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Abbreviations and acronyms

ar	as received
BET	Brunauer-Emmet-Teller
EBC	European Biomass Certificate
EC	Electrical conductivity
IBI	International Biochar Initiative
HTC	Hydrothermal Carbonization
SEM	Scanning electron microscope
SNG	Synthetic natural gas
TGA	Thermogravimetry Analysis
waf	water and ash free
wf	water-free
WHC	Water holding capacity

1 Executive summary

This first deliverable of WP6 "Bioenergy carriers" deals with the experimental characterization of biochar samples from the first two gasification test campaigns performed at VTT (BCFB 21/42 and BCFB 22/04). The feedstock used in these test campaigns were pellets made from bark residue.

The gasification process generates two carbon-rich fractions that are both investigated as potential biochar products: gasifier bottom ash (char separated from bed material by sieving) and filter dust recovered from the filter unit.

The main questions to be answered by this deliverable are:

- Is the biochar suitable for further use and is there a difference between these two char products from the quality and end-use point of view?
- Does the gasification process require some adaption to provide biochar in appropriate quality and is there a need for post-processing?

Furthermore, the deliverable should provide information for defining the most suitable and valuable use of the FlexSNG biochar that will be outlined in deliverable D6.2.

Therefore, ultimate and ash analyses are determined, as well as inorganic and organic impurities, indicators for its combustion and soil amendment applicability as well its surface morphology. The results are compared with the quality requirements of the two voluntary standardization guidelines for biochars from IBI and EBC.

All biochar characteristics are in good accordance with the voluntary standards. Furthermore, combustion and soil amendment characteristics show suitable parameters for the envisaged biochar use. The difference between bottom and fly ash is not very distinguished; biochar pollution with bed material is found, but this is not a barrier for further use of biochar.

Remark and update in August 2022:

This deliverable contains only results for biochar produced from bark pellets but it will be complemented with biochar results derived from other feedstocks as well once new samples become available from the ongoing gasification tests at VTT. The key characteristics of biochar produced from different feedstocks are gathered in table format in Appendix 8.4 to facilitate easy comparison. Proximate and ultimate analyses of the gasifier feedstocks are given in Appendix 8.1.

In August 2022, results of biochar produced from wood pellets and straw pellet feedstocks were included in Appendix 8.4. Similarly to bark, their quality meets the requirements of the two voluntary EBC and IBI standardization guidelines.

2 Introduction

The vision of the FlexSNG project is to develop and validate a flexible and cost-effective gasification-based process for the production of pipeline-quality biomethane (bio-based synthetic natural gas, bio-SNG), high-value biochar and renewable heat from a wide variety of low-quality biomass residues and biogenic waste feedstock. Bio-SNG and heat are already marketable products. For biochar, the situation is much less developed but already today, biochar is considered to be valuable e.g. for soil amendment or carbon sequestration.

Even the term "biochar" is not well-defined. Biochar is often used more or less synonymous with "charcoal", "pyrochar", "black carbon" "torrefied biomass" or "hydrochar". All terms are closely related to the different biochar production processes: pyrolysis, gasification, torrefaction or hydrothermal carbonization.

Following the definition in [1], biochar can be described as a "stable carbon-enriched substance produced from biogenic feedstock through thermal treatment in a no or low oxygen atmosphere". This broad definition includes products from torrefaction, pyrolysis, gasification as well as from hydrothermal carbonization.

Other definitions have a narrower understanding of biochar. Besides the process itself, they are often based on carbon content, production temperature or feedstock. In [2], the carbon content of biochar should be within the range of 50-80%, whereas in [3] the carbon content should exceed at least 50% with a black carbon content 10-40% of total carbon, a molar O/C ratio below 0,4 and a molar H/C ratio below 0,6. The carbonization temperature is also considered sometimes as criteria; excluding biochars from torrefaction and Hydrothermal Carbonization (HTC) due to temperatures below 350°C and therefore low carbonization degrees [4]. Furthermore, the prefix "bio" can emphasize the biogenic origin of the feedstock as well the final use for soil amendment and carbon sequestration [5].

In the frame of the FlexSNG project, biochar refers to the solid, black carbonaceous by-product of the gasification process received from the bottom and fly ash removal. This definition is in line with the voluntary, non-legal binding European Biochar standard described in [6], where gasification is considered to be part of pyrolysis technology. However, this definition does not limit the further utilization of the FlexSNG biochar to either energetic or material usage.

3 Biochar production

With addition of sufficient heat and a lack of oxygen, biomass is converted into carbon-rich products, including biochar, either from pyrolysis or hydrothermal carbonization.

Pyrolysis is a thermochemical conversion process converting dry organic materials into solid biochar and gaseous volatiles, where the latter ones are split after condensation into liquid pyrolysis oil and permanent gases. The organic matter present in the biomass starts to decompose at around 250°C and proceeds until 700–800°C without the presence of air/oxygen. Depending on the feedstock composition as well as reaction parameters like temperature, pressure, residence time, heating rate as well as reactor design and configuration, yields and quality of the three products char, oil and gases vary significantly.

Gasification can be considered as a high-temperature pyrolysis process. At elevated temperatures above 650°C and understochiometric air ratio, more permanent gases (mainly CO, CO_2, CH_4 and H_2) are formed than for low-temperature pyrolysis. However, significant amounts of biochar are still formed due to incomplete conversion of the feedstock. Within the FlexSNG concept, the gasifier is run in a biochar producing mode ("co-production mode") to increase the plant flexibility by production of storable biochar.

Hydrothermal carbonization (HTC) is often described as "pressure cooking" or "dewatering" of biomass, converting wet biomass into a solid fuel. HTC takes place at mild conditions in liquid water of about 200°C and corresponding pressures of about 20 bars. Feedstock can be used without any pretreatment and there are no restrictions regarding its composition. HTC takes place at temperatures above 200-220°C. The solid product is often referred to as biochar, but it is different than products of pyrolysis or torrefaction. The detailed reaction scheme is a complex mixture of hydrolysis, decarboxylation and dehydration of carbohydrates, followed by recondensation, aromatization and polymerization of the in situ formed intermediates on the remaining carbon skeleton.

Due to the different technologies, manifold process configurations and various feedstock sources, there is no one biochar. In contrast, biochars differ in a broad range of their chemical and physical properties, which in turn affect the final end use valorization.

4 Biochar utilization

Biochars are produced since thousands of years, mainly as fuel for heating and metallurgic processes. Furthermore, slash-and-burn land clearance or natural wildfires forms biochar as well, attracting a lot of interest from research and industry in the recent decade due to positive effects of biochar as organic fertilizer and soil amendment. More industrial applications of biochars comprise the use as filter material, as pharmaceutical additive for farm animals and humans, as adsorption material for soil recovery or as construction material additive. Furthermore, biochar is considered to play an important role as negative carbon emission technology.

Figure 1: Biochar applications [7].

The global biochar market is expected to grow up to 2 billion € by 2026, with an annual growth rate above 10% [8]. For Europe, the market volume in 2021 was 600 million €, with an average growth rate of 67% per year from 2019-2022 [7]. About 90% of biochar used in Europe goes into the agricultural sector.

Despite the strong growth of the biochar market, no legal framework for biochar is released in the EU. So, all European and national legislation has to be considered before placing biochar in the market, e.g. fertilizer and waste regulations.

However, two voluntary standardization certificates are implemented so far, one European Biochar Certificate (EBC) [6] and the one from International Biochar Initiative (IBI) [9]. The goal of both initiatives is to define common quality and practices for biochar utilization. The

IBI standardization guideline is from 2015. The latest one is the renewed EBC guideline from the beginning of 2022, and is chosen as benchmark for FlexSNG biochar. The EBC guideline defines five certification classes and all of them include carbon sink certification. EBC-BasicMaterial is the minimum standard based on the EU-REACH regulation. The other certificate classes are oriented on final end use of biochar: EBC-Feed for fodder, EBC-Agro and EBC-AgroOrganic for agricultural, EBC-Urban for non-food soil amendment and EBC-ConsumerMaterials as well as EBC-BasicMaterials for all non-soil uses.

Both voluntary standards comprise very similar parameters and characterization methods for biochars, feedstock material as well as chemical and physical parameters. These include proximate and ultimate analyses, nutrient content, pH value, electrical conductivity, bulk density and particle size distribution and pollutant concentrations.

In this deliverable, the experimental results obtained from FlexSNG biochars are compared with the requirements of the EBC guideline requirements, to gain a first insight into possible biochar valorization routes. However, the experimental results are not limited to the certification guidelines, but also provide information regarding alternative biochar uses as adsorption or cathode material or for substitution of coal-derivatives in metallurgic processes or tire production.

5 Biochar samples

The biochar samples discussed in this deliverable were collected during the first two gasification campaigns conducted at VTT in October 2021 (BCFB 21/42[1]) and January 2022 (BCFB 22/04[1]) in the frame of WP4 of the FlexSNG project. The initial feedstock was bark pellets. The proximate and ultimate analysis of the feedstock is given in Table 1.

Table 1: Proximate and ultimate analysis of bark pellets that were used in the first two gasification campaigns at VTT.

Feedstock	**Bark pellets**
Test campaign	BCFB 21/42 & BCFB 22/04
LHV, MJ/kg (d.b.)	18,9
Moisture, wt-%	9,2
Volatile matter, wt-%	73,1
Fixed carbon, wt-%	23,1
Dry matter analysis	**wt-%**
C	51,9
H	5,9
N	0,4
O (as difference)	37,9
Ash	3,8
S	0,03
Cl	0,008

During the gasification campaigns, biochar was sampled at two different points; at the gasifier bottom and in the dust filter. The initial goal in the gasification test campaigns was to recover the majority of the biochar product through bottom ash removal and subsequent separation from the bed material by sieving. Only the very fine particles are entrained at the gasifier top

[1] BCFB xx/yy (xx=year, yy=week)

and captured in the filter dust unit. This fraction typically becomes more contaminated by bed material as the separation is more difficult. In this deliverable (unless otherwise mentioned), the carbonaceous material sieved from gasifier bottom ash is referred to as “biochar” and the material recovered as fly ash from the filter unit as “filter dust”, respectively.

During the 1st campaign, only 40 g of biochar could be captured at the gasifier bottom. Due to the limited amount of sample available, only a part of the envisaged biochar characterization experimentation could be done for this campaign. Most of the solid material passed the gasifier and was captured in the fly ash fraction. The filter dust sample was mixed with bed materials dolomite and/or sand (Figure 2). The separation of the solids was quite challenging, time-consuming and not to a complete extent. Thus, the fly ash sample still contains some bed material.

In the 2nd campaign, the gasifier conditions were optimized to recover more biochar, in particular as bottom ash: the fluidizing velocity was lowered and the gasifier was operated below 700 °C without an external bed material. This type of operation regime enabled effortless biochar recovery through bottom ash removal. Therefore, a sufficient amount of biochar material was collected for a comprehensive characterization. The biochar sample details along with the corresponding gasification conditions are summarized in Appendix 8.2.

Figure 2: Biochar from the 1st campaign with bed material included.

Conclusion:

Regarding the EBC guidelines, bark is a possible feedstock because of its non-fossil carbon. The amount of unavoidable impurities with fossil carbon sources like plastics is limited to 10 wt-% for non-soil uses and to 1 wt-% for all soil and fodder uses, which are usually not exceeded for bark residues. Furthermore, a non-contaminated (e.g. paints, solvents, flame retardants) and non-organic-free feedstock is claimed. For virgin biomasses like bark, this is not an issue. However, for wastes streams like waste wood discarded material, this could be a limiting factor. For agricultural biomass feedstock and wood, a sustainable production is requested, e.g. a PEFC or FSC certificate for woody biomass or residues.

5.1 Ultimate analysis

Ultimate analysis of the biochar samples was performed according to the corresponding standards (DIN51719, DIN51724, DIN51726, DIN51732 and DIN51733). The results are shown in Table 2. The moisture content of all biochar samples is below 2 wt-%; storage at air for 72 hours showed no significant increase of moisture content for all samples.

Table 2: Ultimate analysis of biochar from bark (wt-% of water-free biochar).

Sample	Carbon [wt-%]	Hydrogen [wt-%]	Nitrogen [wt-%]	Sulfur [wt-%]	Oxygen [wt-%]	Ash [wt-%]
Filter dust 1st campaign	64,8	0,7	0,5	<0,1	4,5	29,4
Biochar 2nd campaign	83,1	0,9	0,5	<0,1	4,2	11,0

The different ash amounts are related to the presence of bed material in the samples derived from the 1st campaign. In the 2nd campaign, the amount of bed material in the biochar sample is significantly reduced as the char fraction could be more easily separated from the bed material by sieving and towards the end of the test run, the gasifier was even operated without an external bed material. On an ash-free basis, the composition of the two samples is very similar (see

Table 3).

Table 3: Ultimate analysis of biochar from bark (wt-% of water- and ash free biochar).

Sample	Carbon [wt-%]	Hydrogen [wt-%]	Nitrogen [wt-%]	Sulfur [wt-%]	Oxygen [wt-%]
Filter dust 1st campaign	91,9	1,0	0,7	<0,1	6,4
Biochar 2nd campaign	93,6	1,0	0,6	<0,1	4,7

As expected for high-temperature pyrolytic biochar, the carbon content (and also the degree of carbonization and its long-term stability, see [10]) increases compared to the initial feedstock bark, which is in accordance with literature results (e.g. [4], [11], [10]). Regarding the EBC and IBI certification standards, the total organic carbon content (TOC) is a crucial parameter. TOC is determined by the difference of total carbon and total inorganic carbon. For both samples, TOC is well above the envisaged threshold of the two certificate standards, which target a TOC of above 50%.

Table 4: Total organic carbon (wt-% of water- and ash free biochar).

Sample	Carbon [wt-%]	TIC [wt-%]	TOC [wt-%]
Filter dust 1st campaign	91,9	0,6	91,3
Biochar 2nd campaign	93,6	0,8	92,4

Based on the above ultimate analysis results, the molar ratios of H/C_{org} respectively O/C_{org} are calculated, see Table 5. Both values are more accurate indicators for the degree of carbonization and distinction to other carbon products like biomass, lignite, hardcoal or their derivatives. The lower both ratios, the more carbonized (and so coal-like) the biochar is.

Table 5: H/C_{org} and O/C_{org} values.

Sample	H/C_{org}	O/C_{org}
Filter dust 1st campaign	0,09	0,053
Biochar 2nd campaign	0,12	0,038
EBC & IBI limits	<0,7	<0,4

Conclusion:

The results from ultimate analysis show that the FlexSNG biochar from bark is in good accordance with the requirements from the EBC and the IBI standardization for biochars. The biochar is a highly carbonized product, which enables its energetic use as gasifier fuel (co-fed with challenging waste feedstocks) like envisaged in the FlexSNG concept, as fuel for heat production or for metallurgic processes. The results also suggest sequestration is another promising valorization option. However, a more detailed investigation of the biochar decomposition rate over a longer period of time is required to provide deeper insights in its real long-term stability.

5.2 Ash analysis

Ash composition and amount reflect mainly the feedstock inorganics, but also bed material used in the gasifier and abrasion materials from plant parts. Ash composition and amount are important characteristics for the energetic valorization route of the biochar, determining the ash melting behavior and thus slugging and fouling of pipes and heat exchangers in combustion or gasification units. Furthermore, for agricultural use, the concentration of heavy metal pollutants has to fall below the threshold values of the corresponding national and European legislation, e.g. EU 2019/1009 and EU 2019/2164.

The ash analysis (Table 6) was conducted according to DIN-51729-11.

Table 6: Ash composition (wt-% of ash) of biochars produced from bark.

Sample	Filter dust 1st campaign	Biochar 2nd campaign
Ash (815°C), wt-% (wf)	29,4	11,0
Ash composition, wt-% of ash		
Al_2O_3	6,1	4,8
CaO	41,3	28,4
Fe_2O_3	3,2	2,2
K2O	3,5	6,7
MgO	17,1	3,7
MnO	0,9	1,2
Na_2O	1,6	2,1
P_2O_5	3,1	2,7
SO_3	0,4	1,2
SiO_2	20,2	25,7
TiO_2	0,2	0,1

The total ash amount is much lower for biochar obtained from the 2nd campaign due to the absence of external bed material in the gasifier, whereas a mixture of dolomite ($CaMg(CO_3)_2$) and sand (SiO_2) was used in the 1st campaign. Both bed materials are present in the filter dust sample obtained from the 1st campaign, which can be seen as elevated Ca and Si contents. The switch to using sand as bed material in the second campaign and ultimately operating the reactor with no external bed material is reflected in the ash composition. The amount of bed material in the biochar is significantly decreased in the second gasification campaign where only some remaining sand bed material from previous set points is included in the sample.

Furthermore, the ash melting behavior was determined for biochar produced in the 2nd campaign to identify possible plugging or fouling problems. The ash melting temperatures are far above the gasification temperatures (750-850°C) as well as typical biomass combustion boiler temperatures (1000-1100°C). Therefore, plugging and fouling are not very likely for biochar of bark residues.

Table 7: Ash melting temperatures of biochar produced from bark.

Sintering temperature, °C	1250
Softening temperature, °C	1460
Hemisphere temperature, °C	>1500
Flow temperature, °C	>1500

The amount and chemical composition of biochar ash is no longer required by the most recent EBC guidelines from 2022 but the total ash amount declaration is still required for the IBI certificate. For the EBC certificates, the amount of the inorganic nutrient phosphorus, potassium, magnesium, calcium and iron have to declared; for agricultural and fodder use it is mandatory. The IBI certificates only require the nitrogen content for biochars. No upper or lower limits are claimed so far, except for the concentration of Pb, Cd, Cu, Ni, Hg, Zn, Cr, As and Ag (see Figure 3).

	EBC-Feed	EBC-AgroBio	EBC-Agro / EBC-Urban / EBC-ConsumerMaterials	EBC-BasicMaterials
Pb	10 g t^{-1} (88%DM)	45 g t^{-1} DM	120 g t^{-1} DM	no limit value, only declaration required
Cd	0.8 g t^{-1} (88% DM)	0.7 g t^{-1} DM	1,5 g t^{-1} DM	
Cu	70 g t^{-1}DM	70 g t^{-1}DM	100 g t^{-1} DM	
Ni	25 g t^{-1} DM	25 g t^{-1} DM	50 g t^{-1} DM	
Hg	0.1 g t^{-1} (88% DM)	0.4 g t^{-1} DM	1 g t^{-1} DM	
Zn	200 g t^{-1} DM	200 g t^{-1} DM	400 g t^{-1} DM	
Cr	70 g t^{-1} DM	70 g t^{-1} DM	90 g t^{-1} DM	
As	2 g t^{-1} (88% DM)	13 g t^{-1} DM	13 g t^{-1} DM	
Ag	no limit value, only declaration required			

Figure 3: Thresholds for heavy metal concentrations for the EBC classes [6].

Due to costly determination, the low amount of biochar available from the 1st campaign and the use of virgin biogenic feedstock with typically low concentrations of heavy metals, only the biochar sample from the 2nd campaign was analyzed (see Table 8). Analysis was done according to DIN22022-1. All concentrations are far below the strictest EBC limits for the EBC-Feed class.

Table 8: Amounts of heavy metals (g/t) from biochar (ar).

Element	Pb	Cd	Cu	Ni	Hg	Zn	Cr	As	Ag
g/t	< 2	< 0,2	16	11	<0,07	87	13	<0,8	< 5

Conclusion:

Biochar produced from bark is in accordance with the EBC guideline standards. There are no limitations regarding its use - even the use as fodder additive is possible. Regarding the use for agricultural purposes, the amount of nutrients is very low, and it is even worsened by the fact that only parts of the nutrients are available for plants. Therefore, the biochar use for fertilizing seems questionable, at least without additional loading of nutrients. For all other uses (soil amendment, construction material, sequestration), the low nutrient content is no barrier.

5.3 Thermogravimetry (TGA)

Thermogravimetry provides insights into the thermal and chemical stability of the biochars. In particular, the amounts of VOCs condensed on the biochar surface during pyrolysis are a crucial characteristic of biochars. These volatiles are released during TGA temperature increase. The content of volatile matter can have effects on plant growth; toxic compounds like aromatics can inhibit plant growth, while labile saccharide derivatives can serve as carbon source for microbes and thus lower the long-term storage carbon amount.

Thermogravimetric measurements were carried out with a thermobalance (DuPont 951 thermogravimetric analyzer). Sample sizes were about 10–15 mg, and the heating rate was 10 K/min up to 800°C with a final holding time of 60 minutes. The helium purge gas flow was 100 ml/min for all experiments and each material was analyzed in triplicate. The data acquisition from the thermobalance was done by a PC with LabVIEW. For the samples from the 1st gasification campaign with high ash content (due to inclusion of bed material in the sample), pure carbon particles were manually selected for the TG measurements. The weight loss between 100°C and 750°C is considered as the volatile matter content of the biochar samples, whereas the remaining mass reduced by the ash amount (determined before, see 5.2) is considered as the fixed carbon content.

Thermograms for samples from the first two gasification campaigns are shown in Figure 4 and Figure 5. The volatile matter of all samples is quite low, between 5 – 15%. This is in full accordance with biochars reported in the literature [6]. In [10], a higher pyrolysis temperature leads to a more stable biochar with less volatiles for different wood species. A similar trend is observed in the thermograms of FlexSNG biochar samples produced at different gasification temperatures. The trend is even more pronounced for biochars from the 2nd campaign. No difference is found between bottom and fly ash samples for the 1st campaign. Therefore, it can be concluded that the biochar in both samples is the same. Considering the ash amounts, the fixed carbon content of the 1st campaign is around 56 wt-%, whereas the carbon content for the 2nd campaign is around 75-85%. So far, the reason is unknown. However, inhomogeneities due to the small TG sample sizes are most likely responsible.

There is no restriction from both guidelines, only the declaration of TG measurement is claimed. TGA is used to determine the volatile content and the final pyrolysis temperature. Due to high temperatures for gasification (600-850°C) and the temperature limit of the thermobalance (750°C), the latter one cannot be determined properly from the thermograms. But, the final gasification temperature of biochars exceeds the final TG temperature.

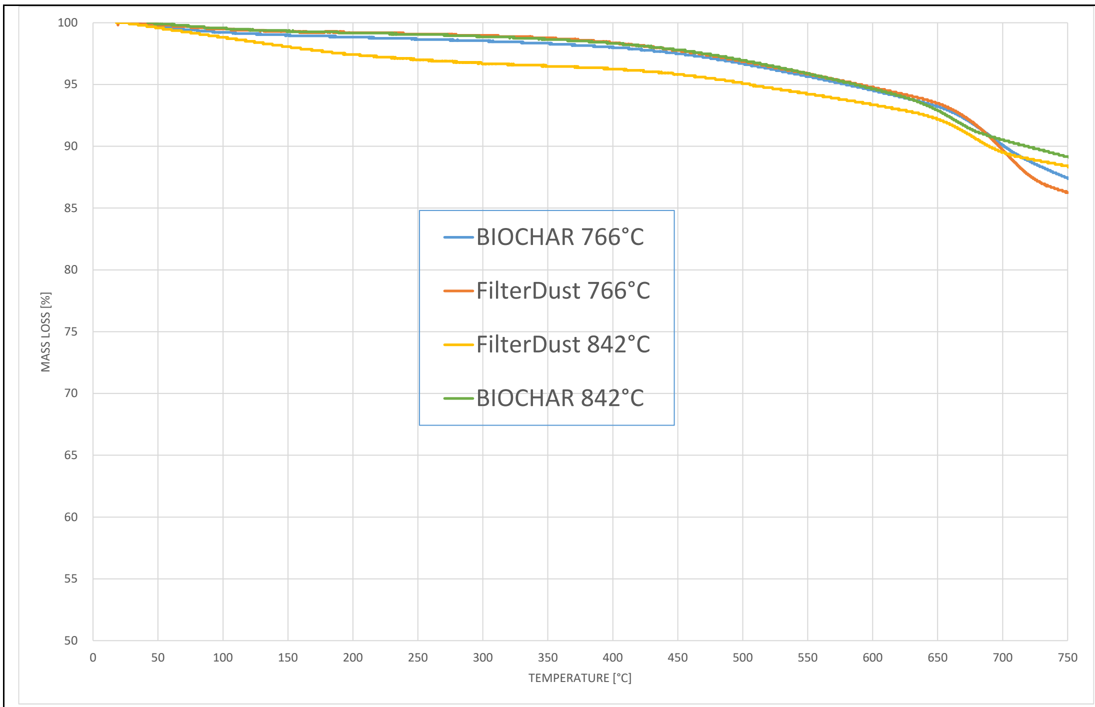

Figure 4: Thermogravimetry of biochar and filter dust from the 1st gasification campaign.

(Biochar 766°C & Filter dust 766°C from set point BCFB 21/42E, and Filter dust 842°C & Biochar 842°C from set point BCFB 21/42B1)

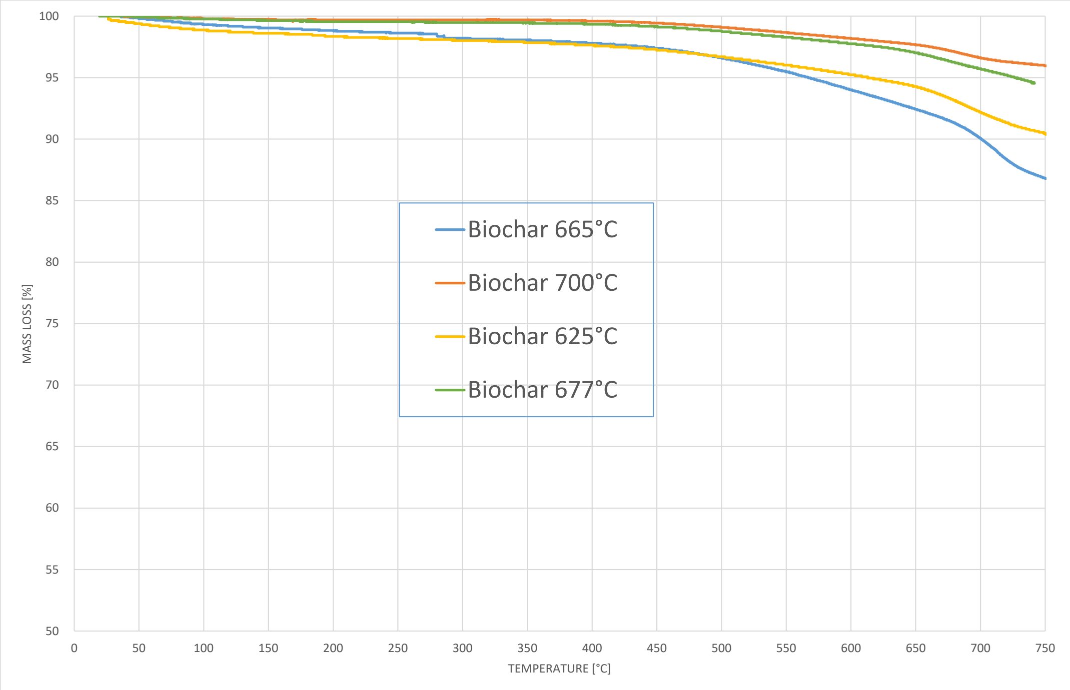

Figure 5: Thermogravimetry of biochar samples from the 2nd gasification campaign.

(Biochar 655°C, 700°C, 625°C and 677°C from set point BCFB 22/04D2)

Conclusion:

TGA measurement provides no barriers for biochar use. In contrast, the very low volatile content has positive effects on the combustion behavior. For metallurgic uses, no or very low volatile contents are mandatory to avoid dangerous formation of flames or explosions.

5.4 Combustion characteristics

As already mentioned, the volatiles of the biochar account for about 5 – 15%, in contrast to 73% for the feedstock bark. Additionally, the heating values for biochar samples were determined by calorimetric measurements according to DIN 51900. The results are shown in Table 9. The difference between the two campaigns is attributed to different ash amounts. On a water and ash-free basis, the biochar HHV is around 30 MJ/kg for all samples.

Table 9: Heating value for biochar samples.

Sample	HHV (wf) [MJ/kg]	Ash (wf) [wt-%]
Biochar 1st campaign	20,4	29,4
Filter dust 1st campaign	20,1	29,8
Biochar 2nd campaign	29,9	11,0
Filter dust 2nd campaign	29,7	10,9

Conclusion:

The biochars show good fuel properties, in particular the high heating value as well as the low volatile amount are very advantageous. due to their increased heating value. The high ash amount of is challenging, because only dedicated industrial boilers or gasifiers are capable of dealing with high-ash containing fuels, e.g. grate boilers for straw, waste wood or waste incineration. However, the main part of the ash amount comes from the bed material, which chemical composition and resistance to high temperatures is only a minor issue for boilers. Therefore, no severe limitations regarding the fuel usage of the biochar have to be considered for future biochar valorization.

5.5 Polycyclic Aromatic Hydrocarbons (PAHs)

During the production of biochar, pollutants can be introduced and enriched by the biogenic feedstock, which is usually the case for inorganic pollutants. In contrast, organic pollutants can be either degraded due to the elevated process temperatures (e.g. residues from drugs [12]), but also formed during the reductive atmosphere during the pyrolysis or gasification step (e.g. PAHs or even dioxins if a high number of halogens are present, [13]).

According to the results of various studies of PAH concentration in biochars ([14], [15], [16]), the simplest PAH naphthalene is the most highly concentrated of the 16 most abundant PAHs, but no elevated dioxin concentrations have been found so far. The processes and conditions for the production of biochar with low PAH levels are not yet fully understood or known. However, the studies show as well that for some biochars, the amount of total PAH exceeds the limits of the Guidelines for European Biochar Certificate [6]. Besides the pure presence of PAHs in biochar, the bioavailability of these components is the more crucial parameter. The bioavailability of PAHs and dioxins were found to be far below the total levels in the biochars studied [16]. Nevertheless, the amount of PAH is a very important parameter for placing biochars in the market, either to fulfill the EBC & IBI requirements, but also to respect European and national legislation for agricultural, disposal, landfilling, wastes or chemicals.

Determination of PAHs was done according to DIN 16181 (Soxleth extraction with toluene and PAHs quantification with GC-MS) by an external supplier (Eurofins GmbH; Freiberg).

The sample amount received from the 1st campaign was not sufficient for PAHs determination, but analysis could be performed for the samples of the 2nd campaign. VTT determined PAH concentrations from two biochar samples (sieved from bottom ash) and one filter dust sample (see Appendix 8.3). The results show more PAHs in the filter ash (26 mg/kg) than in bottom ashes (0,8 mg/kg and < 0,05 mg/kg). Two additional samples were analyzed by EIFER where the total PAH values are <2 mg/kg for both biochar and filter dust (see Table 10). The results are within the envisaged expectations, with higher PAH amount at the filter ash samples due to longer contact times with the tar-containing syngas; however, the total amount of PAHs is still at a level that does not exclude the general material utilization of the biochar.

The PAHs limits differ between the IBI and the EBC standards. For IBI, thresholds are between 6- 300 mg/kg, whereas lower limits exist for EBC due to stricter EU regulation (EBC-AgroOrganic class <4 mg/kg; EBC-Agro class <6 mg/kg). For all other EBC classes, only declaration of PAH amounts is required.

Table 10: Concentration of PAHs for biochar and filter dust samples of the 2nd campaign.

Concentration, mg/kg	**Biochar** 2nd campaign (bark)	**Filter dust** 2nd campaign (bark)
Naphthalene	0,3	1,2
Acenaphthylene	<0,1	<0,1
Acenaphthene	<0,1	<0,1
Fluorene	<0,1	<0,1
Phenanthrene	<0,1	0,3
Anthracene	<0,1	<0,1
Fluoranthene	<0,1	<0,1
Pyrene	<0,1	<0,1
Benzo[a]anthracene	<0,1	<0,1
Chrysene	<0,1	0,1
Benzo[b]fluoranthene	<0,1	<0,1
Benzo[k]fluoranthene	<0,1	0,2
Benzo[a]pyrene	<0,1	<0,1
Indeno[1,2,3-cd]pyrene	<0,1	<0,1
Dibenzo[a,h]anthracene	<0,1	<0,1
Benzo[ghi]perylene	<0,1	<0,1
Benzo[e]pyrene	<0,1	<0,1
Benzo[j]fluoranthene	<0,1	<0,1
Sum of PAHs, mg/kg	**0,3**	**1,4**

Conclusion:

The EBC limits are exceeded for one the filter dust samples but not for the biochar samples (sieved from gasifier bottom ash). The biochar PAH concentrations even fall below the strictest EBC limit for some samples, which shows the general capability to produce high-quality, low-PAH containing biochar from gasification. The further envisaged gasification test campaigns with other fuels and gasifier set point conditions within the project time will be used to get more insights on this topic.

Regarding the less strict IBI standards, all samples analyzed are within the limits. Therefore, no restrictions regarding the utilization of biochar from FlexSNG process are found.

5.6 Soil amendment characteristics (pH, EC and WHC)

The pH and electrical conductivity (EC) values are important parameters to determine the effects of biochar in soil amendment use. The amount and the composition of salts are important factors of soils for plant growth and thus for biochar as well. Soils as well as biochars differ strongly in their salt composition and amounts; to avoid negative and maximize positive effects for plant growth, both parameters have to be determined. The pH and EC values of a biochar suspension are proportional to the amount of soluble salts of the biochar itself. From literature it is well known that increased pyrolysis temperatures up to 600°C lead to higher pH and EC values [17]., expecting both values for biochar from gasification (at even higher temperatures than pyrolysis) at the upper level of pyrolytic biochars. Both parameters depend as well from the initial feedstock composition and from the carbonization process. The ph and EC values have to be declared before placing biochar at the market. However, no lower or upper limits are demanded so far.

The pH value of different biochar samples was measured according to DIN 10390 with a WTW pH 7110. 0,5 g of biochar were suspended in 25 ml of 0,01 m $CaCl_2$ solution, stirred for approximately 2 hours and afterwards the pH value was measured within the suspension directly. The measurement was repeated three times for each sample.

The conductivity of the biochar samples was measured according to DIN 11265 with a WTW LF 197. 0,5 ml of biochar were suspended in 50 ml of 0,01 m $CaCl_2$ solution, stirred for approximately 1 hour and afterwards the pH value was measured within the suspension directly. The measurement was repeated three times for each sample. The results are shown in Table 11.

Table 11: Mean pH, EC and WHC values for biochar samples produced from bark.

Sample	pH	EC [µS/cm]	WHC [%]
Sand	6,6	52	n.a.
Dolomite	7,4	95	212
Filter dust 1st campaign	9,9	2430	141
Biochar 1st campaign	9,5	1880	166
Biochar 700°C 2nd campaign	9,7	1148	145
Biochar 665°C 2nd campaign	9,8	1190	159

All biochar samples are alkaline, mainly due to the high amounts of Mg- and Ca components. The values are in the upper range compared with literature values for biochars but still within the typical range of 4-12 ([10], [17]). The bed material itself shows a slight acid or neutral character, with no significant (or only low) effect on the biochar pH and EC values.

The EC values have slightly more variation, since they are more sensitive to the detailed ash compositions. Nevertheless, the EC values are also within the range reported in the literature of 0,04-54,2 mS/cm [17].

The water holding capacity (WHC) is a crucial parameter describing the behavior of biochars with liquids, e.g. for water management or plant availability of liquid fertilizer like digestates, or balancing moisture content of biochar-containing materials. The WHC was determined according to DIN 14238. About 10 g of the biochar was placed in a vertical glass cylinder closed with cotton wool at the bottom. After weighing, the cylinder was put in a water-bath for 24 hours. Afterwards, the free water was removed for 2 hours in a sand bed, and the water uptake of the samples was subsequently determined by weighing. The measurement was repeated three times for each sample. The results are shown in Table 11. The biochar and the filter dust samples have quite similar WHC of around 150%; a trend depending on gasification temperature cannot be found like for pH and EC values.

Conclusion:

Both standardization guidelines require only a declaration for pH, EC and WHC values. No thresholds exist. However, these values are important indicators for the final end use, e.g. to avoid further increase or decrease of the acidity of a soil.

So far, there are no limitations or restrictions for FlexSNG biochar uses based on these results.

5.7 Surface morphology (SEM and BET)

The surface morphology of the biochar was investigated by SEM (Fei Quanta 200F). SEM pictures of biochars have already shown that various biomasses, procedures and temperatures lead to changes in the surface morphology of the initial biomass particles [11] .The higher the temperature, and thus also the carbonization degree of the initial biomass particle, the more pores are formed through evolution of the volatiles inside the biomass particle, see macropores in Figure 6 and Figure 7. However, still some structures of the initial bark can be found, as seen in the fiber structures in Figure 8. At higher resolution, the numerous microstructure pores and the very uneven surface area are obvious (Figure 9). Furthermore, the high temperatures and the very fast heating rates in the fluidized-bed gasification process lead to the breaking of the initial particles into smaller ones with sharp fracture surfaces and stress cracking (Figure 10 and Figure 11). All these effects increase in the specific surface area determined by macro- and micropores.

More detailed information about the pore sizes and amounts was obtained by BET measurements. The specific surface area (N2 SBET) was determined according to DIN 9277 using the BELSORP-mini2 (BEL Europe GmBH) and N_2 adsorption at 77 K in liquid nitrogen. Before experimental investigation, the samples were dried at 40°C in a vacuum and degassed. The specific surface area correlates with the pyrolysis temperature: the higher the temperature, the higher the specific surface area due to release of volatiles [11]. This corresponds well with the results of gasification biochar, which temperatures of 650-900°C are above the typical pyrolysis temperatures of 400-600°C. All biochars are above the typical value range of pyrolytic biochar of 150 m²/g.

Table 12: Specific surface area S and average pore diameter of biochar and filter dust samples.

Sample	Biochar 1st campaign	Filter dust 1st campaign	Biochar 2nd campaign	Filter dust 2nd campaign
S_{BET} [m^2/g]	217	224	281	348
Av. pore diameter [nm]	3,01	3,25	2,22	2,32

Conclusion:

For specific surface area, no limits are claimed by IBI or EBC standards, only its declaration. For EBC, a specific surface area above 150 m^2/g is recommended. All samples are above this threshold.

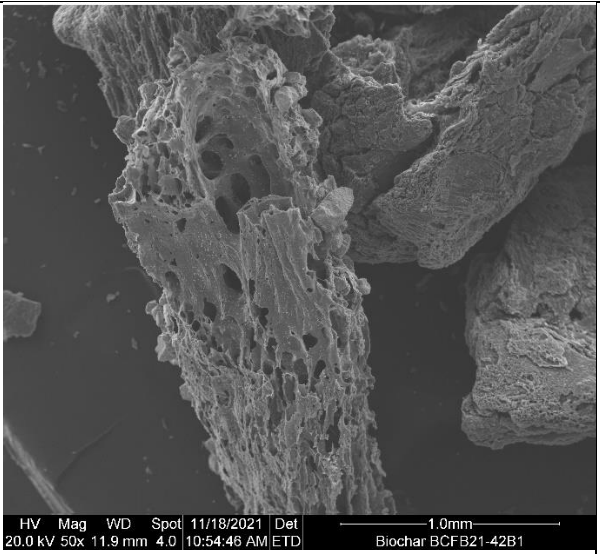

Figure 6: Biochar 1000 µm (1st campaign).

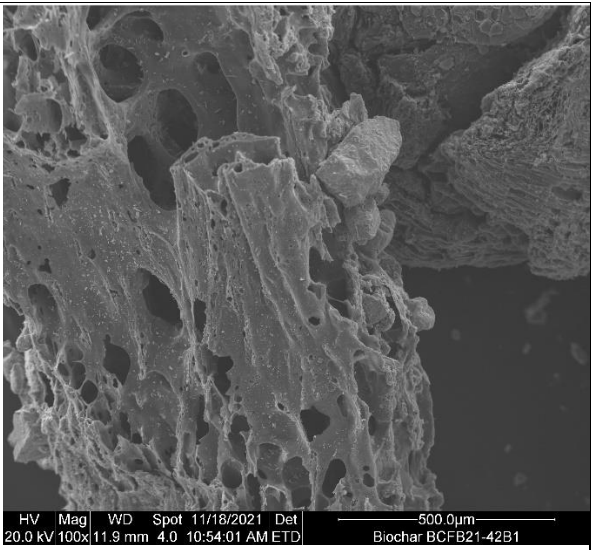

Figure 7: Biochar 500 µm (1st campaign).

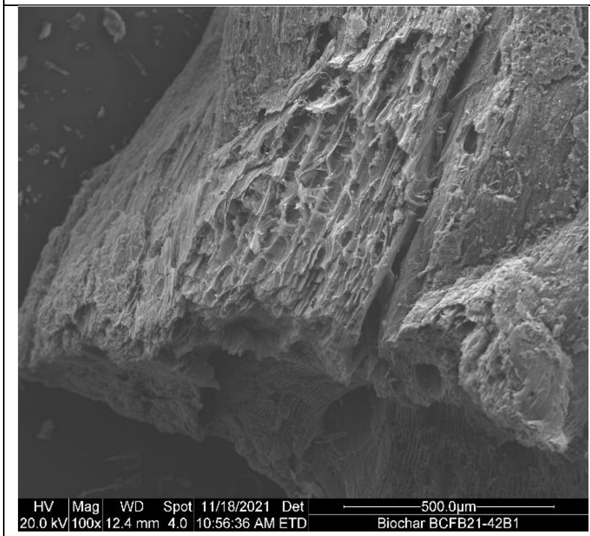

Figure 8: Filter dust 500 µm (1st campaign).

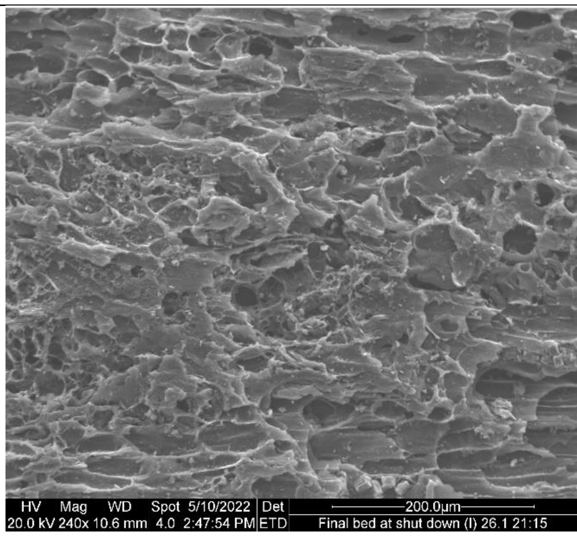

Figure 9: Biochar 200 µm (1st campaign).

Figure 10: Biochar 500 μm (2nd campaign).

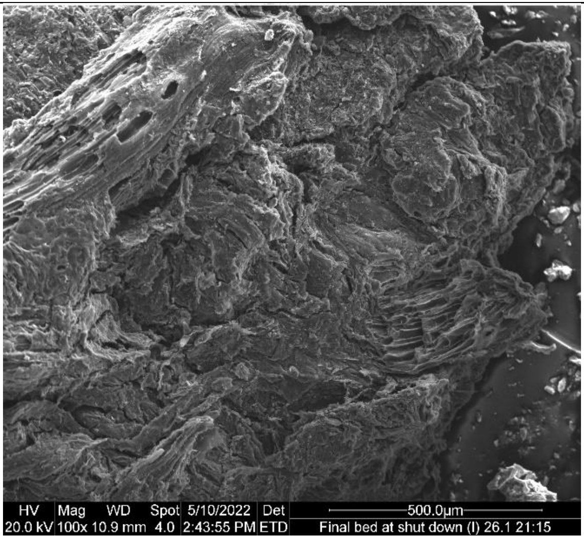

Figure 11: Filter dust 500 μm (2nd campaign).

6 Summary

This report comprises the results of the experimental investigation of biochar produced from bark pellets. The measurements include proximate and ultimate analyses, ash composition and melting behavior, amount and composition of polyaromatic hydrocarbon impurities, TGA, pH, EC and WHC as well as surface characterization with BET and SEM measurements.

The FlexSNG biochar is able to meet the requirements for the two voluntary EBC and IBI standardization guidelines; therefore, its utilization besides energetic use is a feasible option worth to be considered further. The most crucial parameter regarding the further use is the concentration of PAH, which will be further analyzed during the upcoming next validation gasification campaigns.

Besides the two voluntarily standards, national and European standards have to considered for its fodder, agricultural and soil amendment use. Regarding the use as construction material additive, the PAH amount seems to be a less crucial parameter, due to the fact that biochar immobilizes PAHs on its surface and the biochar itself is immobilized in the construction material.

The differences between biochar (sieved from bottom ash) and filter dust (fly ash) are quite low, with only minor effects regarding the voluntary standardization guidelines.

All of the above experimental investigations will be repeated for biochars produced in the next gasification test campaigns from other feedstocks, such as wood pellets and straw. At least for wood pellets, no significant challenges or problems are expected according to literature review. For straw, the higher ash and chlorine load in the initial feedstock could lead to higher PAHs concentrations.

This report will be continuously updated after completion of the experimental characterization of biochars obtained from the FlexSNG gasification campaigns. A comparison of the key characteristics of biochars produced from various feedstocks will be compiled in Appendix 8.4, which will be made available for the project consortium as well as the interested public at the end of the project.

These results also provide valuable insights and fundamental data for the upcoming deliverable D6.3 “Biochar utilization”, including more detailed technical and economic considerations for future FlexSNG biochar valorization.

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7 Appendices

7.1 Analysis of the feedstocks used in the gasification test campaigns

Feedstock	**Bark pellets**	**Clean wood pellets**	**Straw pellets (Lithuania)**
Test campaign	BCFB 21/42 & BCFB 22/04	BCFB 22/18	BCFB 22/18
LHV, MJ/kg (d.b.)	18,9	18,9	17,2
Moisture, wt-%	9,2	7,5	7,7
Volatile matter, wt-%	73,1	78,0	74,8
Fixed carbon, wt-%	23,1	21,7	18,9
Dry matter analysis	**wt-%**	**wt-%**	**wt-%**
C	51,9	50,2	45,9
H	5,9	6,5	6,1
N	0,4	0,1	0,3
O (as difference)	37,9	42,9	41,2
Ash	3,8	0,3	6,3
S	0,03	0,01	0,08
Cl	0,008	0,002	0,087

7.2 Biochar samples and the corresponding operating conditions of the gasifier

Sample	**Biochar** 1st campaign	**Filter dust** 1st campaign	**Biochar** 2nd campaign	**Filter dust** 2nd campaign
Origin of sample	Sieved from gasifier bottom ash	Filter dust	Sieved from gasifier bottom ash	Filter dust
Feedstock used	Crushed bark pellets	Crushed bark pellets	Crushed bark pellets	Crushed bark pellets
Bed material	30% sand+ 70% dolomite	30% sand+ 70% dolomite	No external bed material	No external bed material
Process conditions				
Gasifier temperature (bed/top), °C	766 / 747	766 / 747	< 690 / < 690 (samples after final shutdown during gasifier cooling)	700 / 860
Filter temperature (inlet/outlet), °C	547 / 551	547 / 551	479 / 552	479 / 552
Sample details				
Test campaign: acronym and date	BCFB 21/42 18.-20.10.2021	BCFB 21/42 18.-20.10.2021	BCFB 22/04 24. -26.1.2022	BCFB 22/04 24. -26.1.2022
Set point	BCFB 21/42E	BCFB 21/42E	BCFB 22/04D2	BCFB 22/04D2
Sampling date and time	20.10.2021 02:15-15:15	20.10.2021 02:15-15:15	26.1.2022 21:15-21:37	26.1.2022 14:15-15:15

BCFB xx/yy (xx=year, yy=week)

7.3 Amounts of PAHs from samples of the 2nd campaign (BCFB 22/04)

Sample	Filter dust BCFB 22/04D2	Biochar 1 BCFB 22/04D2	Biochar 2 BCFB 22/04
Compound	**mg/kg**	**mg/kg**	**mg/kg**
1-methylnaphthalene	0,15	0,12	<0,05
2-pfenylnaphthalene	<0,05	<0,05	<0,05
2-methylanthracene	<0,05	<0,05	<0,05
2-methylnaphthalene	0,52	0,13	<0,05
7,12 -Dimethylbenz(a)antracene	0,51	<0,05	<0,05
Anthracene	0,95	<0,05	<0,05
Asenafteen	0,18	<0,05	<0,05
Asenaphthylene	0,81	<0,05	<0,05
Benzo(a)pyrene	0,41	<0,05	<0,05
Benzo(b)fluoranthene	0,4	<0,05	<0,05
Benzo(g,h,i)perylene	0,1	<0,05	<0,05
Benzo(k)fluoranthene	0,59	<0,05	<0,05
Benzo(a)anthracene	1,3	<0,05	<0,05
Benzo(b)fluorene	<0,05	<0,05	<0,05
Benzo[e]pyrene (BeP)	<0,05	<0,05	<0,05
Biphenyl	0,71	<0,05	<0,05
Dibenzo(a,h)anthracene	<0,05	<0,05	<0,05
Dibenzofuran	<0,05	<0,05	<0,05
Dibenzothiophene	<0,05	<0,05	<0,05
Phenanthrene	4,8	0,094	<0,05
Fluoranthene	3,6	<0,05	<0,05
Fluorene	0,23	0,05	<0,05
Indeno(1,2,3-cd)fluoranthene	<0,05	<0,05	<0,05
Indeno(1,2,3-cd)pyrene	<0,05	<0,05	<0,05
Coronene	<0,05	<0,05	<0,05
Chrysene/triphenylene	2,5	<0,05	<0,05
Naphthalene	4,5	0,25	<0,05
Perylene	<0,05	<0,05	<0,05
Pyrene	2,8	<0,05	<0,05
PAH, total sum	**26**	**0,77**	**<0,05**

7.4 Comparison of the EBC key characteristics for different FlexSNG biochars

Feedstock	Bark	Wood	Straw
Origin of biochar sample	Sieved from gasifier bottom ash	Filter dust	Filter dust
C_{org}, wt-%	82	88	86
H/ C_{org}	0,12	0,20	0,18
O/C_{org}	0,04	0,07	0,06
VOCs, %	5-15	10-15	10-15
HHV, MJ/kg (waf)	30-31	31	29
Heavy metals	< EBC thresholds	< EBC thresholds	< EBC thresholds
pH	10	11,2	11,6
Bulk density, g/dm^3	300	280	250
Water content, wt-%	<2	<2	<2
WHC, %	105	110	110
EC, mS/cm	1-2	4-5	12-13
Spec. surface S_{BET}, m^2/g	250-350	270	290
PAHs, mg/kg	6 (0,3-12)	38	45 (13-87)
Nutrients, wt-% (wf)			
N	0,66	0,25	0,37
P	0,38	0,50	0,39
K	0,94	1,10	1,01
Ca	4,20	1,38	2,68
Mg	0,52	8,10	2,10
Fe	0,32	0,71	0,50