clear statement cannot be made. The deviation in the results could be explained by the difference between the original (raw) biomass as well as the sample taking. Another reason could be sample aging because the analysis could not be conducted promptly due to the amount of samples and distribution time.

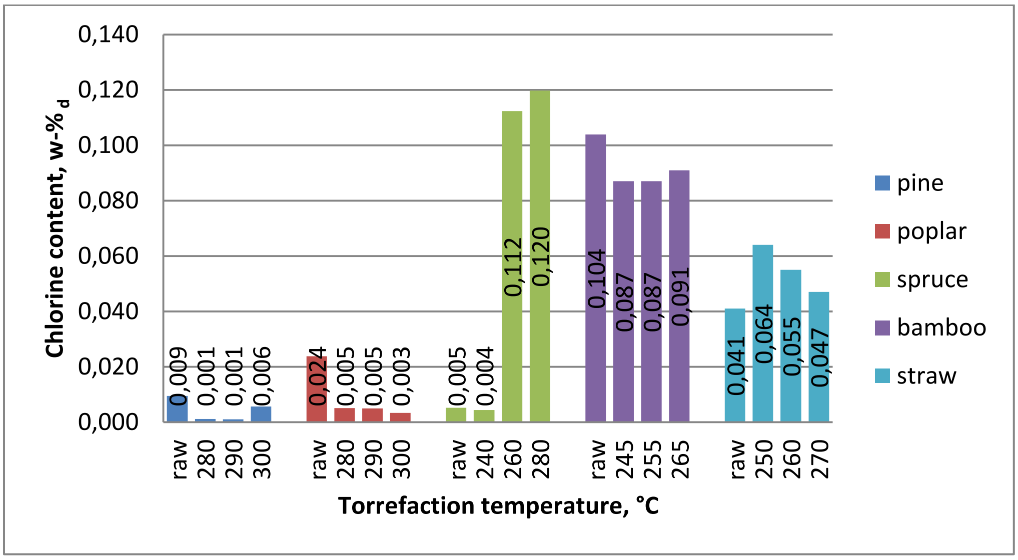

Figure 52: Chlorine content of samples pine, poplar, spruce bamboo and straw at different torrefaction temperatures (240°C-300°C) and the raw material

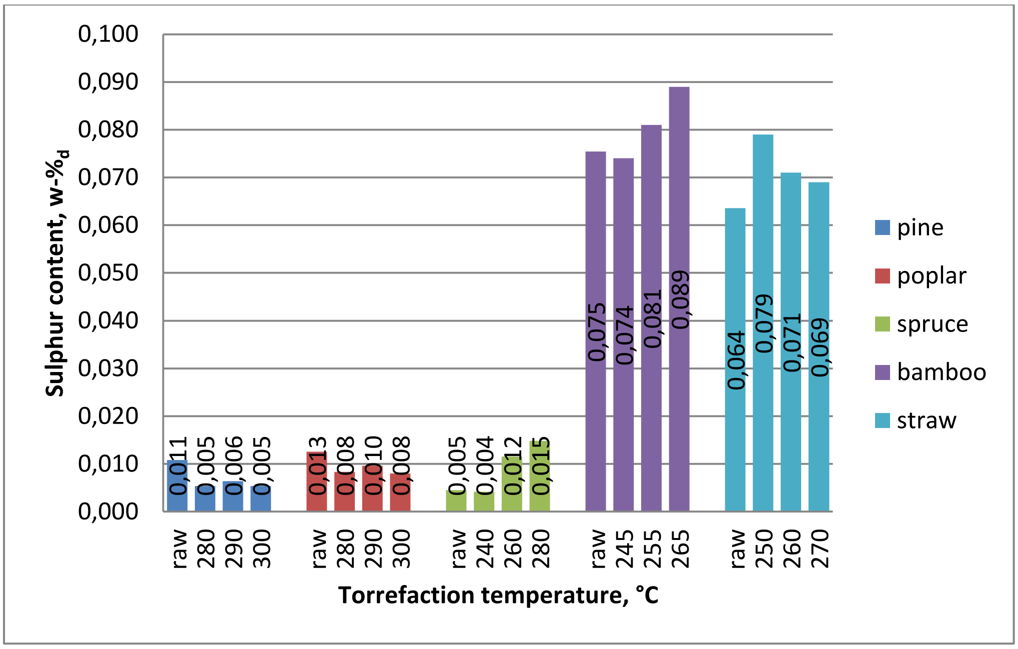

Figure 53: Sulphur content of samples pine, poplar, spruce bamboo and straw at different torrefaction temperatures (240°C-300°C) and the raw material

3.2.6 Ash melting behaviour

A second group of samples were selected for determination of the influence of torrefaction on ash melting behaviour. The criteria for this selection were based on comparable torrefaction methods (same producer), the type of biomass, the torrefaction temperature and the amount of material still available after base characterization.

The selected samples were all tested for ash melting behaviour (Table 9). Hemispherical- and spherical-temperature were not considered, because they did not occur at the majority of the selected biomass types.

Differences in the ash melting behaviour (especially for the deformation temperature) could be detected between raw and torrefied materials. However it is not possible to give a definite statement about the influence of torrefaction on the ash melting behaviour. The changes differ between an increase and a decrease and the amount varies widely. Also the DIN standard for ash melting behaviour (DIN 51730) states a repeatability of 30K, whereby the CEN/TS standard (CEN/TS 15370-1) give no repeatability limits at the moment. This has to be considered when the results are analysed. Therefore further testing is required to determine an influence. The highest change in deformation temperature (110° C) shows the straw samples independent of torrefaction temperature. Interestingly the flow temperature is only affected by the pine sample. The torrefied pine samples show a lower flow temperature of 50 °C.

Table 9: Ash melting behavior of different torrefied samples and corresponding raw material

Sector Sample ID	Material	Torrefaction temperature °C	Deformation temperature °C	Flow temperature °C
CENER_straw-_white chips_NA	Straw	-	980	1160
CENER_straw-250_torrefied-chips_140213	Straw	250	870	1150
CENER_straw-270_torrefied chips_260613	Straw	270	870	1160
CENER_poplar-_white chips_NA	Poplar	-	1210	1500
CENER_poplar-280_torrefied chips_290513	Poplar	280	1260	1500
CENER_poplar-300_torrefied chips_280513	Poplar	300	1220	1480
CENER_pine-_white chips_NA	Pine	-	1380	>1500
CENER_pine-280_torrefied chips_021012	Pine	280	1360	1450
CENER_pine-300_torrefied chips_221112	Pine	300	1360	1450
UmU_willow-_white chips_300513	Willow	-	1400	>1500
UmU_willow-286; 6 min_torrefied chips_300513	Willow	286	1340	>1500
UmU_willow-330; 6 min_torrefied chips_300513	Willow	330	1420	>1500
CENER_beech-_white chips_NA	Beech	-	1330	1500
CENER_beech-270_torrefied chips_120912	Beech	270	1340	1490

3.2.7 Mechanical Durability

There are only a limited number of pellets produced from samples within the SECTOR-project and no pellets are made from the original, raw sample of biomass. Because of this, it is not possible to compare the mechanical durability and determine the influence of torrefaction, but it is possible to compare the results with current certification criteria for untorrefied wood pellets (e.g. EN ISO 17225-2, for A1 DU ≥ 97.5 %).

By comparing the data acquired during the SECTOR-project, a huge difference between the pellet-samples in mechanical durability is recognizable (Table 10). The values range between 80.6 % and 97.7 %. While the high mechanical durability is comparable with pellets made from untreated biomass, the samples with low mechanical durability of just above 80 % are significantly below the limit-values which exist for untorrefied wood-pellets.

There is no evidence recognizable, that specific types of biomass or torrefaction parameter lead to the production of pellets with higher or lower mechanical durability. Therefore it is assumed that the main influence for an improvement of mechanical durability is the pelletizing technology.

Table 10: Mechanical Durability of different torrefied pellets with corresponding moisture content

SECTOR sample ID	Moisture content w-%, $_{ar}$	Mechanical Durability %
CENER_straw-260_torrefied pellets_	9.0	92.0
CENER_straw-270_torrefied pellets_	10.5	97.9
UmU_forest residue-308_torrefied pellets_190613	5.9	86.5
CENER_beech-270_torrefied pellets_170912	13.4	95.7
ECN_poplar-270_torrefied pellets_060513	3.4	97.9
CENER_poplar-290_torrefied pellets_100713	7.1	94.2
CENER_poplar-300_torrefied pellets_090713	6.7	92.7
ECN_pine-270_torrefied pellets_060513	4.7	80.6
UmU_pine-285_torrefied pellets_150913	2.8	83.9
CENER_pine-290_torrefied pellets_060613	6.9	89.1
CENER_pine-300_torrefied pellets_310113	5.9	90.6
UmU_willow-308_torrefied pellets_190613	9.6	83.9
ECN_spruce-260_torrefied pellets_180113	1.7	97.2

3.3 Influence of varying torrefaction time and temperature

If the changes in chemical properties of raw and torrefied biomass are compared regarding differences in torrefaction temperature and time, it shows that an increase of the temperature has a greater influence than an alteration of the process time.

The changes in chemical properties (increased calorific value, increased carbon content, removed volatile matter, etc.) are more intense at the samples with a higher torrefaction temperature, even if the torrefaction time is less. Based on the small amount of available samples with varying torrefaction time, it is not possible to give a more profound statement of the relation between process time and temperature in regard of the progress of the torrefaction process. The most significant properties of the samples with altering torrefaction time are shown in the Table 11. There is one discrepancy at the anhydrous weight loss for the samples of pine. The sample torrefied at 286°C for 12 minutes should have a higher anhydrous weight loss (=degree of torrefaction) then the sample torrefied at the same temperature for 6 minutes. All properties that were determined in the laboratory show the trend that is expected for samples with a longer torrefaction time at the same temperature.

Table 11: Samples with different torrefaction times and torrefaction temperatures

SECTOR sample ID number	Torrefaction temperature	Torrefaction time	Anhydrous weight loss %	Net calorific value MJ/kg$_d$	Volatile Matter w-%$_d$
UmU_forest residue-286; 6min_torrefied chips_180613	286°C	6 min	12.6	20.9	73.3
UmU_forest residue-286; 12min_torrefied chips_170613	286°C	12 min	13.3	21.8	70.2
UmU_forest residue-308. 9min_torrefied chips_120613	308°C	9 min	19.3	22.1	68.4
UmU_forest residue-330; 6min_torrefied chips_180613	330°C	6 min	28.5	22.7	66.2
UmU_forest residue-330; 12min_torrefied chips_170613	330°C	12 min	29.7	23.7	62.1
UmU_willow-286; 6min_torrefied chips_300513	286°C	6 min	6.6	19.4	79.4
UmU_willow-286; 12min_torrefied chips_310513	286°C	12 min	11.1	19.4	78.3
UmU_willow-308. 9min_torrefied chips_030613	308°C	9 min	17	20.3	76.7
UmU_willow-330; 6min_torrefied chips_300513	330°C	6 min	24.8	21.0	73.3
UmU_willow-330; 12min_torrefied chips_310513	330°C	12 min	34.8	22.9	64.3
UmU_pine-286; 6 min_torrefied chips_	286°C	6 min	12.2	20.1	81.7
UmU_pine-286; 12min_torrefied chips_	286°C	12 min	11.9	20.4	81.2
UmU_pine-330; 6 min_torrefied chips_	330°C	6 min	19.2	21.2	77.9
UmU_pine-330; 12min_torrefied chips_	330°C	12 min	26.7	22.0	73.5

3.4 Freezing behaviour

In cooperation with WP6 some small scaled test about the storage behaviour of torrefied pellets were developed and realised. A report about leaching tests and a storage test has been published in D6.3 “Final report on pellet characteristics after renewed tests with optimised torrefied materials”. Furthermore the effect of freezing was analysed. Therefore torrefied pellets were frozen under different conditions and afterwards the mechanical durability (according to EN 15210) was measured. These tests were conducted in combination with water absorption tests to analyse the loss of mechanical durability.

3.4.1 Method

For the tests six different torrefied pellets samples and one conventional “white wood” pellets sample were used. In the following table (Table 12) the samples are listed.

Table 12: Used samples for the freezing behaviour tests

Sample ID	SECTOR No.	SECTOR sample ID number / description	Provider
406775-7	3018	CENER_pine-300_torrefied pellets_310113	CENER
406775-10	2030	UmU_willow-308_torrefied pellets_190613	UmU
406775-67	2028	UmU_pine-285_torrefied pellets_150913	UmU
406775-68	4027	Topell_wood residues-_torrefied pellets_	Topell
406775-81	3042	CENER_straw-270_torrefied pellets_	CENER
406775-82	3043	CENER_straw-260_torrefied pellets_	CENER
411828	-	conventional wood pellets	-

These samples were tested under different freezing conditions. However all samples were stored at least 48 hours in a chest freezer to guarantee completely frozen samples. After freezing, the pellets were stored at ambient atmosphere in order to defrost for at least 24 hours. After the defrosting the mechanical durability was tested. The pellets were frozen under three different conditions:

1) dry frozen – D_u-1

The pellets were not prepared before freezing. The sample was frozen with the humidity absorbed during storage. After the defrosting the mechanical durability was tested.

2) wet frozen – D_u-2

First an immersion test (see method description water absorption), was done. After the dripping time the pellets were frozen. The mechanical durability was measured after defrosting with the wet pellets.

3) wet frozen with drying – D_u-3

The pellets were treated as described in point 2. After the defrosting, the pellets were dried to constant mass (max. 24 hours) at 105°C. The dried pellets are left at ambient atmosphere in order to stabilize for at least 24 hours. Afterwards the mechanical durability was tested.

3.4.2 Results

Additionally to the durability tests, also the moisture content of the pellets before the mechanical durability test was measured (Table 13).

Table 13: Moisture content of the torrefied pellets before mechanical durability tests

Sample ID	w-%-original	w-%-2	w-%-3
406775-7	5.6	38.7	3.6
406775-10	9.4	36.8	3.6
406775-67	2.7	27.6	3.9
406775-68	10.4	31.5	4.3
406775-81	9.7	39.6	5.0
406775-82	8.3	-	-
411828	6.4	-	-

w-%-original............................	original moisture content of the sample
w-%-2	moisture content of the sample in test 2 after defrosting and before mechanical durability test
w-%-3	moisture content after drying and before mechanical durability test in test condition 3

The following graph (Figure 54) shows all measured mechanical durabilities for the three different conditions and the original mechanical durability:

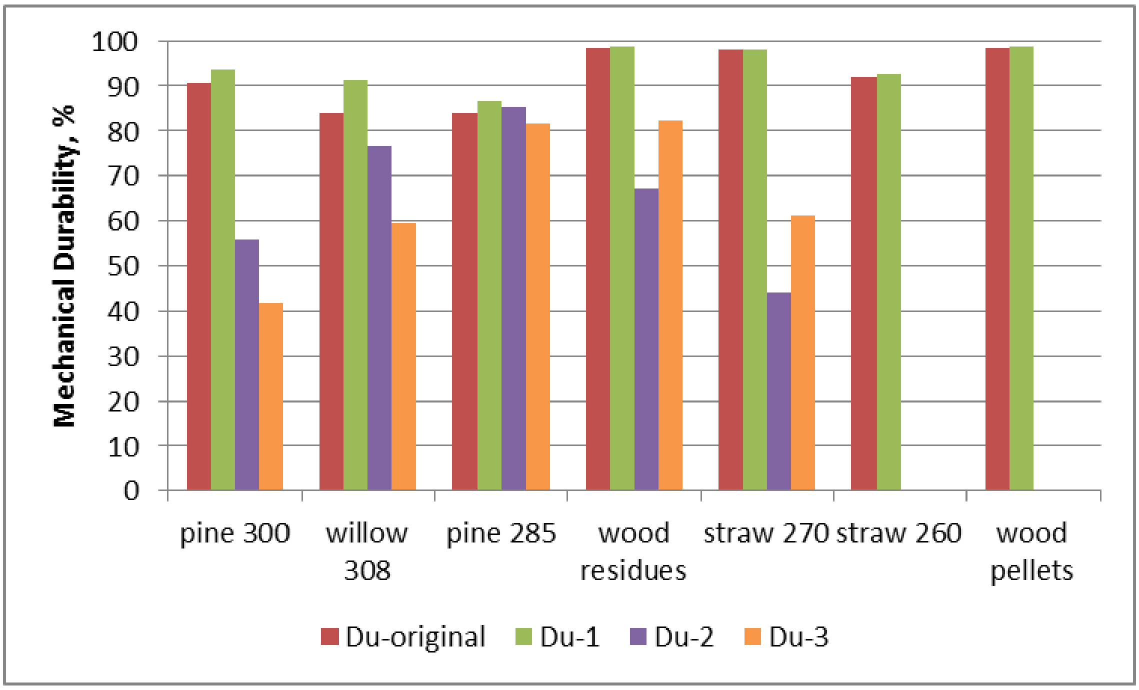

Figure 54: Results of the durability tests after freezing (Du-1 no preparation before freezing; Du-2 water absorption test before freezing; Du-3 water absorption test before freezing and drying before mechanical durability)

It is clearly recognizable that the mechanical durability of dry frozen pellets does not decrease. On the contrary, the durability after freezing is in all cases higher as the original durability. As known from the water absorption test (immersion tests), the mechanical durability decreases after immersion in water. As expected also the mechanical durability in test 2 also decrease. In this case the durability test was made with wet pellets. This approach influences the results of the durability test. The results are in some cases better than they really are: because of the high moisture content the fine dust sticks to the pellet and therefore adulterates the result of the mechanical durability tests. Test 3 (water absorption and drying before mechanical durability) results in a higher mechanical durability as test 2 (except for sample pine 285° C) but shows also a lower mechanical durability compared to the raw material and test 1 samples.

Figure 55 shows the mechanical durability from the samples after a "water absorption test" (method description: water absorption) and the mechanical durability from test condition three. This is a water absorption test with freezing after the immersion and drying before mechanical durability tests.

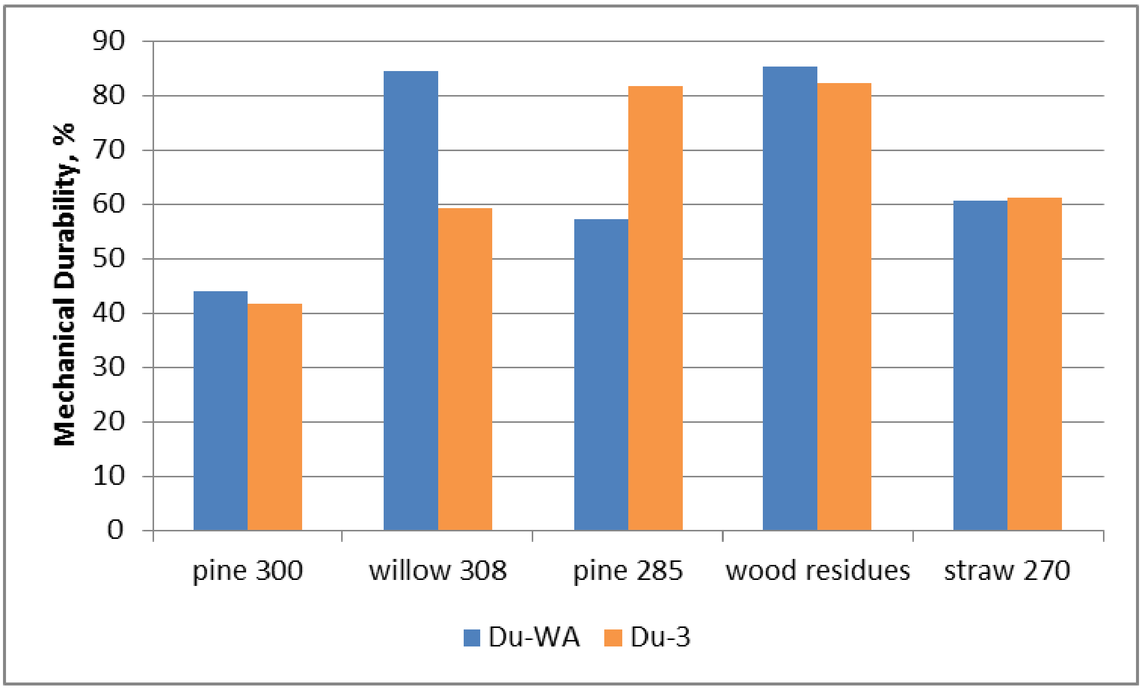

Figure 55: Comparison between conventional water absorption (Du-WA) and water absorption with freezing test (Du-3)

It is assumed that the freezing decrease the durability more than a single immersion in water. During the freezing, the water extends and breaks the structure of the pellet. However with the present findings this assumption cannot be confirmed.

3.5 Summary & Conclusion

For a better description of torrefied material the chemical parameters and behaviour is essential. In Round Robin I it was shown that the standards for biomass are applicable for torrefied materials. Therefore samples produced within the SECTOR project were analysed according to standard and then compared.

The most notable result is the increase in calorific value which is highly important for the increase of the energy density. This increase can be mainly explained by the increase carbon content with increasing torrefaction temperature. The correspondence of calorific value and carbon content is linear.

Due to torrefaction process the volatile matter is decreasing with increasing torrefaction temperature. This statement is valid for all samples but the amount of change differs from sample to sample. Bamboo shows the highest reduction of volatile matter whereas straw shows a small change in volatile matter.

Another important parameter for possible applications is the ash content which is increasing on a low level. Also the ash melting behaviour was evaluated and only minor influences concerning the deformation temperature and flow temperature is notable. Of the nine torrefied biomass samples four showed a change in the deformation temperature, but with no trend and two out of nine samples showed change in flow temperature compared to the raw material.

For emission crucial parameters chlorine and sulphur show no trend or correlation concerning the sample type or torrefaction temperature. Some torrefied biomass samples (pine and poplar) showed a lower level of sulphur and chlorine, whereas other samples (e.g. spruce) showed the opposite behaviour. Hence, a bigger data set should be investigated due to the importance of these parameters in thermochemical conversion processes.

Concerning the mechanical durability of pellets from torrefied material the results a widely spread. Out of 13 considered samples only two reach the criteria A1 according to EN ISO 17225-2. The main influence of the parameter mechanical durability is the pelletisation process.

Different process parameters like torrefaction temperature and torrefaction time have an influence on the parameters. But a comparison of time and temperature in the torrefaction process showed that the influence of temperature is higher than of torrefaction time.

Another parameter evaluated was the freezing behaviour because the storage type for torrefied material is still evaluated. In some European countries freezing temperatures are normal in winter therefore the freezing behaviour and the link with the mechanical durability and water absorption was investigated. As a result could be mentioned the pellets frozen with no further pre or post treatment show a slightly higher mechanical durability compared to the original mechanical durability. Torrefied pellets frozen after water absorption result in loss of mechanical durability compared to the original mechanical durability.

This comparison and evaluation of different biomass properties and analysis give an insight on the sample torrefied biomass. This information has high value for producers and end-users for an improvement of the production as well as for the decision for the type of end use. Also ongoing evaluation of the results gained from analysis and its standards is essential for improvement of torrefied material. Further research concerning the dependency of the single biomass analysis parameters should be persued.

3.6 References

EN 15210-1 2010-02: Solid biofuels - Determination of mechanical durability of pellets and briquettes - Part 1: Pellets

EN 14774-2 2009-12: Solid biofuels. Determination of moisture content. Oven dry method. Total moisture. Simplified method

EN 14775 2012-11: Solid biofuels - Determination of ash content

EN 15148: 2009 12: Solid biofuels - Determination of the content of volatile matter

EN 15104: 2011 04: Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods

EN 14918: 2010 02: Solid biofuels - Determination of calorific value

EN 15289: 2011 04: Solid biofuels - Determination of total content of sulfur and chlorine

CEN/TS 15370-1 2006 12: Solid biofuels - Method for the determination of ash melting behaviour - Part 1: Characteristic temperatures method

DIN 51730 2007-09: Testing of solid fuels - Determination of fusibility of fuel ash

EN ISO 16993 2013-03: Solid biofuels - Conversion of analytical results from one basis to another

EN ISO 17225-2 2014-09: Solid biofuels - Fuel specifications and classes - Part 2: Graded wood pellets

D6.3 “Final report on pellet characteristics after renewed tests with optimised torrefied materials”

4 Annex

4.1 Annex A

Size classification by image analysis – Calibration of the instrument

Draft standard method for discussion in ISO 238 WG4

Elaborated by:

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Developed within SECTOR Project (WP 8)

1 Introduction

Instruments for determination of size and shape criteria by image analysis are continuously being developed and several technical solutions are applied. Therefore it is not possible to create a standard for the functioning of a measuring device or for applicable principle itself. But it is rather the aim of this standard to define a procedure for testing and calibrating the instrument in order to evaluate the reliability of the created results as relevant for biofuels.

Additionally, there can be a wide scope of output parameters as provided by an image analysis device (e.g.: Feret-diameter, Maximum Length, Martin Diameter, Maximum Chord, Particle Shape Factor, Sphericity, Roughness, etc.). But it is not the aim of this standard to suggest meaningful size parameters for the characterisation of biomass fuels. Instead of that, a selection of simple key parameters is made in order to identify whether the image analysis instrument is able to determine certain particle dimensions at a sufficient accuracy.

2 Scope

This document specifies a method for the testing of measuring instruments which provide data concerning dimensions of all particles in a given biomass fuel sample. It is applied for instruments which can at least determine the Minimum Feret-diameter, the Maximum Length and the Standard Length. The definitions of these dimensions are given in Clause 3.

This standard applies for instruments which are constructed in such way, that the particles of a sample are first singularized and then horizontally transported towards the camera which provides the optical data for calculating the necessary dimensions from the achieved two-dimensional silhouettes of the separated particles. The instruments are assumed to be sensitive towards the particle’s traveling speed when passing the visual field of the camera.

An example of such a device is presented in Figure 1.

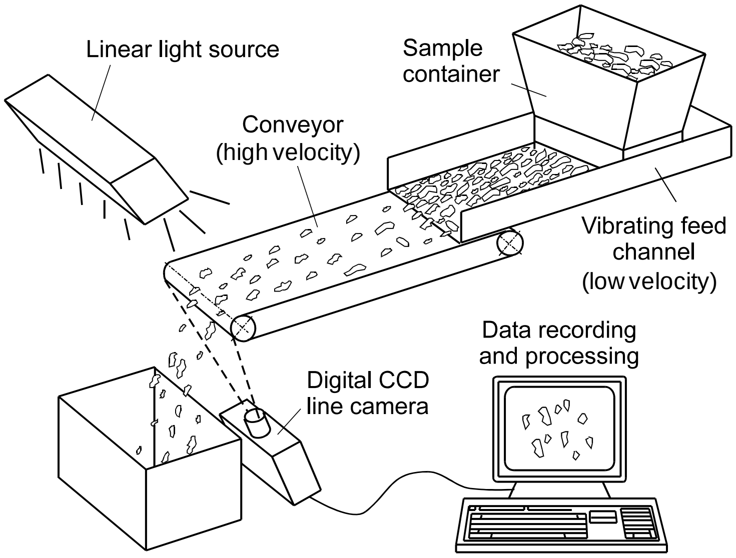


Figure 1 Example of a functional design of a continuously operating image analysis device

3 Terms and definitions

The major particle dimensions which are typically determined by image analysis are presented in Figure 1. For the calibration procedure as presented in this standard the following dimensions are relevant.

- Minimum Feret-diameter (see No. 6 in Figure 2)
- Maximum Length (see No. 4 in Figure 2)
- Standard Length (see No. 7 in Figure 2), it is defined as the longest dimension which is perpendicular to the minimum Feret-diameter

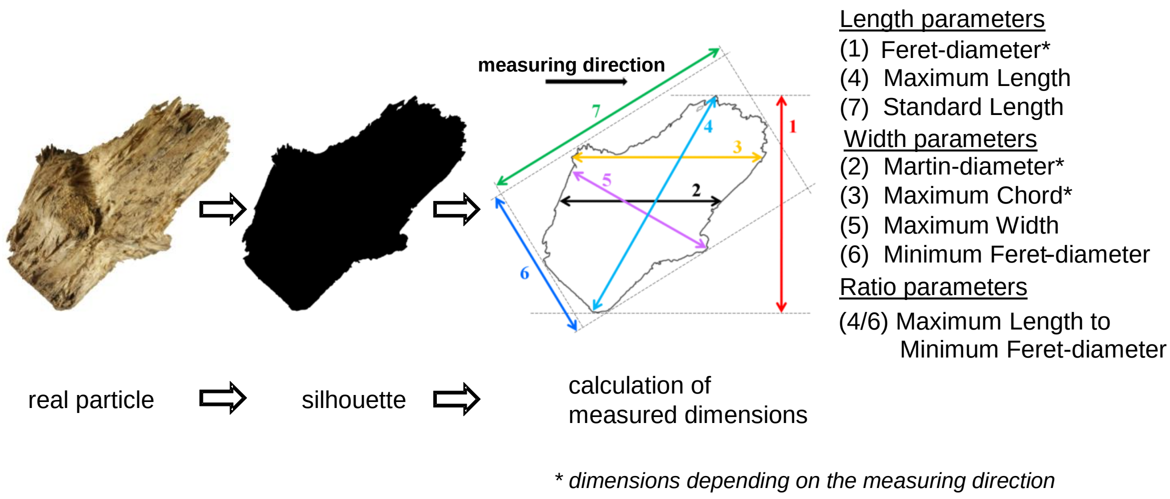


Figure 2 Transformation of a particle's image into a silhouette and calculation of typical dimensions as performed by image analysis devices

4 Principle

Reference sample material (test pieces) with defined dimensions are used for test runs with the regarded image analysis device. The test piece dimensions as measured by the applied instrument and the results are compared to the given dimensions as previously determined by hand measurement using a calliper.

5 Apparatus and materials

5.1 Calliper or micrometer gauge

A calliper or a micrometer gauge with an accuracy of 0,05 mm is required.

5.2 Reference sample material

5.2.1 Test piece properties and dimensions

The reference sample material shall consist of several groups of homogeneously shaped steel plates with uniform dimensions. These test pieces shall be produced from of stainless steel.

Note: The use of stainless steel is required because the material must be hard and highly resistant towards wear and abrasion and shall remain in shape within the range of usual conditions of application (temperature, humidity, radiation). Corrosion shall in any case be avoided.

The shape of the test pieces are cuboid but very flat, thus approaching an almost two-dimensional shape. The cuboids shall be sharp edged.

The reference sample material consists of 11 classes of test pieces. Each class consists of 10 uniform pieces (see Table 1). The maximum thickness of each piece is 1 mm.

Table 14 Nominal dimensions of test pieces used as reference sample material

Test piece class No.	Length (mm)	Width (mm)	Height (mm)
1	5	5	≤ 1
2	10	5	≤ 1
3	20	5	≤ 1
4	60	5	≤ 1
5	10	10	≤ 1
6	25	10	≤ 1
7	40	10	≤ 1
8	80	10	≤ 1
9	30	30	≤ 1
10	70	30	≤ 1
11	120	30	≤ 1

Measure all three dimensions of each test piece (length $\overrightarrow{AE}$, width $\overrightarrow{AB}$ and height $\overrightarrow{AC}$ as shown in Figure 3) by hand measurement using the calliper or micrometer gauge as described in Clause 5.1. From these results calculate the relative coefficient of variation (CV in %) for each test piece class.

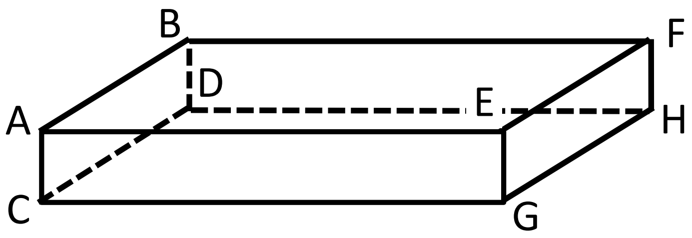


Figure *3* Basic schematic design of a test piece

The maximum relative coefficient of variation (CV) shall be:

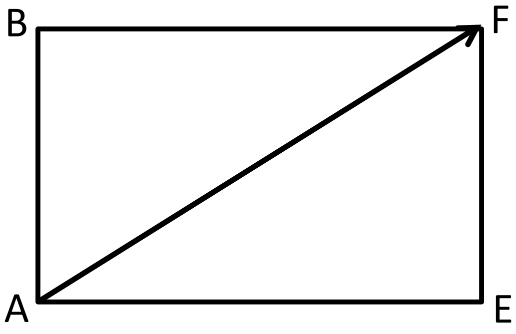
length: 0.5 %

width: 0.5 %

height: 2.0 %

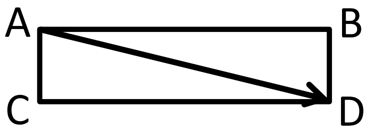
5.2.2 Determination and calculation of the diagonals of test pieces

The determination of the diagonals of all reference test sample pieces is performed by calculation using the measurement of the three edges of each cuboid piece (length $\overrightarrow{AE}$, width $\overrightarrow{AB}$ and height $\overrightarrow{AC}$) as determined in Clause 5.2.1. From these measurements the face diagonal $\overrightarrow{AF}$, the two side diagonal $\overrightarrow{AD}$ and $\overrightarrow{AG}$ and the space diagonal $\overrightarrow{AH}$ are calculated as described in Figures 4, 5, 6 and 7.



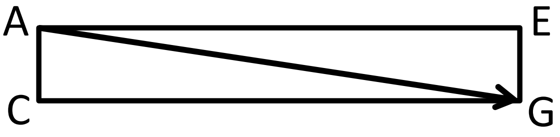
$$\overrightarrow{AF} = \sqrt{\left(\overrightarrow{AB}\right)^2 + \left(\overrightarrow{BF}\right)^2}$$

Figure 4 Calculation of the face diagonal $\overrightarrow{\mathbf{AF}}$



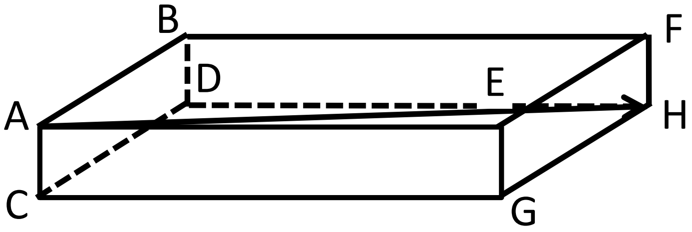
$$\overrightarrow{AD} = \sqrt{\left(\overrightarrow{AB}\right)^2 + (BD)^2}$$

Figure 5 Calculation of the side diagonal $\overrightarrow{AD}$



$$\overrightarrow{AG} = \sqrt{\left(\overrightarrow{AE}\right)^2 + \left(\overrightarrow{EG}\right)^2}$$

Figure 6 Calculation of the side diagonal $\overrightarrow{AG}$



$$\overrightarrow{\boldsymbol{AH}} = \sqrt{\left(\overrightarrow{\boldsymbol{AC}}\right)^2 + \left(\overrightarrow{\boldsymbol{CG}}\right)^2 + \left(\overrightarrow{\boldsymbol{GH}}\right)^2}$$

Figure 7 Calculation of the space diagonal $\overrightarrow{AH}$

From the results for each diagonal calculate the mean value of each of the four determined diagonals $\overrightarrow{AF}$, $\overrightarrow{AD}$, $\overrightarrow{AG}$ and $\overrightarrow{AH}$ for each of the 11 test piece classes. These results are used as reference values for the calibrations performed with the tested apparatus.

6 Procedure of instrumental test runs

The prepared standard sample pieces are applied for test runs with the regarded image analysis device. This is done in such way, that all test piece classes (of which each class consists of 10 test pieces) are processed in separate test runs. Repeat the first run for each class 9 times to gain a total of 10 measurements per class. Process all 11 test piece classes in the same way.

Note: Before performing the calibration tests it can be useful to test and adjust the traveling speed following the procedure in Annex A in order to achieve better test results.

Record the measured results for the Minimum Feret-diameter, the Maximum Length and the Standard Length after each replication separately for each test piece class.

7 Calculation

From the image analysis test runs in Clause 6 calculate the mean values for each test piece class of

- the Minimum Feret-diameter,
- the Maximum Length and
- the Standard Length.

8 Instrumental requirements for image analysis devices

8.1 Accuracy

Depending on the orientation of the test pieces towards the measuring plane of the image analysis device the smallest and the largest possible dimension of the three regarded sizes are variable.

In the case of the Minimum Feret-diameter any result which is equal to or between the distances $\overrightarrow{AB}$ (i.e. smallest possible size) and $\overrightarrow{AD}$ (i.e. the largest possible minimum Feret-diameter) would be 100 % conform with the reference values of the sample.

In the case of the Maximum Length any result which is equal to or between the distances $\overrightarrow{AF}$ (i.e. smallest possible size) and $\overrightarrow{AH}$ (i.e. largest possible size) would be 100 % conform with the reference values of the sample.

In the case of the Standard Length any result which is equal to or between the distances $\overrightarrow{AE}$ (i.e. smallest possible size) and $\overrightarrow{AG}$ (i.e. largest possible size) would be 100 % conform with the reference values of the sample.

The readings for the three regarded mean particle dimensions from the image analysis shall not deviate more than 3 % from the reference dimensions as described above. Calculate the tolerable 3 % deviation from the reference material's dimension to achieve the lower and upper boundary values (see columns B and D in Table 2). This calculation is made for each of the 11 test piece classes and for each of the three target parameters. All values measured with the tested image analysis device (see column C in Table 2) shall be between the determined lower and upper boundary values.

Note: The boundary values are derived from the hand measured and calculated dimensions as described in Clause 5.2. Under usual application conditions their determination is required only once and the reference data achieved for the sample material remains valid for several test further on.

4.2 Annex B

Solid biofuels - Method for the determination of bridging properties

This draft is mainly an outcome of the project Bionorm2, elaborated by TFZ Straubing, to be presented and discussed in WG4 of CEN TC 335. It was modified in 2013 to include the method specifications derived from the trials within the ongoing SECTOR project.

Responsible author: Hans Hartmann, TFZ

Introduction

This document is a working document

Bridging is the phenomenon where particles form a stable arch above an opening. All particles regardless of the size could potentially form an arch and in the case of biofuels this is in particular a problem in the internal transport systems of heating plants and infeed mechanism in the boilers.

Several parameters influence the bridging tendency. Fuel related parameters include e.g. mean particle size, proportion of long particles and moisture content. Handling related parameters include e.g. friction against surfaces and angle of repose. Bridging as measured with the method described in this Technical Specification is thus a relative measure of the particular measured sample’s tendency to form a bridge in the described apparatus. The method can be used for comparisons between fuels, e.g. between fuels already in use in a heat plant and new fuels considered to be used.

1 Scope

This draft standard describes a method of determining the bridging properties of particulate biofuels.

The method is applicable to all particulate biofuels that either have been reduced in size (such as most wood fuels or cut straw) or which are physically in a particulate form (such as olive stones, nut shells, grain etc).

Note Bridging is not an absolute value, therefore the result of a test of the bridging properties of a fuel is only a measure of that particular fuel. Parameters such as the particle size and shape, the number of overlong particles, the sample moisture content are decisive for the bridging properties; therefore it may be useful to determine these parameters parallel.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication applies (including amendments).

CEN/TS 14588:2003, Solid biofuels – Terminology, definitions and descriptions

CEN/TS 14778-1, Solid biofuels – Sampling – Part 1: Methods for sampling

CEN/TS 14778-2, Solid biofuels – Sampling – Part 2: Method for sampling particulate material transported in lorries

CEN/TS 14779, Solid biofuels – Sampling – Method for preparing sampling plans and sampling certificates

CEN/TS 15149-1, Solid biofuels – Methods for the determination of particle size distribution. Part 1: Oscillating screen method using sieve apertures of 3,15 mm and above

CEN/TS 15149-3, Solid biofuels – Methods for the determination of particle size distribution. Part 3: Rotary screen method

CEN/TS 14774-1:2004, Solid biofuels – Determination of moisture content – Oven dry method, Part 1: Total moisture – Reference method

CEN/TS14774-2:2004, Solid biofuels – Determination of moisture content – Oven dry method, Part 2: Total moisture – Simplified procedure

3 Terms and definitions

For the purpose of this European Standard, the terms and definitions given in CEN/TS 14588:2003 shall apply.

Bridging is the phenomenon where loose particles form a stable arch across an opening.

4 Principle

A sample is subjected to bridging by placing it over an expandable slot opening facilitating the building of a bridge. The opening width of the slot is taken as a measure for the bridge building properties of the sample.

Note Bridging cannot be determined with methods based on shear strength tests, as most solid biofuels are elastic.

5 Apparatus

5.1 Bridging apparatus

For the test a box with a bottom area of 1,1 × 2,0 m (± 0,01 m) and a minimum height of 0,75 m (± 0,01 m) shall be used. The sides of the box shall be made of oriented strand board (OSB); the bottom shall be made of two flexible mats with rubber surfaces.

An expandable slot divides the middle of the box’s bottom. The slot is formed by round edges. These round edges form a quarter of a circular arc with an effective radius of 125 mm. When the bottom is fully closed, the two mats meet in the centre of the box' length without forming any slot. The mats shall be fully even and horizontal to the ground, except at the round edges (see Figure 1). The slot shall be capable of being gradually expanded while the edges are parallel and the bottom is prevented from becoming inclined during any phase of the opening procedure. The expansion shall be executed in a way, which ensures, that the mats remain in place, except at the rounded edges, where they are sliding over a plate which forms the rounded edges (Figure 1). Alternatively they could also be rolled onto a pair of rollers.

Note 1 This design avoids that any friction between the bottom and the fuel sample in the box can occur when the slot is being expanded.

Note 2 If a pair of rollers is used the effective radius is variable. An excess of the given tolerance shall then be avoided by the choice of a mat with a suitably low thickness.

The opening movements of the two bottom halves shall be synchronic, thus ensuring that the slot is widening without changing its position. The maximum opening width shall be 1,5 m. The edges of the slot shall remain parallel during the opening procedure, a tolerance of 10 mm is acceptable. This is measured as the difference of the opening widths at both ends of the slot and it applies for the full range of the slot opening.

The opening speed shall be 180 mm /minute (± 50 mm/minute).

The container shall be positioned firmly at a height, which ensures that all sample material can freely fall through the slot without causing any blockages (e.g. 1,5 m height of container bottom).

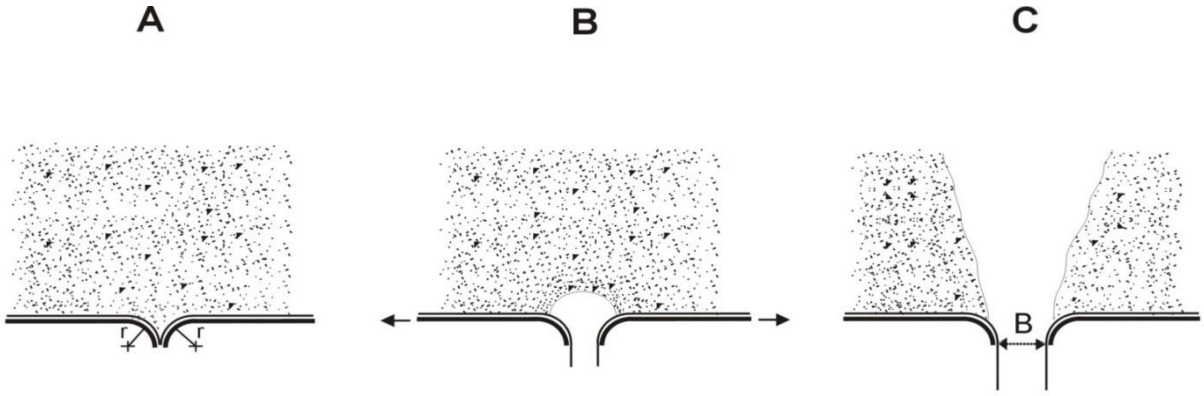


Figure 1: Operation principle of the bridging tester

5.2 Metric rule

A metric rule capable to measure the opening width between the rollers to the nearest centimetre.

5.3 Shovel

A shovel to level out the sample

6 Sample preparation

The minimum volume of the test portion shall be 1,5 cubic meter loose volume and shall be sampled according to prCEN/TS 14778-1, prCEN/TS 14778-2 and prCEN/TS 14779.

7 Procedure

Fill the container by pouring the sample material from a height of maximum 500 mm above the rim of the container without applying any compaction to the sample. Level out the surface so that the sample is evenly spread in the container.

Note Loading of the sample could be performed e.g. using a wheel loader.

Generate a slot opening under the sample by starting the slot opening procedure. The sample material will form a bridge, which overstretches the slot.

Note: Fine and pourable fuel samples such as pellets or kernels may require some time to percolate through the slot opening. The opening of the slot can be continued, if it is certain, that a stable bridge will be built-up.

As soon as the bridge collapses, the slot opening motion shall be stopped and the slot width shall be measured at both sides of the container and reported as average to the nearest centimetre. The reading is conducted at the minimum horizontal distance between the slot edges as indicated in Figure 1 by the letter "B"**.**

Unify the remaining sample with the sample material, which has fallen through the slot by emptying the container completely.

Reload the container with the unified sample and repeat the procedure until 10 repetitions is performed.

8 Calculation

The relative bridging property shall be calculated as the arithmetic mean and standard deviation of the 10 replications.

9 Precision and bias

Because of the varying nature of solid biofuels covered by this Technical Specification it is not possible at this time to give a precision statement (repeatability or reproducibility) for this test method.

10 Test reporting

The test report shall include at least the following information:

- Identification of the laboratory and the testing date.
- Identification of the product or sample tested.
- A reference to this working document.
- Any deviation from the working document.
- Conditions and observations, e.g. unusual occurrences during the test procedure, which may affect the result
- The test results, i.e. arithmetic mean and standard deviation

Bibliography

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Jensen, P.D., Mattsson, J.E., Kofman, P.D. and Klausner, A.: Tendency of wood fuels from whole trees, logging residues and roundwood to bridge over openings. Biomass and Bioenergy 26 (2004) 107 – 113

Mattsson J.E.: Tendency to bridge over openings for chopped Phalaris and straw of Triticum mixed in different proportions with wood chips. Biomass and Bioenergy 12 (1997) 199–210.

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4.3 Annex C

Determination of the angle of repose of bulk material

Draft standard method for discussion in ISO 238 WG4

Elaborated by:

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Technology and Support Centre of Renewable Raw Materials (TFZ), Straubing, Germany

Developed within SECTOR Project (WP 8), based on Technical specification FEM 2581 by Fédération Européenne de la Manutention (FEM).

1 Sample volume

A sample of more than 700 litres is required

2 Equipment needed

- lifting device (e.g. crane or fork lifter)
- big bag, capable to accommodate more than 700 l sample volume, with a discharging opening at the bottom and capable to be fixed onto a lifting device
- yard stick
- ferrule to block the discharging opening of the big bag (e.g. metal ring).

3 Pre-arrangement

Mark on the floor by two exact squares (one within the other) with the following measurements: outer square: 2.5 m x 2.5 m, the inner square 2 m x 2 m. Mark the common center of these two squares with a cross (Figure 1).

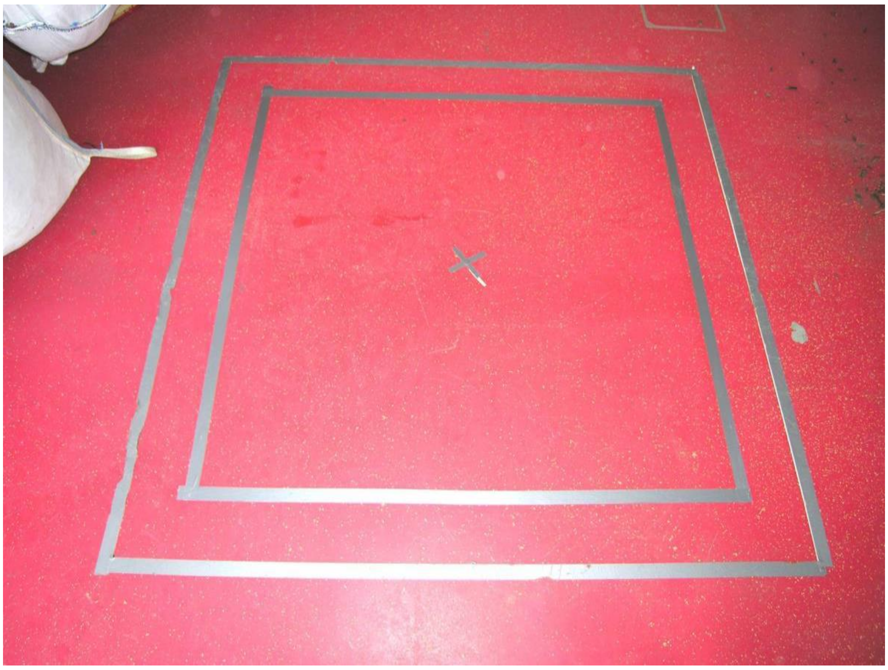

Figure 1: Example of marked square on the laboratory floor

4 Procedure

The sample of minimum 0,7 m³ volume is stored in the big bag. Position the big bag on the lifting device with the discharge outlet pointing to the bottom and move it in a way that the discharge outlet is situated vertically above the centre of the two squares (Figure 2). Thereby the lifting device shall not stand within the squares to allow an undisturbed creation of the angle of repose. Then put the ferrule around the discharge outlet of the big bag and fix it. Lift the big bag until the ferrule is located at 1,0 m above the floor.

Note: The ferrule is used to achieve a slower and more even flow of the tested fuel, particularly when easily flowing materials are tested.

Figure 2: Position of the filled big bag before opening the lower outlet for unloading

Then open the outlet and let the fuel percolate on the floor.

Note 1: If the fuel is blocked in the outlet of the big bag, take a stick and try to dissolve the blockage by stirring within the big bag. This shall be conducted from above, to guarantee an undisturbed angle of repose. A ladder may be needed for an unproblematic stirring. By stirring the fuel, try not to shake the big bag and the outlet.

Note 2: If the particle size of the fuel is too big for an undisturbed flow, dismount the ferrule and note this.

The percolation shall be interrupted, when about 2/3 of the big bag's content is on the floor. Then reduce the gap between the outlet and the top of the formed cone to about 10 cm and discharge the last third of the sample volume onto the cone.

Note: This reduction is performed in order to get an even angle of repose (cone). Without reducing the distance, the cone might build a plateau on the top and not a peak.

The height (*h*) of the cone shall be measured as mentioned in Figure 3 by using a board and placing a water level on it. Avoid any compaction of the peak. A second person is required to use the yard stick. Record the measured height.

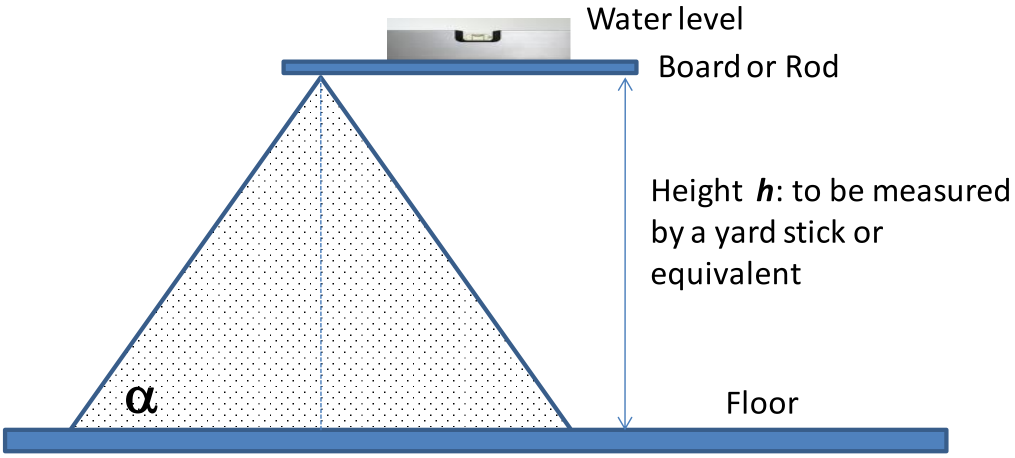

Figure 3: Method to determine the height h for calculating the angle of repose

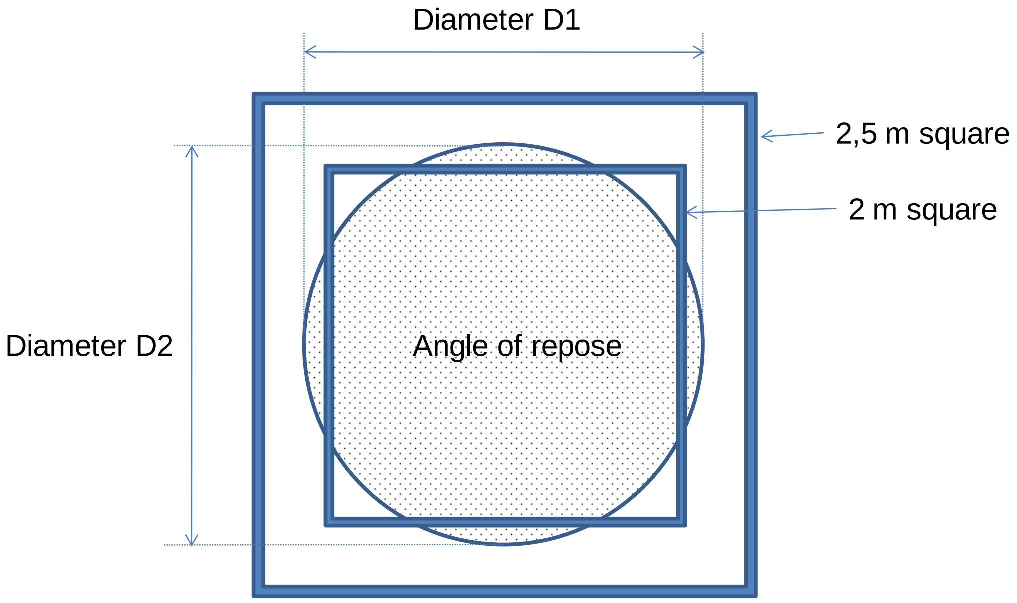

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Figure 4: Method to determine the diameters D1 and D2 for calculating the angle of repose

According to Figure 4 measure the two diameters *D1* and *D2* of the sample cone and record them. The squares shall help to orientate and to be sure, that the two highest diameters will be measured.

Note 1: Sometimes the angle of repose will not be exactly circular, therefore start measuring diameter *D1* where the diameter is highest.

Note 2: The circumference of the cone on the floor ends where the sample cone dues not any more build a closed surface (this means that no floor is shining through; i.e. single particles are not regarded as part of the sample cone).

5. Calculation

The angle of repose α (in °) is calculated using equation [1], where h is the height and D_1 and D_2 are the diameters as recorded in Clause 4 (in cm) (see Figures 3 and 4).

$$\alpha = arc\ \tan \frac{4*h}{D_1+D_2} \qquad [1]$$