Annex 2
Analytic, Checks, Tests and Examples of Coal containing residues and by-products out of small-scale thermo-chemical wood gasification CHP plants

Elaborated by
Dipl.-Ing. Dieter Bräkow
Working Group Gasification of Biomass of the FEE e.V.
Society for the Promotion of Renewable Energies FEE e.V.

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1. Introduction

The following remarks would like to make a contribution to steer more steps in the direction of the re-use of residues from the thermo-chemical gasification of biomass (TGB). They refer to the presentation of previous knowledge on the handling of real waste materials from the point of view of the corresponding working group (WG) of the Society for the Promotion of Renewable Energies FEE e.V.

They are based on the small-scale gasification plants < 1 MW_{el} geared to CHP, which in Germany provide electricity and heat simultaneously from solid dry biomass in continuous operation and in which residual materials have to be removed. This primarily involves those technologies which have not yet been geared to a third product, i.e. a by-product[1]. The aim is to clarify the still existing learning and clarification process in order to handle given residual materials even more appropriately in accordance with the valid regulations. In subsequent steps, they are to be recycled as far as possible in order to reduce costs and achieve additional revenues as far as possible.

Without claiming to be exhaustive, the focus will be on the groups of residual substances that really arise and are essential and typical for the industry. By means of their physicochemical systematisation and description, it should then be shown which regulations (laws, ordinances and practiced procedures) can make their properties more usable for by-products than before.

After initial considerations it will become clear that it is appropriate to concentrate solely on solid residues from the small-scale gasification of untreated wood. Waste gas utilisation and discharge from the gasification of sewage sludge, fermentation residues or waste wood must be reserved for separate consideration. Also the occupation with liquid phases, which were important in the history of thermo-chemical gasification, e.g. as specific tar fractions of the raw gas, as well as the relatively insignificant condensates remain omitted in this article.

The above limitations are associated with the fact that reference is made primarily to German framework conditions, albeit in close connection with EU directives.

It should be noted at the outset that, as elaborated in the main contribution [0], residual materials can only be brought to utilization if this makes the operation of the individual plants more economical. To this end, an interweaving of contradictions must be resolved, in which not so much the lack of knowledge and technical solutions, but rather the basic attitude towards the subject and the expenditure per plant represent hurdles. Combined with the small quantities of often less than 5-25 t/year, the search for upgrading of residual materials from individual plants is therefore often broken off at the outset. It is very difficult to "do business" separately with the residual materials. Therefore, based on the composition of the typical residual substances, the dualism of valuable properties and organic loads should be referred to and suggestions for the reintegration of valuable elements and compounds into the cycle of substances should be made.

The explanations can only touch on some problems and should primarily be understood as a contribution to the discussion.

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[1] However, reference is always made to the first concept of SynCraft® from Austria known to the author, in which a by-product was already being worked on in the course of development.

2. Terms

Even among those directly involved in the thermo-chemical gasification of biomass, terms such as residual materials, ash, coal and by-products are used with different meanings. For orientation, therefore, a pictorial representation of the division of the dry mass of the resulting substances into inorganic and carbon-influenced fractions, ordered by loss on ignition (LOI), is chosen.[2].

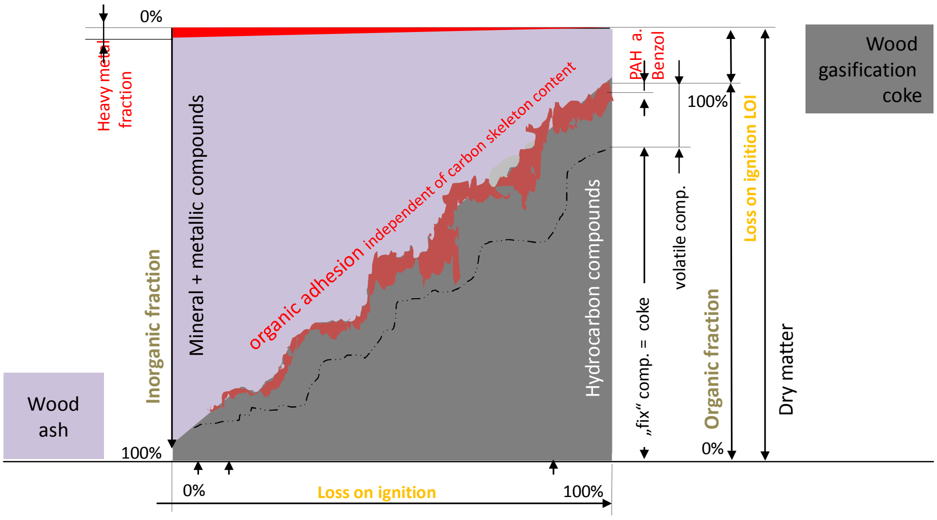

Fig. 1 Order of residues from thermo-chemical biomass gasification via the annealing losses

Residual materials are here (already narrowed down by the introduction) as a collective term for solid untreated materials, which after optimization of the design and operation at individual wood gasification plants can no longer be further converted. They have undergone the gasification or/and gas purification processes, which is why they differ from those which occur during the handling of the fuel but which are not treated here.

In thermo-chemistry, **ashes** are solid mineral combustion residues after (technically almost complete) oxidation of the (Hydro-) carbon compounds. Since no reactions take place completely on a technical scale, it is proposed to speak of ash in relation to the solid residues of wood gasification only as long as they can be land filled in accordance with the Landfill Ordinance [1]for DK II (i.e. on domestic waste landfills). Limit values for this are losses on ignition (LOI) of < 5 m% and TOC values of < 3 m%.[3] Because of the chemical identity with ash from wood combustion, the term wood ash (from thermo-chemical gasification) is used in the following. This term is bound to quality criteria by the stakeholders of wood combustion and is increasingly restricted to wood combustion. As explained in more detail under section 10, owners of wood ashes from gasification with LOI < 5 M%, based on analyses by this quality association, should follow.

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[2] In a subsequent step, it is planned to qualify this system, which is stoichiometrically more accurate, applied over the total organic carbon content (TOC). Weidner, M [2], for example, has already begun the further clarification of carbons.

[3] An extension of the term to substances which are taken to landfills of DK III or used as backfilling agents with LOI < 12 M% is suggested but not applied here.

From a thermo-chemical point of view, **coals** are $C_xH_yO_z$ compounds with mineral components which have been formed in geologically relevant periods of time under exclusion of air, pressure and temperature from masses of plant residues by oxygen and hydrogen extraction.

Wood gasification coke In contrast to geological processes, carbonized residues from the thermo-chemical gasification of wood are produced in technical processes, mostly under near atmospheric pressure and at high temperatures (with few exceptions between 850 and 1200°C) in an extremely short time (max. in a few minutes). This results in the pore structures that characterise them physically and chemically and their adhesion with ring-shaped hydrocarbons. They thus correspond to "coke" of wood gasification or "wood gasification coke". As can be seen in Fig. 1, in addition to the relatively fixed carbon skeleton, volatile and ash constituents as well as mostly tar components are also present. This specificity forms the basis for the transfer to by-products. For this reason, the term "wood gasification coke", which is better applicable than coal, is used below for residual materials dominated by carbon (even if it is an unwieldy term). As will still become clear, wood gasification coke will differ from one gasification process to the next depending on the wood used and the space-temperature-time ratios for the reactions. Therefore, it cannot simply be replaced by "charcoal", which itself is also a very specific coke made of wood.

Mixtures from wood ash and wood gasification coke belong between LOI > 5 and < 85 M% to the reality of the wood gasification and are therefore specifically treated starting from section 5.

By-product should only be used as a term if wood ashes or wood gasification coke have taken on properties through the gasification sub-processes or through after-treatments which allow their use by third parties. The term is legally defined in Europe. Because it is so important for the upgrading of residual materials, it will be dealt with specifically below.

3. Circular Economy Act and the closing of cycles

Owners of the residual substances defined above must ultimately dispose of these substances (with a few exceptions). Therefore, in practice they are usually regarded as waste. This view is supported by the Circular Economy Act (KrWG) [3] which under §3 "Definitions", in paragraph (3), point 1, assigns "Substances .., which are produced during energy conversion ...." even immediately to "wastes". Waste suggests de-valuation and so it follows in the everyday life of waste that owners try to get rid of these substances with as little effort as possible.

This was already opposed by the original – and is now further opposed by the $KrWG_{2012}$ in implementation of the European "Directive 2000/98/EC ...on waste..."[4] with specifications on the "waste hierarchy" (§ 6). The consideration of the details of the KrWG and the mentioned EC Waste Framework Directives cannot be relieved of the plant suppliers and waste owners.

However, in anticipation of the specific properties of the residual materials to be considered (see point 6), it is important to emphasise that their overall composition with its advantageous and disadvantageous components must be taken into account. A basic prerequisite for the upgrading of waste within the framework of the waste hierarchy (in accordance with EC Waste Framework Directive [4] Art. 4 and KrWG § 6 (2) Sentence 1) is that the protection of people and the environment in the generation and management of waste must be ensured taking into account the precautionary and sustainability principles.

The following quotation from the EC Waste Framework Directive [4] can then be read as a "definition for by-products", especially as Article 6 also specifies the criteria.

Article 5

By-products

(1) A substance or object, resulting from a production process, the primary aim of which is not the production of that item, may be regarded as not being waste referred to in point (1) of Article 3 but as being a by-product only if the following conditions are met:

a) further use of the substance or object is certain,
b) the substance or object can be used directly without any further processing other than normal industrial practice;
c) the substance or object is produced as an integral part of a production process; and
d) further use is lawful, i.e. the substance or object fulfils all relevant product, environmental and health protection requirements for the specific use and will not lead to overall adverse environmental or human health impacts.

(2) …

Article 6

End-of-waste status

(1) Certain specified waste shall cease to be waste within the meaning of point (1) of Article 3 when it has undergone a recovery, including recycling, operation and complies with specific criteria to be developed in accordance with the following conditions:

a) the substance or object is commonly used for specific purposes;
b) a market or demand exists for such a substance or objec;
c) the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products; and
d) the use of the substance or object will not lead to overall adverse environmental or human health impacts.

If there is to be a market or at least a demand for the conversion of the residues treated here into by-products, then they must have or receive a material and sales value. Furthermore, all parties involved must be clear about possible hazards that may arise from the specific residual substances or that are limited.

According to the provisions of the EC Waste Framework Directive [4], as well as the almost literal §§ 4 and 5 of the KrWG, "by-products" themselves are ultimately subject to product law and, because they correspond to chemicals, the regulations under REACH [5] apply. As a rule, their consideration requires the use of specialised agencies or offices and must be omitted here.

Fundamental consideration: As with all bioenergy technologies, the starting materials for the thermo-chemical conversion treated here are taken from the biosphere and above from the soil. This not only interferes with the material cycle of the economy, but also of nature. In the sense of a sustainable, balanced natural balance, these removals actually require the risk-free return of nutrients and trace substances to the soil for the biomass that is to grow back again. The KrWG [3] with § 11 "Circular economy for bio-waste and sewage sludge" provides the basics for this and refers to related laws and regulations, of which the Fertilizer Ordinance (DüMV) [6] and the Federal Soil Protection Ordinance (BBodSchV) [7] are to be referred to with regard to residual substances.

In this context, it should be emphasised that, when converting these residues into by-products, preference should be given to those which help to close the biological cycles and/or enrich the biosphere again.

4. Historic development

The study of residual materials from small-scale plants with thermo-chemical gasification of biomass took place in the following stages (reduction from point 1.2 of the main contribution [1]):

- In the 1940s, the first major application phase of discontinuous gasification, at that time mainly for mobility purposes, very little attention was given to the outputs. However, the dangers posed by their use have already become apparent.
- This was taken into account in the reactivation of biomass gasification for CHP continuous operation applications from the 1990s onwards. At that time, however, the primary objective was first to restore functional efficiency and then to achieve high availability.
- With the achievement of long-term operation of the first prototypes from 2005/6 onwards, environmental authorities already drew attention to the need to pay due attention to emissions. This applied first with regard to the regulations for keeping the air clean and then, somewhat later, with regard to the handling of solid and liquid residues. The pioneer was the Bavarian State Office for the Environment LfU [8].
- While the development of the process had already taken very precise account of specifications for exhaust gas values, efforts to comply with limit values for solid and liquid phases were rather hesitant. With the parallel efforts in the direction of Biochar and Terra Preta [9] and the intensive work with wood ashes [10], residue utilisation seemed to be clarified.
- It was not until around 2011/12, with the growing success of the first series products in continuous operation, when disposal became a real task, that the problems became clear. Most residual materials proved to be contaminated with organic and/or heavy metals and did not fit into the disposal system.
- Starting with the two German market leaders, and subsequently with almost all developers and manufacturers, a tenacious clarification process has taken place since then (first an intellectual one and then finally as a result) in the form of the confrontation with the regulations and corresponding technical and organisational solutions.
- With the publication of the "Implementation Notes ... " [11] there has been a binding scope of legal requirements for the handling of residual materials in Bavaria since 2013, combined with information on subsequent use. With Chapter 7 of VDI-RL 3461 [12], they have been updated and disseminated.
- As a result, since 2017/18 new plants of the leading technological manufacturers in the German-speaking region have had technical equipment for the proper handling of solid residual materials. In addition, the first routines for proper disposal have been confirmed.
- In addition to the recognition of the sale of "vegetable charcoal" by the Austrian Syncraft GmbH, Burkhardt GmbH was the first German company to succeed in obtaining and offering certified wood gasification coke from wood gasification as a by-product under chemicals law. A third supplier has applied for the thermal utilisation of said coke in accordance with waste legislation.
- Solutions to residual material issues have become company know-how and thus the object and advantage of intensified competition.

Overall, however, the industry still has to rid itself of the image of not having completely sorted out and solved its problems with residual materials. Above all, stocks of plants from the years of the first series are still pushing for recycling. In many cases, there are still paths to be taken to ensure proper disposal. The belief of operators that only nature-compatible residues can be produced from untreated wood must be overcome.

Note on the latter two points
Contaminated wood gasification coke, which until recently was considered hardly to be in conformity with the Directive, is now accepted as a by-product in one case in Germany and is on its way to being thermally recycled in a second case, for which an application has been made under waste law. To have marked out these paths are services, i.e. the know-how of two companies that cannot yet be generalised. This article therefore discusses the external use of wood gasification coke as a task that still needs to be solved, until Point 11 again refers briefly to the pioneers in recycling.

5. Residues and places of occurrence (status quo)

In order to switch from the basic considerations to the actually given residual materials, the following overview was prepared, from which the systematisation shown in Section 6 was then derived. For this purpose, 10 technologies were examined in more detail in continuation of the limitation[4] already made at the beginning. From the author's point of view, these technologies produce the majority of residual materials in Germany and represent typical small-scale CHP technologies with thermo-chemical gasification of untreated wood in continuous operation. In order to also take into account the technologies with double-fire gasification, which have shaped the gasification development with all their ups and downs, in one of the cases mentioned, the most stable version from Stans (CH) to date was included. Where the concepts were similar, preference was given to those that had already proved their suitability for operation over several years, including prototypes. Technologies which have not yet been in customer hands in Germany or which have not been offered since 2017/18 have not been taken into account. Sources were generally accessible publications by the manufacturers, supplemented by requests from the team for the author.

In the diagram, the assembly on which the ejections take place is highlighted in red for each process chain. Black arrows stand for the discharge of defined wood gasification coke, grey arrows for those which, according to the design, represent or should represent wood ash.

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[4] Limitation to small-scale CHP gasifier units in the power range < 1 MW_{el} in continuous operation, from solid dry biomass, providing electricity and heat in Germany

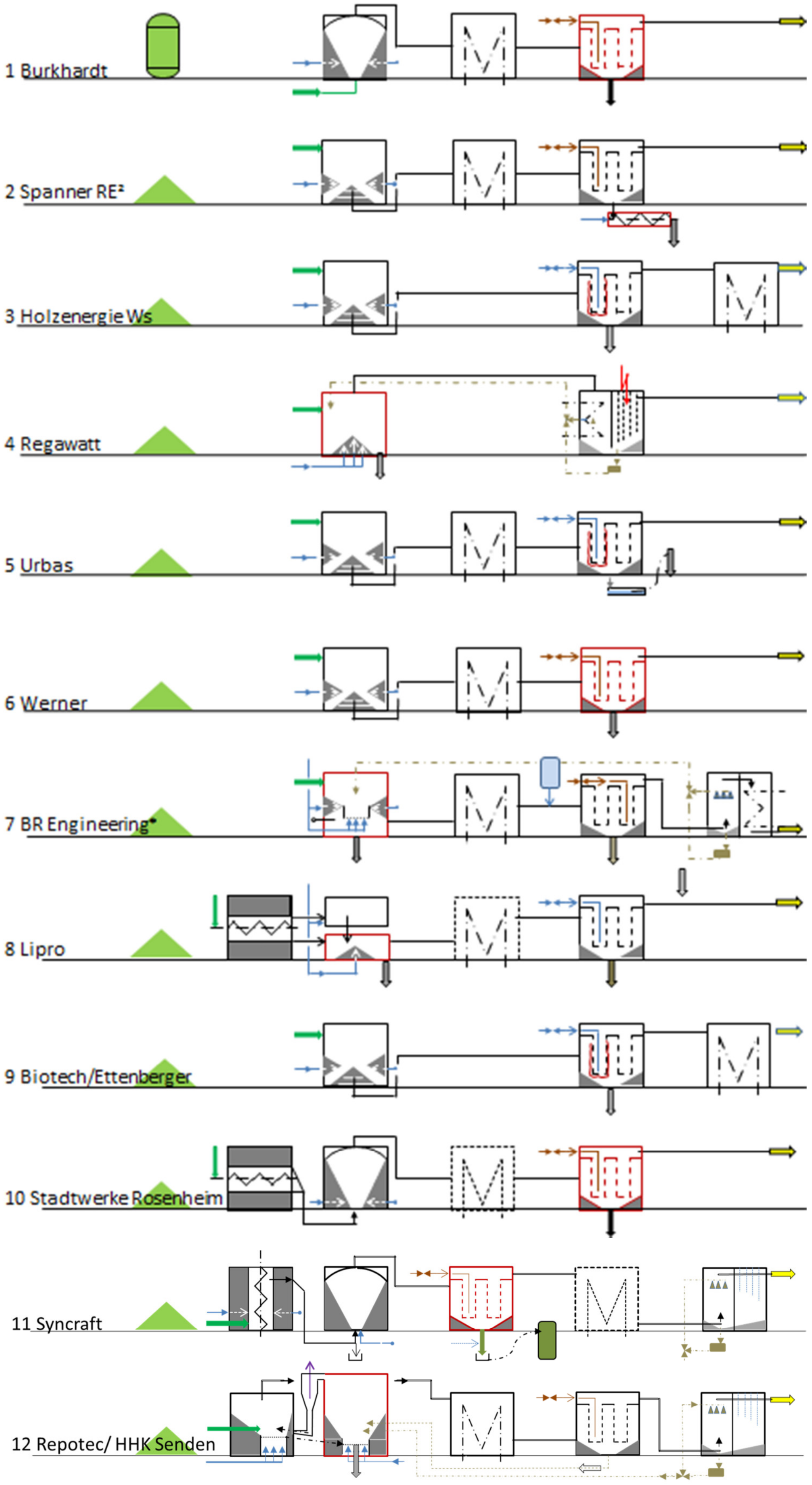

Fig. 2 Plant concepts for thermo-chemical wood gasification and its ejections

Figure 2 also shows at which points in the process chains residual materials occur internally, are partly recycled or post-treated and highlights where they are ultimately discharged.

In order to enable a comparison with at least one large plant, the plant of the wood-fired cogeneration plant in Ulm/Senden was included, which is known to work with fluidised beds according to Repotec technology. In order to relate to the process, which was designed from the outset for electricity, heat and vegetable coal, the concept of Syncraft ® operated in Austria was also presented.

In summary, it can be said for the small-sized processes:

- Of the 4 solid or liquid outputs[5] that are classified as basically possible in the literature and in [0], Sections 1.4.2 and Fig. 4, only one or seldom two types of residues occur in reality when technologies are in operation.
- Washing agents (with the exception of a few existing plants) have not been discharged for years. Sludges from washing agents are re-circulated, gasified or incinerated within the process. Permanent condensate discharges are exceptions. This is confirmed by the initial limitations and the concentration on solid dry residues.
- Grate or gasifier chamber residues (such as ashes, slag and dust, in order to establish an analogy to combustion) are only produced in processes with fixed-bed counter-current gasification and those with double firing.
- In contrast to wood combustion, the decisive residual material retention in the previously predominant direct current processes is achieved by gas cleaning. In most processes, it is even the only place where residual materials are discharged.
- Untreated carbon-dominated filter residue (in DE) is currently only produced by two technologies. These can, however, be disposed of in the meantime (as already mentioned) as a by-product or shortly before external thermal utilisation.
- The majority of manufacturers, who also produce filter residues, convert these into oxidised residues when cleaning the filter media or in combination with post-combustion processes in or directly at the plants. (The post-combustion gases enter the fuel gas internally).
- Even if individual manufacturers are still working on such after-treatments and proofs still have to be provided, the majority of the processes have meanwhile been designed in such a way that either relatively defined carbon-dominated or largely oxidised residues have to be discharged.
- This does not yet mean that the entire plant inventory connected to the grid in Germany operates according to these either/or ejections, but that the plants that still discharge mixtures can be put in this position by additional machine and/or control technology as well as the exchange of know-how.
- At present, the main problem is to obtain the possible residual material qualities from operators and to dismantle existing stock/contaminated sites.

The volume of residues in Germany in 2017 can be estimated at

- approx. 3,200 t mineral characterized,
- approx. 3,000 t carbon-dominated as well as
- approx. 2,300 t of mixed residual materials, which tend to be mineralized.

These data are based on surveys of the WG TGM of the FEE e.V. with status 8/2018 and findings on the fundamentally different properties of the residual materials, depending on where they are discharged from the process.

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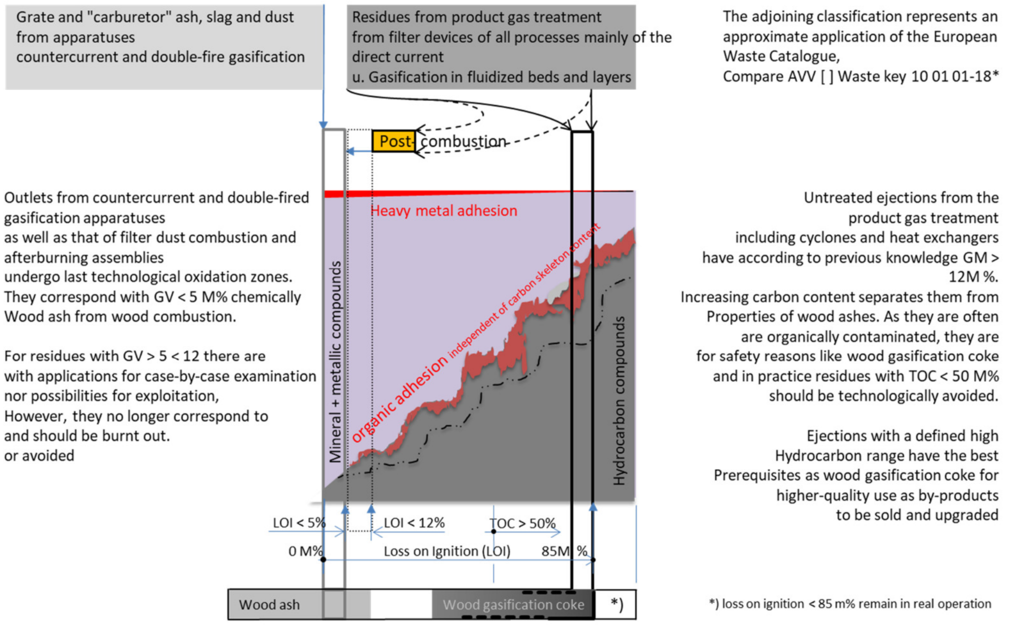
[5] Ash/Coal +Dust/Ash/Filtercake plus Sludge plus Wastewater

6. Systematization of the ejections according to places of occurrence and material properties

In the two figures below, the separation given in practice between the discharge of wood ashes on the one side and wood gasification coke with their places of occurrence on the other hand was again ordered by the loss on ignition. Thus, an assignment of basic properties can already be illustrated for them and their mixtures.



Grate and "carburetor" ash, slag and dust from apparatuses countercurrent and double-fire gasification

Residues from product gas treatment from filter devices of all processes mainly of the direct current u. Gasification in fluidized beds and layers

The adjoining classification represents an approximate application of the European Waste Catalogue, Compare AVV [ ] Waste key 10 01 01-18*

Outlets from countercurrent and double-fired gasification apparatuses as well as that of filter dust combustion and afterburning assemblies undergo last technological oxidation zones. They correspond with GV < 5 M% chemically Wood ash from wood combustion.

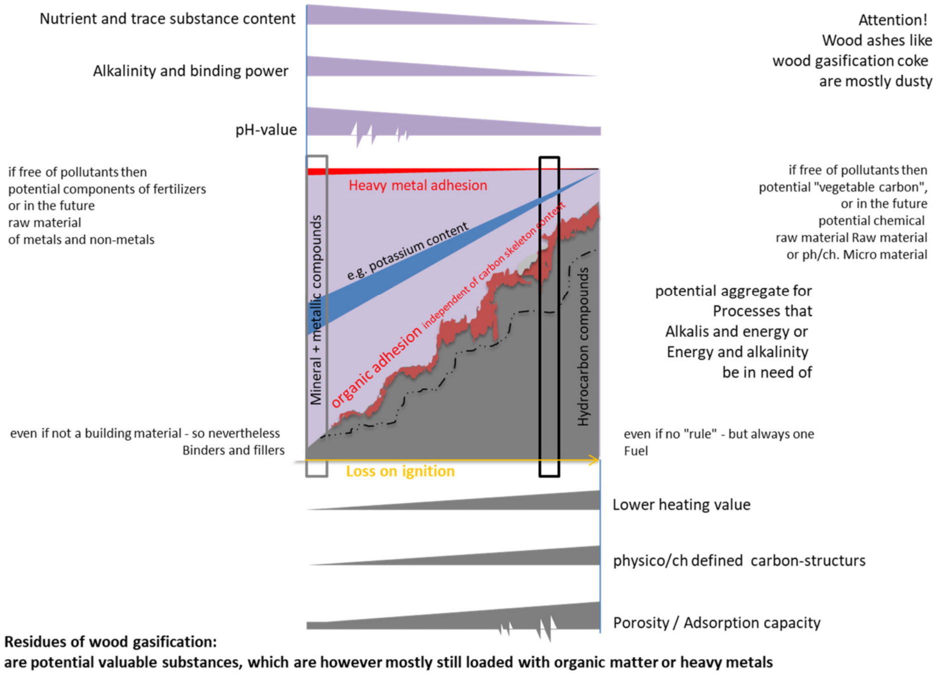
For residues with GV > 5 < 12 there are with applications for case-by-case examination nor possibilities for exploitation, However, they no longer correspond to and should be burnt out. or avoided

Untreated ejections from the product gas treatment including cyclones and heat exchangers have according to previous knowledge GM > 12M %. Increasing carbon content separates them from Properties of wood ashes. As they are often are organically contaminated, they are for safety reasons like wood gasification coke and in practice residues with TOC < 50 M% should be technologically avoided.

Ejections with a defined high Hydrocarbon range have the best Prerequisites as wood gasification coke for higher-quality use as by-products to be sold and upgraded

*) loss on ignition < 85 m% remain in real operation

Fig. 3 Outward transfers of thermo-chemical wood gasification sorted according to their proportion of wood ash and wood gasification coke



Attention! Wood ashes like wood gasification coke are mostly dusty

if free of pollutants then potential components of fertilizers or in the future raw material of metals and non-metals

if free of pollutants then potential "vegetable carbon", or in the future potential chemical raw material Raw material or ph/ch. Micro material

potential aggregate for Processes that Alkalis and energy or Energy and alkalinity be in need of

even if not a building material - so nevertheless Binders and fillers

even if no "rule" - but always one Fuel

Residues of wood gasification:
are potential valuable substances, which are however mostly still loaded with organic matter or heavy metals

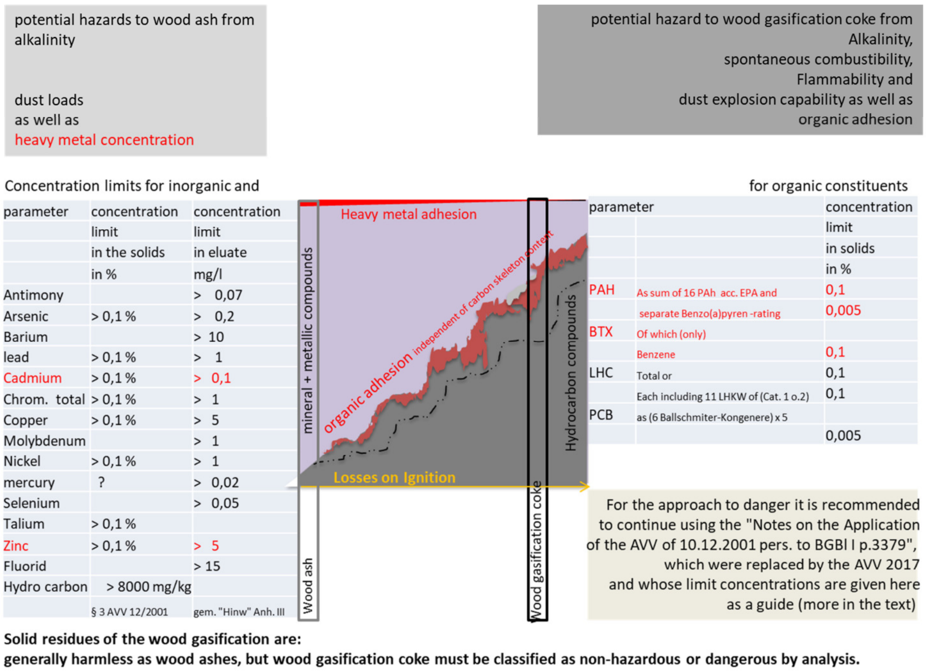
Fig. 4 Residual materials of thermo-chemical wood gasification sorted according to their basic characteristics (both are enlarged in the appendix)

7. Structure and hazard of solid residues

Improper handling of tar phases was the trigger for reservations about dry solid residues as well. These were further reinforced by the actions of many operators, who relied on the belief that carbon-derived residues, as "bio-carbons", had the ability to improve soil as they accumulate. In practice, the residues treated here have therefore been assumed to be dangerous as a precautionary measure. It must be taken into account and, where appropriate, refuted. Slowly, the grey area between the simplest self-recycling still practised and increasing disposal in accordance with the regulations is becoming smaller and smaller, combined with the first steps towards re-use.

Hazard-relevant properties of substances that are regarded as **waste** are disclosed in Annex III of the EC Waste Framework Directive (2008/98/EC) [4]. They must be observed by manufacturers, owners, disposers and recyclers of residues. The first two in particular have to deal with the effects that their residual substances can have on the range from "1. explosive" to "14. ecotoxic". Since 2017, criteria and limit concentrations for hazardous substances as part of the residue mixtures can be found solely in Annex I, Parts 2 - 5, of the European Chemicals Directive CLP, Regulation EC 1272/2008 [13], regardless of whether they are utilized in the application of the waste regime or are removed as a by-product.

Consultants and offices have specialized in the classification of substances according to these regulations. In order to obtain an initial assessment of the hazard relevance itself, it is proposed to withdraw from the "Notes on the Application of the Waste Catalogue Ordinance of 10 December 2001, BGBl. I p. 3379 ..." [14], which were binding until the previous year.[6] [14]



potential hazards to wood ash from
alkalinity

dust loads
as well as
heavy metal concentration

potential hazard to wood gasification coke from
Alkalinity,
spontaneous combustibility,
Flammability and
dust explosion capability as well as
organic adhesion

Concentration limits for inorganic and

parameter	concentration limit in the solids in %	concentration limit in eluate mg/l
Antimony		> 0,07
Arsenic	> 0,1 %	> 0,2
Barium		> 10
lead	> 0,1 %	> 1
Cadmium	> 0,1 %	> 0,1
Chrom. total	> 0,1 %	> 1
Copper	> 0,1 %	> 5
Molybdenum		> 1
Nickel	> 0,1 %	> 1
mercury	?	> 0,02
Selenium		> 0,05
Talium	> 0,1 %	
Zinc	> 0,1 %	> 5
Fluorid		> 15
Hydro carbon	> 8000 mg/kg	
	§ 3 AVV 12/2001	gem. "Hinw" Anh. III

for organic constituents

parameter		concentration limit in solids in %
PAH	As sum of 16 PAh acc. EPA and	0,1
	separate Benzo(a)pyren -rating	0,005
BTX	Of which (only)	
	Benzene	0,1
LHC	Total or	0,1
	Each including 11 LHKW of (Cat. 1 o.2)	0,1
PCB	as (6 Ballschmiter-Kongenere) x 5	
		0,005

For the approach to danger it is recommended
to continue using the "Notes on the Application
of the AVV of 10.12.2001 pers. to BGBl I p.3379",
which were replaced by the AVV 2017
and whose limit concentrations are given here
as a guide (more in the text)

Solid residues of the wood gasification are:
generally harmless as wood ashes, but wood gasification coke must be classified as non-hazardous or dangerous by analysis.

Fig. 5 Residual materials from thermo-chemical wood gasification - limits of hazard

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[6] Siehe https://www.bmu.de/fileadmin/Daten_BMU/Download_PDF/Abfallwirtschaft/avv_erlaeuterungen.pdf.

As already derivable from basic knowledge and illustrated above, the wood ashes and wood gasification coke are two distinctly different groups of residual substances that are afflicted with typical chemical elements and compounds that can have a dangerous effect on humans and the environment. From the characterization of these two groups it is possible to draw conclusions about substances with LOI between 5 and 85 M%.

In addition to the predominant part of salts and oxides, **wood ash** also contains heavy metal compounds as a characteristic of dangerousness in addition to alkalinity. They were absorbed by the wood while growing and gathered in the system during gasification until they were discharged. To the best of our knowledge, none of the heavy metals listed above reaches proportions of > 0.1 % of the dry solid mass. (This applies with regard to hazards to humans and the environment, but does not exclude the possibility that limits for certain uses, e.g. as a starting material for fertilizers, will be exceeded).

The assessment is often more critical if the transition of heavy metal ions to eluates is tested in the second step. If the special Annex III of the above-mentioned "Notes" [14] is used for this purpose, it is not uncommon for the elements Cd and Zn to exceed the limits.

Besides, still the relatively high pH-values of the wood-ashes between 12 and 13 must find attention, especially in connection with the dust-form prevailing with the residues.

Of cause, **wood gasification coke** always consists to a subordinate extent of the wood ashes characterized above. More important, however, is that charred, structured, pore-rich residues of the original wood form the part. Heavy metal contents are so diluted and do not limit uses (as known so far).

By the thermal transformation between 850 and 1200 °C, and altogether with oxygen-deficiency, they have a similar construction, but another pore structure as "unburned" from the combustion, pyrolysis-coke from plants or charcoal from retorts and/or milks. By modification, adsorption and condensation, ring-shaped molecules typical for wood gasification are formed proportionally (primarily depending on the temperature). As PAH, BTX[7] and phenol derivatives, several of them in their pure form are harmful to health and/or can also cause cancer.

With increasing carbon content, the proportion of not completely gasified hydrocarbon compounds of the frameworks also increases, but the potential hazard is mainly characterized by the detachable (extractable) proportions of the three ring-shaped compound groups mentioned. The contents of benzene and PAH_{16EPA} (the latter characterized by naphthalene, acenaphthylene+acenaphthene and phenanthrene) frequently determine that the limit concentration of <0.1 M% is exceeded. Of untreated filter residues, values around 2,000 mg/kg benzene are common and for PAH_{16} even amounts ranging up to 8,000 mg/kg, but also those exceeding 1 M%. Benzo[a]pyrene concentrations usually remain clearly < 0.05 M%, but exceedances are also known as individual values. Compared to the PAH load of e.g. consumer articles made of soft plastic with e.g. approx. 500 mg PAH_{16}/kg or road break-up to be classified as hazardous waste, these loads are to be assessed as seriously high

On the other hand, as analyses have shown[8], contamination with PCBs and LHCs[9] in ashes and coke from wood gasification can be excluded as hazardous components. This also applies to dioxins and

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[7] PAH Polycyclic aromatic hydrocarbons; BTEX aromatic hydrocarbons benzene, toluene, ethylbenzene and the xylenes

[8] acc. to 50 analyses of Spanner RE² GmbH

furans, because their formation is rather unlikely due to the reducing conditions in wood gasification processes.

The contents shown are independent of rising carbon skeleton components (above the LOI ordered). In addition to the source material, the gasification principle and the operating mode of the plants, they are essentially dependent on the extraction points and cycles, as well as on the physicochemical conditions before and during ejection or thermal after-treatment. The conditions for separating the residual particles from the product gas or the exhaust gas of the after-treatment system play an important role here.

In addition to this hazard potential, which is typical for this technology and is significant for humans and the environment, the explosion- and fire-protection-relevant properties of wood gasification coke and the still relatively high pH values between 11 and 12 must also be taken into account.

Note: It should be noted that the detection of the organic contamination is strongly dependent on the analytic methods and their handling. In the industry, the PAH determination in accordance with EN 15527, i.e. after extraction using toluene, and the determination of benzene in accordance with DIN 38407-F9-1(MSD) are gaining acceptance.

Observation: Evaluations of PAH determinations show that, depending on which solvent, which overflow, at which temperatures and time are used for extraction, loads of different magnitudes are detected, which sink to the µg range per litre during elution (in water). From this it can be deduced that due to the strong adsorption forces of the carbon frameworks between the chemically/analytically determined loads on the one hand and the release of benzene and PAH from the mixtures of wood gasification coke under natural conditions on the other hand, extreme differences can also be expected in the effects.

Suggestion: Therefore, it should be compared which real environmentally relevant effects of wood gasification coke and e.g. soil and/or bitumen break-up, which are analytically similarly organically contaminated, emanate. This should not call into question potential hazards, but should make it possible to collect the residues in question, transport them and recycle them at suitable physicochemical sites in a manner that is appropriate to the effort involved. Procedures and technologies should mature in order to transform the carbon frameworks into higher-value by-products in the near future. Today, a classification as hazardous and residues to be declared with an asterisk* often even blocks their external thermal re-use (and this on the basis of still uncertain PAH_{16} analyses with regard to carbon matrices).

Conclusion: The efforts to reliably identify the true PAH_{16} contents and to clarify the real risks posed to humans and the environment by the carbon-dominated residues of wood gasification are an important prerequisite for the increased conversion to by-products with higher utility value (than the one to be recovered from the calorific values).

8. By-product options

The starting point for the systematisation envisaged in the following figure is the loss on ignition (LOI) of 5 M% at which recovery or disposal separates.

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[9] PCB Polychlorinated biphenyls; LHC Highly volatile halogenated hydrocarbons

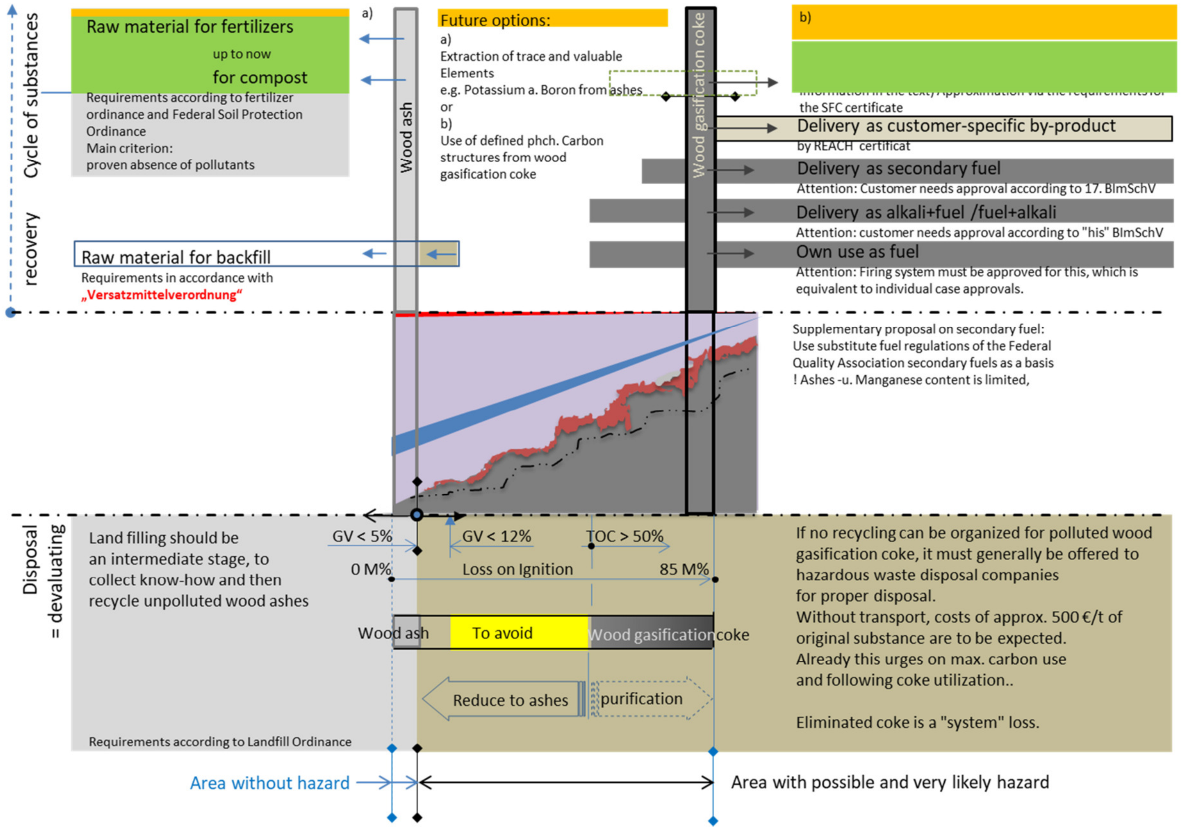

Fig. 6 Residual materials from thermo-chemical wood gasification - recycling options

If the ignition loss of representative samples is less than 5 M%, the residual material is considered suitable for landfill, which in practice is also handled as free of hazards.

This is usually the case for wood ashes. If the LOI< 5 M% is confirmed, there is a good basis for testing the suitability for recycling in the sense of the Fertilizer Ordinance. This opens up possibilities for recovery in line with a true circular economy, as should become the rule for bioenergy technologies.

If the residual material has LOI values of 12 M%, it can (even if it is organically contaminated) still be used in agreement with the authorities for the production of stowing agents.

If the LOI of 12 M% is exceeded and a TOC value of 50 M% is not yet reached, a mixture is given which can neither be used as wood ash nor as coke without complications. Although such ash-rich mixtures burn, from LOI 10 M% there are, for example, calorific values of approx. 4 MJ/Kg [2], but discharges or self-use as fuel combined with a tendency to slagging then tend to have the character of disposal. As the carbon content increases, the combustion conditions improve and the interest in the energy content of the material increases. To respond to demand from the metallurgy or glass and ceramics industry, where calorific values and alkalinity are needed, have so far failed mainly because of low quantities and the control of the dusts. If incineration dominates, the requirements of the BImSchG must be complied with. If hazardousness cannot be excluded, the 17th BImSchV[10] applies. Although there are numerous plants for this purpose, very few have waste code numbers that correspond to residues from thermo-chemical wood gasification. It is physico-chemically possible to obtain this from the authorities, but it has so far proved unprofitable for bitumen or power and cement plants. Technically and legally feasible subsequent uses as aggregate and/or fuel have so far not been

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[10] BImSchV / BImSchG.

possible in most cases due to the excessively high licensing costs in relation to the low volume. The search for a solution is further complicated by fluctuations in the ingredients, the adhesion with organic substances and thus the hazardousness of the substances, as well as the high costs for analyses, coupled with requirements for dust handling. To supply the mixtures to hazardous waste disposal companies has so far only led to acceptable results for very small quantities. Special waste disposal involves costs (including analyses, declaration, packaging and transport) in the range of 500 - 800 €/t DM [15]. In addition, the contaminated substances, which are mainly associated with valuable properties, are destroyed. They once again serve to provide electricity and heat, but are removed from the cycle of substances.

From the above, the industry has come to the conclusion that residual materials that cannot yet be disposed of in landfills and those with undefined carbon contents must be avoided. As a result, many developers have at least succeeded in incinerating such mixtures before they are discharged. In addition, they also show operators how to achieve only wood ash as the only solid residue. There are considerations for thermo-chemically better post-gassing [16].

With the TOC > 50 M%, there is an orientation for residual materials borrowed from the vegetable coal industry, from which higher-value external uses should be targeted. From LOI of 75 to 85 M% it is really wood gasification coke, which, if it were not contaminated with PAH and benzene, corresponds in its properties to pyrolysis coke and charcoal, which are produced extra from biomass. These substances deserve recycling that goes beyond incineration. This is what is discussed under point 11. For the qualitative upgrading of wood gasification coke at the plants there are laboratory tests [16], but an external processing and conversion to products seems to be more effective.

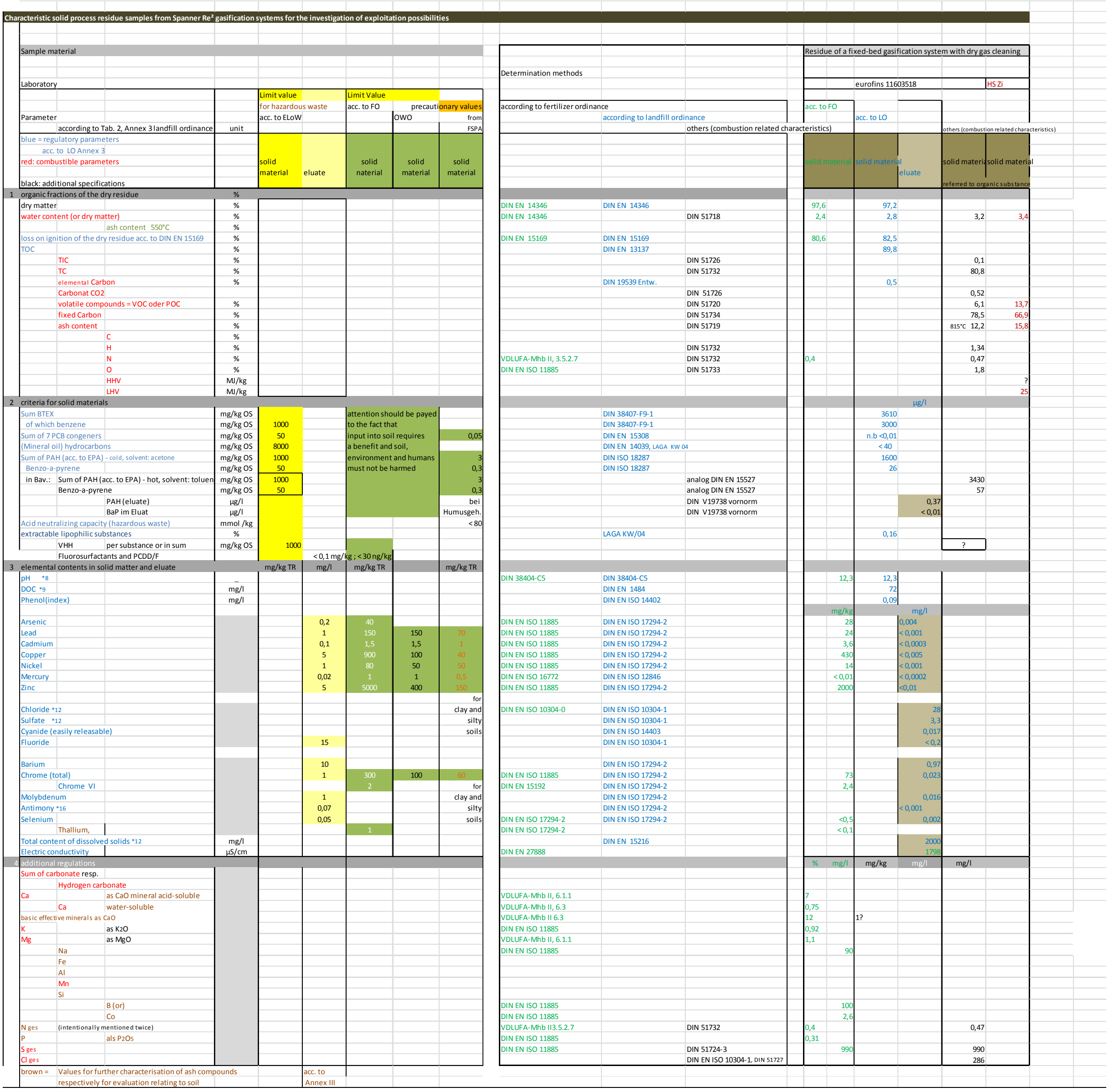
The best chances of releasing wood gasification coke as a by-product exist if the annual volume "justifies" the procedures, the carbon content is as high as possible and the composition remains within relatively narrow technical limits. If the residue is considered to be non-hazardous, this simplifies reuse considerably. More important for the transfer to by-product status, however, is the procedural compatibility between the given qualities and the requirements of the users/processors. If this is balanced by analyses, manufacturers who cause larger wood gasification coke streams, e.g. 1000 t/a, should check with the partner and corresponding service providers whether the customer is able to revalue/produce the product in accordance with waste legislation, or whether the sellers should dispose of their residual materials as partial streams of a certified gasification by-product with a corresponding price after a classification procedure according to REACH. So far there is one application for the latter variant in the industry, obtained from Burkhardt GmbH.

9. Notes on analytics

The analysis of solid residues of the thermo-chemical gasification of wood proves to be a problem area in its own right due to many influencing factors and can only be outlined here.

The main problem is that the relatively labor-intensive and costly analyses always give only a snapshot of the situation at a given point. They can hardly be related to the gasification processes and the conditions that caused the sampled substance to result.

The recognition remains also afflicted with very many coincidences if (storage) stocks are to be analyzed. There are very narrow limits to the methodology used to obtain representative results from as many analyses as possible. The main reasons are the costs of the analyses and the still relatively low market value of the residues as well as the low explosiveness of these questions for scientific work and projects. The data density, for example, is still extremely low compared to that of the technological "neighbours" wood ash and vegetable charcoal. This may apply to many technologies that have only been part of economic life for a few years. What is specific, however, is that with increasing carbon content and associated adsorption forces, conventional waste analysis methods often result in contradictory analyses. This applies in particular to PAH_{16} regulations[11], which determine the hazardousness of residual materials and thus their usability.



Characteristic solid process residue samples from Spanner Re² gasification systems for the investigation of exploitation possibilities

Sample material										Residue of a fixed-bed gasification system with dry gas cleaning				
							Determination methods							
Laboratory											eurofins 11603518			HS Zi
Parameter		Limit value		Limit Value										
according to Tab. 2, Annex 3 landfill ordinance	unit	for hazardous waste acc. to ELoW		acc. to FO	precautionary values OWO	from FSPA	according to fertilizer ordinance	according to landfill ordinance	others (combustion related characteristics)	acc. to FO	acc. to LO		others (combustion related characteristics)	
blue = regulatory parameters acc. to LO Annex 3 red: combustible parameters black: additional specifications		solid material	eluate	solid naterial	solid material	solid material				solid material	solid material	eluate	solid materi	solid material referred to organic substance
1 organic fractions of the dry residue	%													
dry matter	%						DIN EN 14346	DIN EN 14346		97,6	97,2			
water content (or dry matter)	%						DIN EN 14346		DIN 51718	2,4	2,8		3,2	3,4
ash content 550°C	%													
loss on ignition of the dry residue acc. to DIN EN 15169	%						DIN EN 15169	DIN EN 15169		80,6	82,5			
TOC	%							DIN EN 13137			89,8			
TIC	%								DIN 51726				0,1	
TC	%								DIN 51732				80,8	
elemental Carbon	%							DIN 19539 Entw.			0,5			
Carbonat CO2									DIN 51726				0,52	
volatile compounds = VOC oder POC	%								DIN 51720				6,1	13,7
fixed Carbon	%								DIN 51734				78,5	66,9
ash content	%								DIN 51719				815°C 12,2	15,8
C	%													
H	%								DIN 51732				1,34	
N	%						VDLUFA-Mhb II, 3.5.2.7		DIN 51732	0,4			0,47	
O	%						DIN EN ISO 11885		DIN 51733				1,8	
HHV	MJ/kg													?
LHV	MJ/kg													25
2 criteria for solid materials												µg/l		
Sum BTEX	mg/kg OS			attention should be payed				DIN 38407-F9-1			3610			
of which benzene	mg/kg OS	1000		to the fact that				DIN 38407-F9-1			3000			
Sum of 7 PCB congeners	mg/kg OS	50		input into soil requires		0,05		DIN EN 15308			n.b <0,01			
(Mineral oil) hydrocarbons	mg/kg OS	8000		a benefit and soil,				DIN EN 14039, LAGA KW 04			< 40			
Sum of PAH (acc. to EPA) - cold, solvent: acetone	mg/kg OS	1000		environment and humans		3		DIN ISO 18287			1600			
Benzo-a-pyrene	mg/kg OS	50		must not be harmed		0,3		DIN ISO 18287			26			
in Bav.: Sum of PAH (acc. to EPA) - hot, solvent: toluen	mg/kg OS	1000				3			analog DIN EN 15527				3430	
Benzo-a-pyrene	mg/kg OS	50				0,3			analog DIN EN 15527				57	
PAH (eluate)	µg/l					bei			DIN V19738 vornorm			0,37		
BaP im Eluat	µg/l					Humusgeh.			DIN V19738 vornorm			< 0,01		
Acid neutralizing capacity (hazardous waste)	mmol /kg					< 80								
extractable lipophilic substances	%							LAGA KW/04			0,16			
VHH per substance or in sum	mg/kg OS	1000											?	
Fluorosurfactants and PCDD/F			< 0,1 mg/kg ; < 30 ng/kg											
3 elemental contents in solid matter and eluate		mg/kg TR	mg/l	mg/kg TR		mg/kg TR								
pH *8	_						DIN 38404-C5	DIN 38404-C5		12,3	12,3			
DOC *9	mg/l							DIN EN 1484			72			
Phenol(index)	mg/l							DIN EN ISO 14402			0,09			
										mg/kg		mg/l		
Arsenic			0,2	40			DIN EN ISO 11885	DIN EN ISO 17294-2		28		0,004		
Lead			1	150	150	70	DIN EN ISO 11885	DIN EN ISO 17294-2		24		< 0,001		
Cadmium			0,1	1,5	1,5	1	DIN EN ISO 11885	DIN EN ISO 17294-2		3,6		< 0,0003		
Copper			5	900	100	40	DIN EN ISO 11885	DIN EN ISO 17294-2		430		< 0,005		
Nickel			1	80	50	50	DIN EN ISO 11885	DIN EN ISO 17294-2		14		< 0,001		
Mercury			0,02	1	1	0,5	DIN EN ISO 16772	DIN EN ISO 12846		< 0,01		< 0,0002		
Zinc			5	5000	400	150	DIN EN ISO 11885	DIN EN ISO 17294-2		2000		<0,01		
						for								
Chloride *12						clay and	DIN EN ISO 10304-0	DIN EN ISO 10304-1				28		
Sulfate *12						silty		DIN EN ISO 10304-1				3,3		
Cyanide (easily releasable)						soils		DIN EN ISO 14403				0,017		
Fluoride			15					DIN EN ISO 10304-1				< 0,2		
Barium			10					DIN EN ISO 17294-2				0,97		
Chrome (total)			1	300	100	60	DIN EN ISO 11885	DIN EN ISO 17294-2		73		0,023		
Chrome VI				2		for	DIN EN 15192	DIN EN ISO 17294-2		2,4				
Molybdenum			1			clay and		DIN EN ISO 17294-2				0,016		
Antimony *16			0,07			silty		DIN EN ISO 17294-2				< 0,001		
Selenium			0,05			soils	DIN EN ISO 17294-2	DIN EN ISO 17294-2		<0,5		0,002		
Thallium,				1			DIN EN ISO 17294-2			< 0,1				
Total content of dissolved solids *12	mg/l							DIN EN 15216				2000		
Electric conductivity	µS/cm						DIN EN 27888					1798		
4 additional regulations										% mg/l	mg/kg	mg/l	mg/l	
Sum of carbonate resp.														
Hydrogen carbonate														
Ca as CaO mineral acid-soluble							VDLUFA-Mhb II, 6.1.1			7				
Ca water-soluble							VDLUFA-Mhb II, 6.3			0,75				
basic effective minerals as CaO							VDLUFA-Mhb II 6.3			12	1?			
K as K2O							DIN EN ISO 11885			0,92				
Mg as MgO							VDLUFA-Mhb II, 6.1.1			1,1				
Na							DIN EN ISO 11885			90				
Fe														
Al														
Mn														
Si														
B (or)							DIN EN ISO 11885			100				
Co							DIN EN ISO 11885			2,6				
N ges (intentionally mentioned twice)							VDLUFA-Mhb II3.5.2.7		DIN 51732	0,4			0,47	
P als P2O5							DIN EN ISO 11885			0,31				
S ges							DIN EN ISO 11885		DIN 51724-3	990			990	
Cl ges									DIN EN ISO 10304-1, DIN 51727				286	
brown = Values for further characterisation of ash compounds respectively for evaluation relating to soil			acc. to Annex III											

Tab 1 Matrix of analysis data as suggestion for the estimation of recycling of solid residues

Despite the difficulties mentioned above, there are initial basic findings in the identification of residual substances which, among other things, supplement the scheme in Fig. 1 with data, which has already been used several times here. They also strengthen the approach of defining a field of characteristic properties of the said residual substances with as many fundamental considerations as

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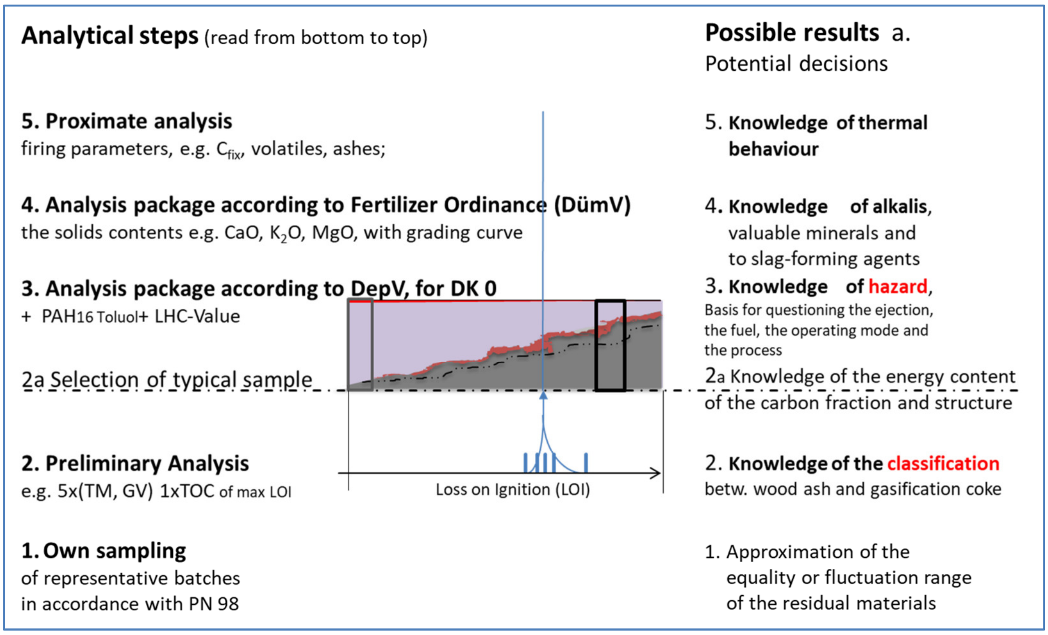
[11] which is why, following the Tar Protocol, reference is made here to the efforts to obtain the "Freiberger-PAH Protocol" [17]

possible and the knowledge of chemical interrelationships, which is gradually specified by analytical results. It was developed in cooperation with the R&D members of the WG TGB, based on generalized analyses of two market leaders, mainly SpannerRe² GmbH, and on the basis of work in the wood ash and vegetable charcoal industries. In line with a more and more intensive engagement with the regulations of waste and fertilizer management, the above-mentioned **analysis matrix** was created. In the meantime, specialist colleagues have been working with it to identify the properties of the residual materials as a whole and the relationships between their elements. It is annexed to this paper not only for the sake of better readability, but also as a recommendation to use it. Its matrix is continuously updated and is available as an electronic version to the members of a pool that has begun to work according to the (here simplified) principle of exchanging anonymised analyses. Further information can be obtained from the FEE e.V. office.

As an introduction to the identification of these residues, it is recommended to familiarise oneself with Appendices 3 and 4 of the Landfill Ordinance (DepV) [1][12] (or similar ordinances of the German Länder). This is also useful if land filling is not considered at all, because the Landfill Ordinance, in conjunction with the sampling regulations for waste [18][13], contains the most important information for analysing wood ash and wood gasification coke.

Those who are quite sure that they only have to analyse wood ash should join the Federal Quality Association for Wood Ash. But those who want to test whether their wood gasification coke has chances to serve soil improvement are advised to deal with the guidelines for the European Biochar Certificate EBC [18][14].

The colouring of the residues or their density (without specific know-how about the fuel and the concrete plant) do not allow a reliable differentiation between the groups of residues (ash:coke) [2]. In order to classify a residue stock that is black step by step, the following steps are proposed in simplified form as examples:



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[12] https://www.gesetze-im-internet.de/depv_2009/DepV.pdf
[13] https://www.laga-online.de/documents/m32_laga_pn98_1503993280.pdf,
[14] http://www.european-biochar.org/en/download.

Fig. 7 Staged analysis of solid residues

Such analyses allow the search for different energetic and/or material (up to primary carbon) uses, preferably as by-products or as chemically defined waste.

If stocks are sampled, it is advisable to observe the continuously occurring residues via the DM and LOI values and randomly also via PAH values for a longer operating phase in order to decide whether (or how) either wood ash or higher-grade coke can be obtained.

10. By-products from wood gasification ashes

Based on what has already been said, Figure 7 below shows an example of a wood ash broken down into its most important chemical elements. Furthermore, ways to their future increased re-use are sketched.

Reacted wood ashes, in contrast to wood gasification coke, are the residual materials that belong to the essence of gasification as an energy conversion technology. This applies if one takes to the main yardstick that developers, manufacturers and operators strive with it to transfer the energy of the raw material at the same time as largely as possible into the main products electricity and heat. All hydrocarbons that are not at least converted to deliver heat at the installation site and remain in the residual material reduce the conversion effect and complicate disposal/recycling. Wood ash is accordingly also the residual material that is produced in the most energy-efficient gasification process, counter-current gasification.

In the meantime, the majority of the plants currently in use have been designed in such a way that they repel wood ash as a residual material according to their design. (Therefore, the subsequent use of wood ash should be stimulated here first, before wood gasification coke is dealt with under point 11 below).

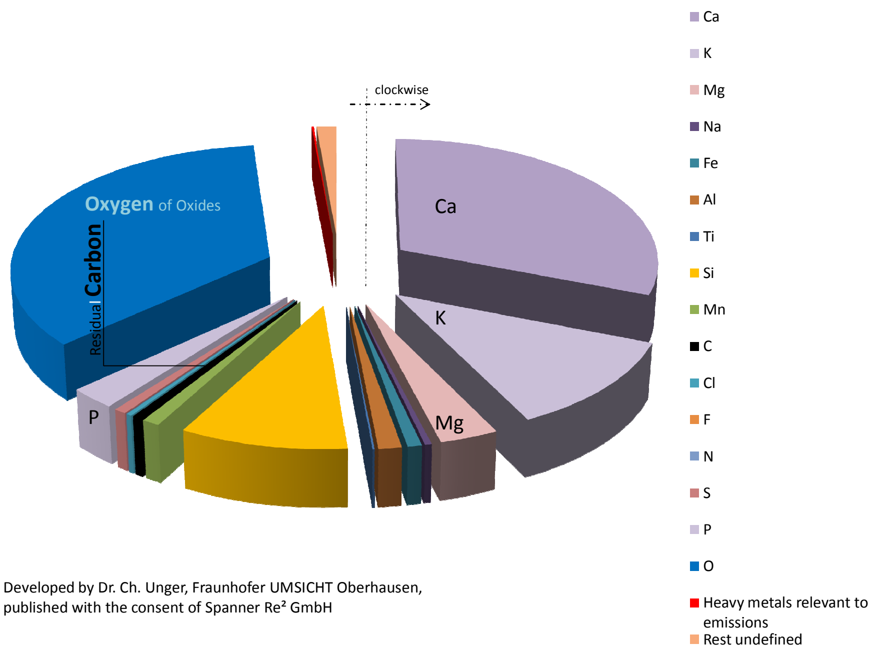

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Fig. 8 Typical composition of a wood ash of a wood gasification plant

The case shown is a wood ash from the afterburning of a direct current gasification with LOI< 5M%, which is also harmless in the other parameters, such as the dissolving behaviour and the content of heavy metals in the eluate. It stands for the fact that manufacturers and operators have a residue which can be disposed of in landfills and which fulfils the requirements to be able to produce by-products without separate cleaning.

What is striking about its composition is its relatively high proportion of the nutrients Ca, K, Mg and P and of oxides. Until now, such ashes have often been spread on fields (even if there are regulations for this), mostly under self-management, often at their own discretion or with a few control analyses[15]. Their inclusion in composting appears to be more favourable. In terms of recycling, the direction is correct, but it should be noted that the nutrients of the wood ash are usually produced in a different proportion than the crops and their soils require. Mixing into liquid manure is only apparently sensible because nitrogen is released in the process. It is therefore advisable to determine the composition more precisely and to offer and hand over the wood ash to fertilizer manufacturers. However, this has so far failed in the case of small-scale plants due to the fact that the residue volume is too low (< 5 to 10 t/a) and the quality proofs required, combined with specifically high analysis costs.

To overcome difficulties in relation to small quantities, the Federal Quality Association wood ash BGH (https://www.holzaschen.de) has been working for some time now, however, in relation to wood ash from combustion. For large wood combustion plants, it has already achieved that their ashes, for example, have become the starting material for the production of mixtures that are used for the remediation of forests through forest liming. As a subsequent step, there are indications that wood ash will increasingly be used to adjust the pH value in biowaste composting. The use of ashes as a component of fertilizer, as specified in Annex 1 of the DüMV [6] as a definition of fertilizer types, is firmly planned. The best possible utilisation of nutrients and trace substances is being worked on. At the same time, efforts are also being made to include small suppliers of wood ashes in such post-use variants by forming pools

It is possible to join these efforts by becoming a member of the BGH. The prerequisite is that the owners of wood ashes from thermo-chemical gasification must also prove their harmlessness and compliance with a quality band in accordance with DüMV analytically (over a period of time to be agreed). Land-filling should be used as the preliminary phase for this. Since wood gasification ashes are usually dustier than commercial fertilizers, it is necessary to produce grading curves and to work on dust handling in addition to chemical analyses (according to DüMV).

Knowledge should be expanded via stages for the greatest possible utilisation of the fertilising properties as far as possible in order to arrive at even higher-priced by-products. Therefore, contents of valuable elements such as potassium, boron and rare metals should be tracked more closely. With a better database than today, R&D should then make it possible to combine fertiliser production processes and the separation of metals, for example, and thus contribute to material cycles and additional income.

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[15] according to fertilizer ordinance

11. By-products of wood gasification coke

In analogy to the consideration of wood ash, thoughts on the possible uses of wood gasification coke shall now be derived from its characteristic chemical composition on the basis of an example of wood gasification coke.[16]

Compared to the wood ash of gasification, wood gasification coke has accompanied the technical development of direct current [fixed and fluidized bed] technologies more sensationally and is thus externally even regarded as the typical residual material for the industry. In the meantime, however, it has become primarily an intermediate product and only a qualitatively defined residual material in 3 out of 12 technologies which is discharged and sorted.

Of course, wood gasification coke batches with strongly fluctuating carbon content and with TOC< 50M% as a problem substance continue to be produced. They must be discharged and disposed of. However, these batches are rarely the result of inadequate design, but originate from malfunctions and/or improper operation, from which there are still enough cases. Such coke then remains rather unsuitable to be led to the by-product. But wood gasification coke of the three companies already mentioned above, which determine the state of the art in residual materials, has a carbon content in the 80 M% range and elementary compositions within relatively narrow limits. Their wood gasification coke has almost evolved from the original sign of procedural shortcomings (without and with organic load) to a mark of quality for know-how.

Today, wood gasification coke is produced by technologies that either generate pyrolysis coke specifically developed and transfer parts of it out, as is the case with the Syncraft® concept. However, it is also the result of weighing up the advantages and disadvantages in the area of conflict between demands for high gas quality and system availability on the one hand and appropriate technical expenditure on the other. This applies to the technologies of Burkhardt GmbH and Stadtwerke Rosenheim GmbH & Co. KG, which do accept carbon that has not been fully converted. However, each of the above-mentioned process carriers has developed its own specific waste disposal system.

- Syncraft GmbH has been working towards the generation and partial ejection of a third party product behind her (low-temperature-) gasification stage, which is now certified and released as a by-product "vegetable coal" in compliance with the limit value for PAK16.
- Burkhardt GmbH has succeeded in classifying polluted residues, which are discharged as polluted filter residues after gasification, as a by-product in view of paying consumers who are particularly interested in accordance with the EC Waste Framework Directive [4] via a “REACH procedure”. In this way, it has given itself and its customers the freedom to trade the untreated residual material like a product. The use itself is one of the company's confidential information.
- Stadtwerke Rosenheim GmbH & Co. KG are working in conjunction with an incineration plant approved in accordance with the 17th BImSchV to expand the incineration process for wood gasification coke, which is also organically contaminated, by the use of waste corresponding to the code number 10 01 18* (waste from waste gas treatment containing hazardous substances) and thus corresponds to wood gasification coke. In the event of a positive outcome, this would

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[16] Due to the concentration on small dimensioned systems, coke from fluidized bed gasification is not considered.

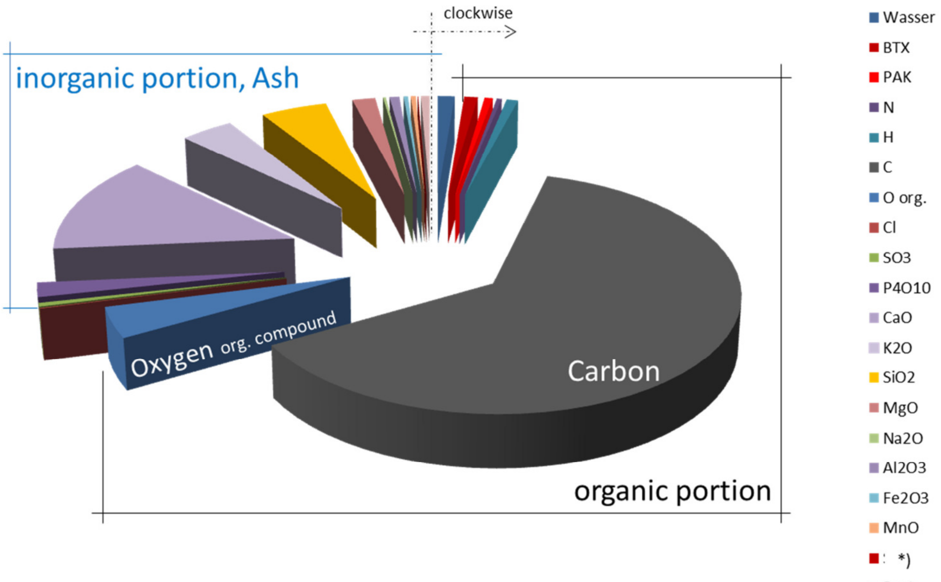
be the first thermal utilisation of a contaminated wood gasification coke in Germany to be accepted under waste disposal law. It would be, if not legally so nevertheless physico-chemically, a by-product.

One year ago, all these efforts were considered too costly and unlikely to be successful. Although they are tied to special circumstances and also to special personal commitment, they also provide an incentive to test and tread similar paths to the use of wood gasification coke. If in this way wood gasification coke becomes increasingly valuable, the concepts presented also give the impetus to examine whether the processes working today with the combustion and afterburning of filter residues (from less defined wood gasification coke) should be retained in the long term. With regard to small scale plants, the search for an approved service provider, who bases his business model on wood gasification coke recycling, is always necessary. In order to promote both the internal and external solution of such questions, Fig. 8 presents a wood gasification coke in its chemical composition, which rather describes the middle field between high-quality and the typical wood gasification coke occurring at filters.

This wood gasification coke is characterized by TOC < 50 M% and 60% < LOI < 85M%. It also originates from a direct current process but without post-treatment and is considered a hazardous substance due to the limit values of benzene and PAH_{16} (highlighted in red) being exceeded. Due to its genesis at temperatures between 1000 and 1200 °C it has a higher stability and a different porosity than coke from pyrolysis. Proposition: Its carbon skeleton should be worth more than its calorific value.

The organic loads can be degraded using hot N, CO_2 and water vapour [16], which opens up the possibility of releasing or further processing the carbon skeleton into a relatively pure and thus usable carbon. Pure dust-like defined carbon structures are of great importance in the technical discussion. This means that wood gasification coke has a good chance of being converted into structures in demand compared to other initial carbon yields, which must be explored. It is fine-grained, dry and already has the microstructures that have to be produced from other raw biomass by pyrolysis or hydrothermal carbonisation (HTC).

In connection with the accompanying elements from the ash, which are largely soluble or detachable or can be useful for special applications, there are also expectations of carbon for micro assemblies or specific adsorbents. In this context, for example, it should also be investigated to what extent indi-



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*) Heavy metals, relevant to emission

Fig. 9 Typical composition of wood gasification coke

vidual salts or metal compounds of wood gasification coke can influence carbon reactions in a directed manner. Carbon with defined pores, which can be adjusted during processing [16], is a valuable material. If wood gasification coke confirms itself as suitable for physicochemical applications, which is to be tested further, then it is absolutely to be aimed at, to process it in small batches high-quality instead of setting it off as mass product.

Nevertheless, it seems appropriate to orientate the production of (or purification into) unpolluted wood gasification coke first at the criteria for vegetable charcoal [19]. By means of recycling stages, e.g. the addition to composting, it should be possible to explore the coke even more precisely. It seems to be confirmed that its pores are the most important good in it, also because they create a habitat for microorganisms. This would allow unpolluted coke (and "unpolluted" coke must be emphasised because it is already used in uncontrolled practice in anticipation of soil improvement) to be brought into effect in the sense of recirculation, as initially envisaged under point 3.

There is much to be said for developing contacts with the plant coal industry, e.g. the Fachverband Pflanzenkohle e. V., www.fvpk.de, and its European representatives, www.ithaka-institut.org. Although their certification conditions [19] do not apply to biomasses charred by gasification, they are a benchmark introduced into practice to determine and negotiate soil-compatible (post) uses of non-hazardous wood gasification coke, as Syncraft® has succeeded in doing (but with coke from pyrolysis). In addition, cooperation with the manufacturers of biomass-based activated carbons is likely to be helpful.

As with wood ash, the dust form is an advantage in terms of process and physicochemical properties for wood gasification coke, but a challenge in terms of handling. Depending on the use, a technical compromise has to be made between the accumulation and use form. Until now, the particle size distribution was too fluctuating for dust firing systems. Pelletizing was often limited by tool wear.

Therefore, pelletizing should be followed up and the transfer into slurry should be considered and tested.

It is becoming apparent that wood gasification coke is a valuable raw material for by-products. If it cannot be generated unpolluted or reused polluted, there is much to be said for leading it to high-quality (by-products) by processing. This seems unlikely at decentralised locations, which is why there is again a field for cross-process R&D here, including legal and logistics issues. It should also be investigated to what extent individual salts or metal compounds of wood gasification coke influence or promote carbon reactions.

12. Recommendations

Residual materials from thermo-chemical wood gasification are not by-products when they are produced (unless they originate from processes which, in addition to electricity and heat, have already been oriented towards a third product during development). They can become by-products as soon as it has been clarified by a preliminary analysis whether they represent wood ash or wood gasification coke and whether, or to what extent, they are either heavy metallic or organic afflicted. Owners of residual substances who illegally dispose of such substances without this knowledge, regardless of the country, endanger the further development of biomass gasification technology. This also applies to developers and manufacturers who leave their customers in the dark about the ingredients.

Anyone striving for by-products must analytically clarify the composition of their residual materials to such an extent that based on the obligation to discharge an offer can be formed which meets with demand for exactly this substance. This is most likely to be the case for unpolluted wood ashes. It is more complicated for organically contaminated wood gasification coke, especially for small quantities.

There are no easy ways to convert residues to by-products, but there is (as was attempted to show in the article) a basic order of paths to move from unknown residues to by-product options. There are no legal ways without effort, but this can be reduced by considerations based on systematic analyses, most advantageously in cooperation.

The aspects related to the solid residues discussed here concern all biomass gasification technologies. Most of them are independent of the size of the plant. If, in addition, the protection of workers and the environment is recognised as a basic prerequisite, then questions regarding residual materials for wood ash or wood gasification coke at all sites must be clarified in a similar way.

The IEAGasification Group Task 33 is therefore proposed to use its nationwide capabilities to raise with the gasification community decision-makers understanding of the following issues:

- The mass of solid residues, which arise untreated during thermo-chemical gasification, consist of valuable substances, which, however, are mostly contaminated with heavy metals organic compounds, which must be determined analytically for each plant.
- Solid residual materials from all bioenergy technologies originate from nature and are gradually returned to the cycle of substances, while strictly respecting the protection of people and the environment.

- Recycling operations have technically and organisationally lower limits, but from a capacity of approx. 25 KWel, collection disposal operations and, growing from this, collection recycling operations should be checked.

The committee is specifically recommended to contribute in a timely manner through e.g. workshops, position papers and projects, as well as technical, legal and organisational work:

- Development of a practicable guideline for the identification of the hazard (y/n) of mixtures of substances, derived from the CLP regulations (regarding parameters, limit values, associated analyses)
- Clarification of the actual hazards posed by contaminated residues to humans and the environment (with determination and consideration of the adsorption capacity especially for PAH16 and benzene)
- Modification of analytical methods regarding carbon-dominated matrices, i.e. for analyses from wood gasification ash to coke, especially for the determination of PAH16, benzene, phenols; but also regarding: LOI; TOC; TC, TIC u. $C_{elementary}$; C_{fix}, volatiles and ash
- Design of the analysis pool and creation of a data base on the overall composition of wood gasification ash up to coke
- Bringing together European manufacturers and operators to prepare and obtain their own key numbers in the European Waste Catalogue and the Waste Catalogue Ordinance – AVV [20]
- Waste legal simplification of the thermal utilisation of wood gasification coke on the basis of adapted emission-safe / tested small dimensioned wood combustion plants

The Task 33 of the IEA is requested to apply for projects of a basic nature and to work on them in cooperation with members, thus contributing to the clarification of the following interrelations:

- the basic chemical and physical relationship of carbons and carbon compounds in solid residues, in conjunction with the C-structure and pore distribution, in relation to their properties (especially adsorption and desorption)
- the combustion, explosion and fire protection technical data from real wood gasification ashes up to coke; tests, derivation of practicable protective measures
- the physical-chemical properties of potentially value-generating constituents of wood gasification ashes and coke

Concluding remark

The team of WG TGW would like to thank National Delegate for Switzerland, Task 33 IEA Bioenergy, Mr. Martin Rüegsegger for the opportunity to enter this contribution into the discussion and is ready for further cooperation.

The contribution was teamwork and stands for a gradual examination of the problems of solid residual materials in wood gasification. It was mainly supported by the market-leading companies in DE, supplemented by the participation of scientists, both as members of the aforementioned WG. The author would like to thank Spanner RE² GmbH and Dr. Christoph Unger of Fraunhofer UMSICHT for the many references to basic relationships in thermo-chemistry, in particular on behalf of the opportunity to generalize knowledge here. He thanks Kristina Hermann, Dr. Ingo Rickert for the editorial support and Dr. Georg Wagener-Lohse for the final version.

Altlandsberg, 10th of September 2018

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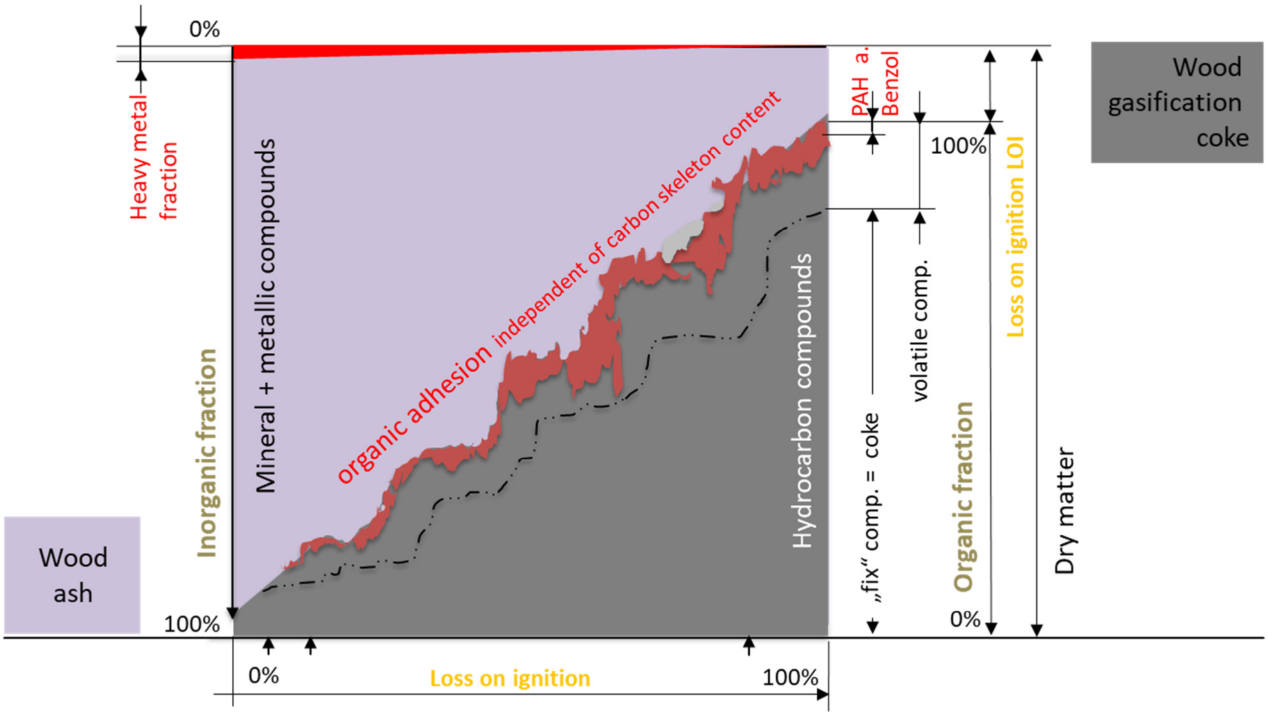


Fig. 1 Order of residues from thermo-chemical biomass gasification via the annealing losses

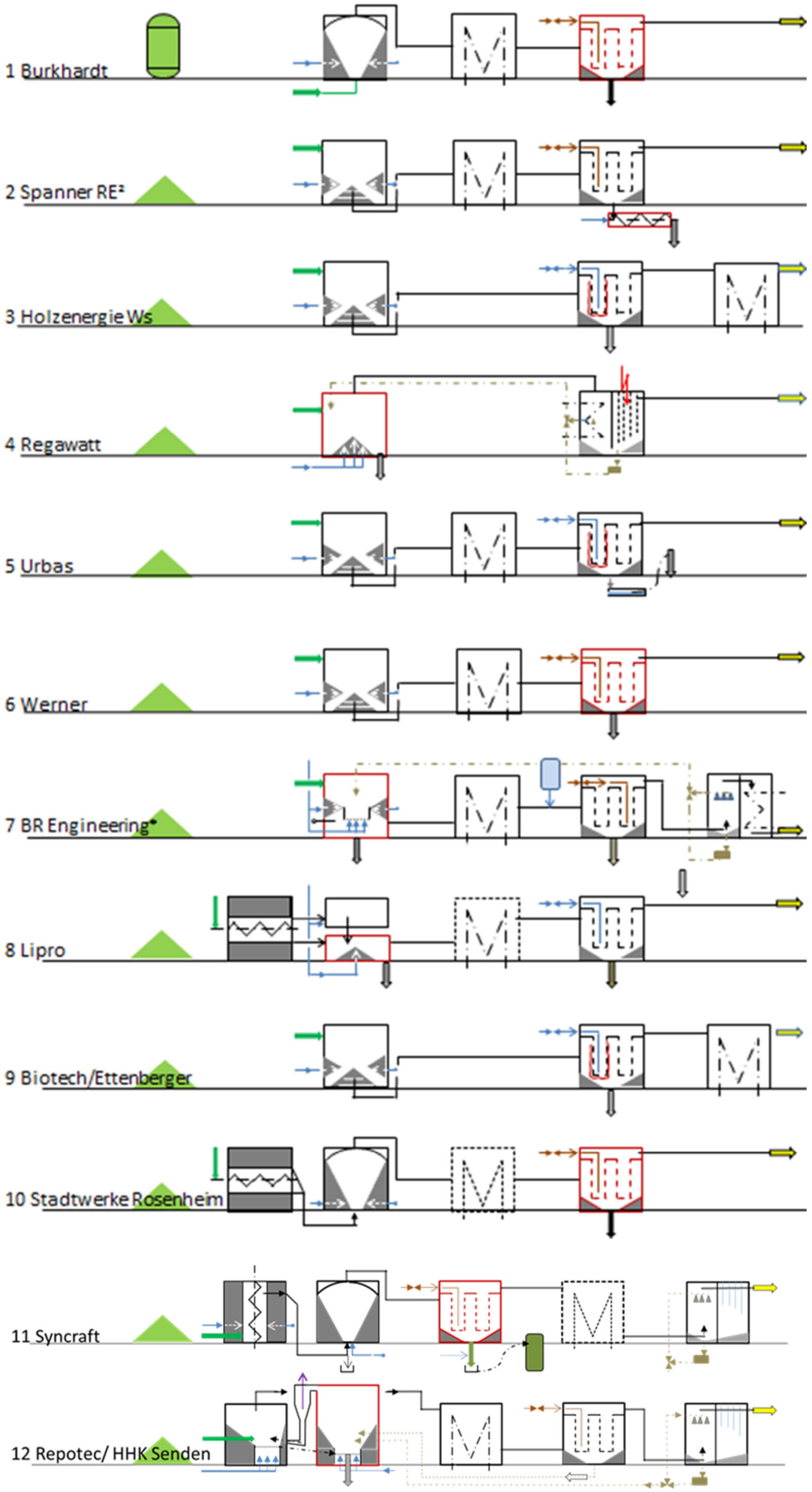
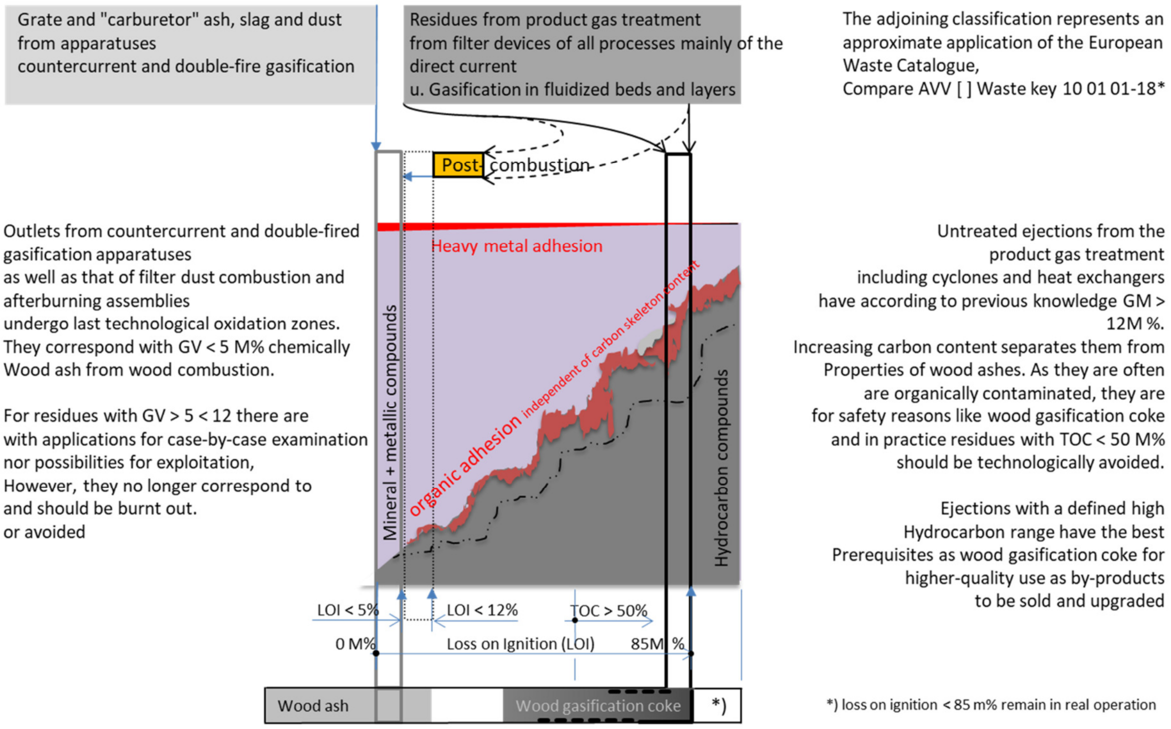


Fig. 2 Plant concepts for thermo-chemical wood gasification and its ejections



Grate and "carburetor" ash, slag and dust from apparatuses countercurrent and double-fire gasification

Residues from product gas treatment from filter devices of all processes mainly of the direct current u. Gasification in fluidized beds and layers

The adjoining classification represents an approximate application of the European Waste Catalogue, Compare AVV [ ] Waste key 10 01 01-18*

Outlets from countercurrent and double-fired gasification apparatuses as well as that of filter dust combustion and afterburning assemblies undergo last technological oxidation zones. They correspond with GV < 5 M% chemically Wood ash from wood combustion.

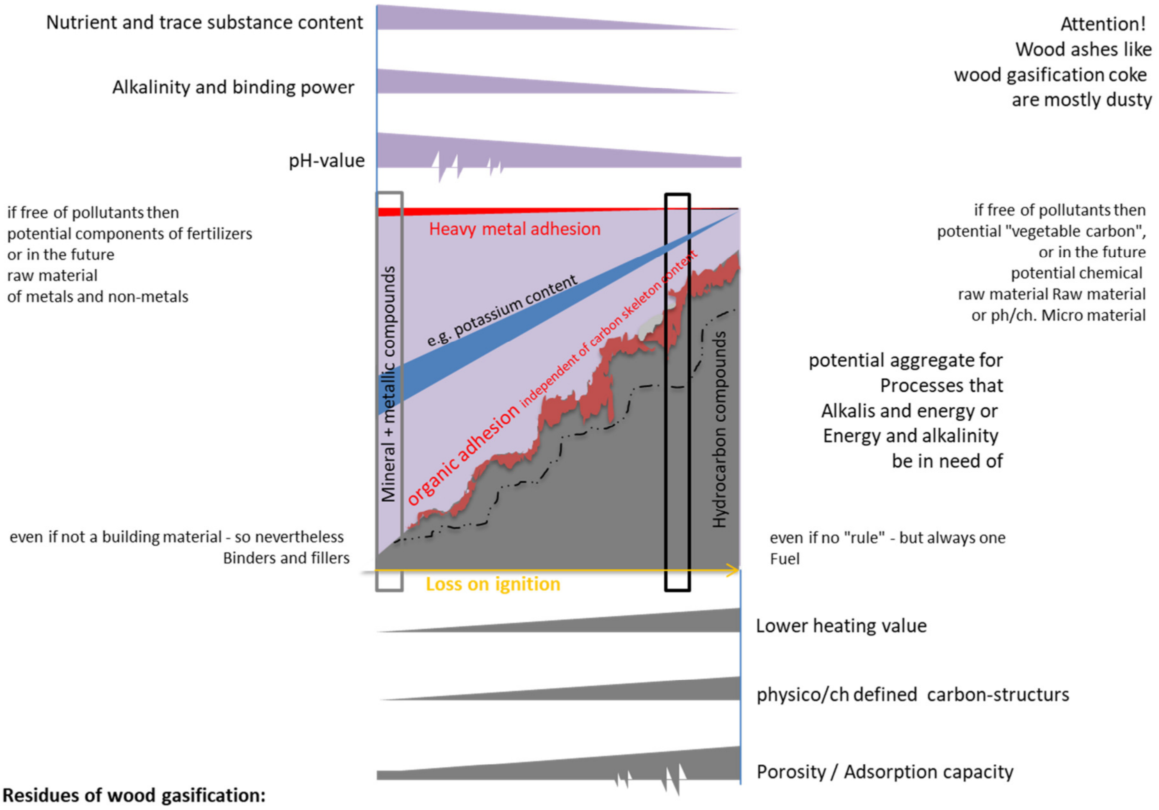
For residues with GV > 5 < 12 there are with applications for case-by-case examination nor possibilities for exploitation, However, they no longer correspond to and should be burnt out. or avoided

Untreated ejections from the product gas treatment including cyclones and heat exchangers have according to previous knowledge GM > 12M %. Increasing carbon content separates them from Properties of wood ashes. As they are often are organically contaminated, they are for safety reasons like wood gasification coke and in practice residues with TOC < 50 M% should be technologically avoided.

Ejections with a defined high Hydrocarbon range have the best Prerequisites as wood gasification coke for higher-quality use as by-products to be sold and upgraded

*) loss on ignition < 85 m% remain in real operation

Fig. 3 Outward transfers of thermo-chemical wood gasification sorted according to their proportion of wood ash and wood gasification coke



Attention! Wood ashes like wood gasification coke are mostly dusty

if free of pollutants then potential components of fertilizers or in the future raw material of metals and non-metals

if free of pollutants then potential "vegetable carbon", or in the future potential chemical raw material Raw material or ph/ch. Micro material

potential aggregate for Processes that Alkalis and energy or Energy and alkalinity be in need of

even if not a building material - so nevertheless Binders and fillers

even if no "rule" - but always one Fuel

Residues of wood gasification:
are potential valuable substances, which are however mostly still loaded with organic matter or heavy metals

Fig. 4 Residual materials of thermo-chemical wood gasification sorted according to their basic characteristics (both are enlarged in the appendix)

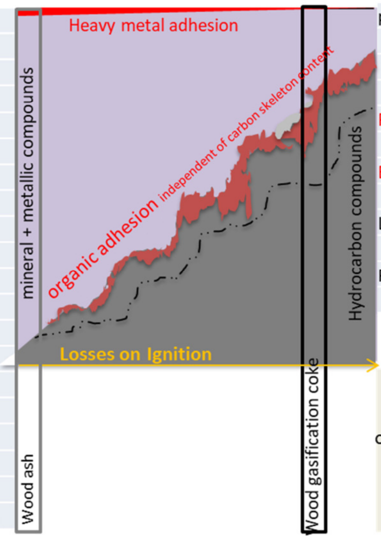
potential hazards to wood ash from
alkalinity

dust loads
as well as
heavy metal concentration

potential hazard to wood gasification coke from
Alkalinity,
spontaneous combustibility,
Flammability and
dust explosion capability as well as
organic adhesion

Concentration limits for inorganic and for organic constituents

parameter	concentration limit in the solids in %	concentration limit in eluate mg/l
Antimony		> 0,07
Arsenic	> 0,1 %	> 0,2
Barium		> 10
lead	> 0,1 %	> 1
Cadmium	> 0,1 %	> 0,1
Chrom. total	> 0,1 %	> 1
Copper	> 0,1 %	> 5
Molybdenum		> 1
Nickel	> 0,1 %	> 1
mercury	?	> 0,02
Selenium		> 0,05
Talium	> 0,1 %	
Zinc	> 0,1 %	> 5
Fluorid		> 15
Hydro carbon	> 8000 mg/kg	
	§ 3 AVV 12/2001	gem. "Hinw" Anh. III

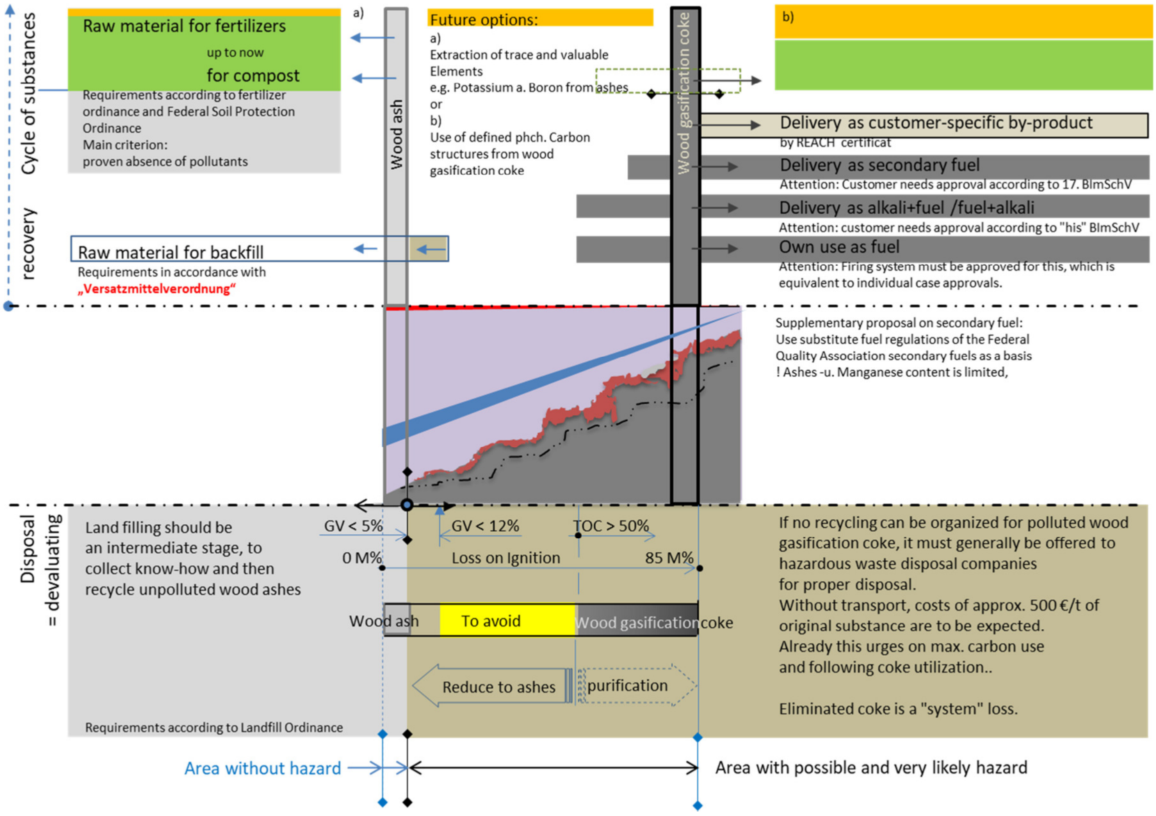


parameter		concentration limit in solids in %
PAH	As sum of 16 PAh acc. EPA and	0,1
	separate Benzo(a)pyren -rating	0,005
BTX	Of which (only)	
	Benzene	0,1
LHC	Total or	0,1
	Each including 11 LHKW of (Cat. 1 o.2)	0,1
PCB	as (6 Ballschmiter-Kongenere) x 5	
		0,005

For the approach to danger it is recommended to continue using the "Notes on the Application of the AVV of 10.12.2001 pers. to BGBl I p.3379", which were replaced by the AVV 2017 and whose limit concentrations are given here as a guide (more in the text)

Solid residues of the wood gasification are:
generally harmless as wood ashes, but wood gasification coke must be classified as non-hazardous or dangerous by analysis.

Fig. 5 Residual materials from thermo-chemical wood gasification - limits of hazard



Requirements according to fertilizer ordinance and Federal Soil Protection Ordinance
Main criterion:
proven absence of pollutants

Requirements in accordance with „Versatzmittelverordnung"

Future options:
a)
Extraction of trace and valuable Elements
e.g. Potassium a. Boron from ashes
or
b)
Use of defined phch. Carbon structures from wood gasification coke

Attention: Customer needs approval according to 17. BImSchV

Attention: customer needs approval according to "his" BImSchV

Attention: Firing system must be approved for this, which is equivalent to individual case approvals.

Supplementary proposal on secondary fuel:
Use substitute fuel regulations of the Federal Quality Association secondary fuels as a basis
! Ashes -u. Manganese content is limited,

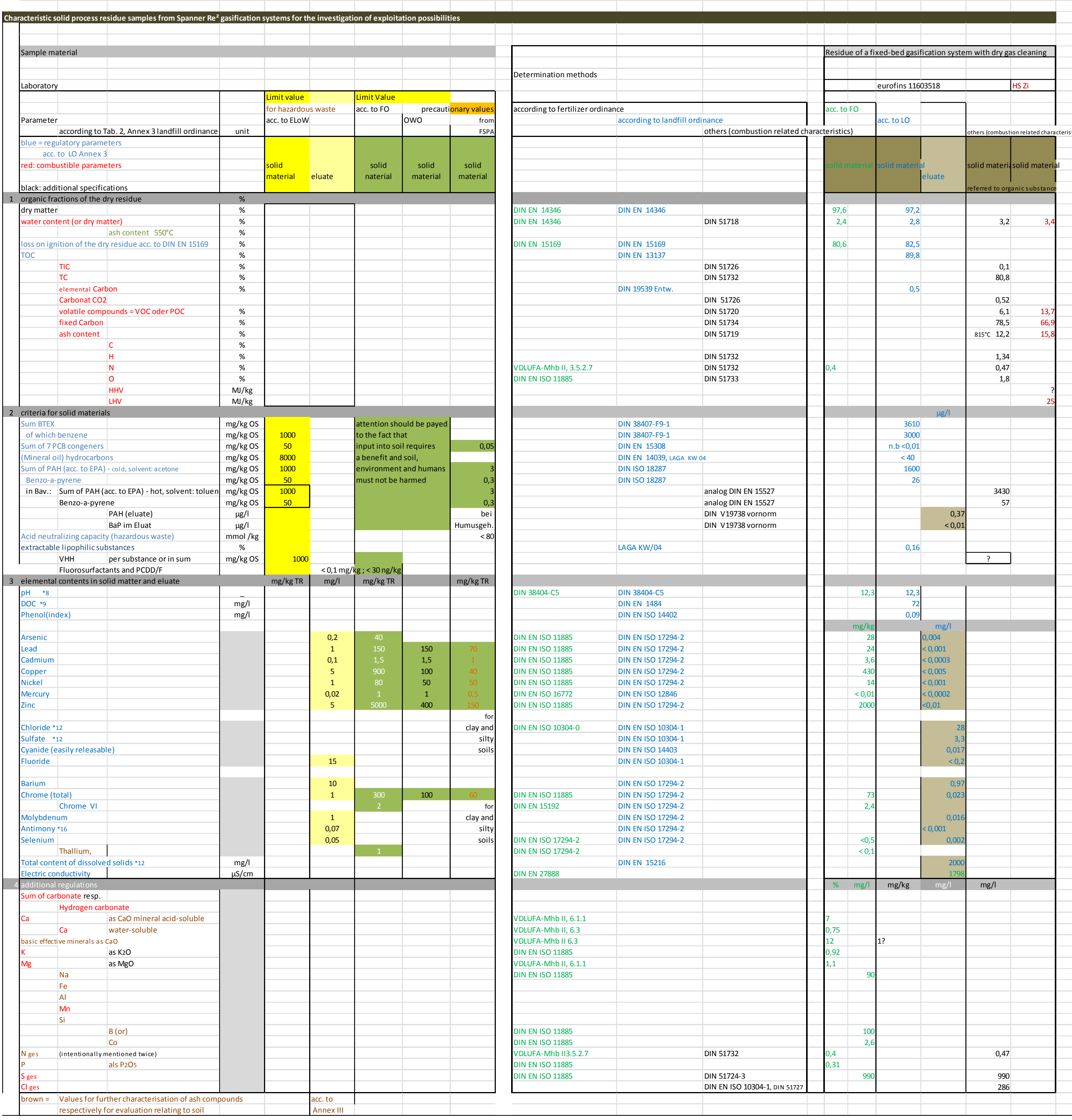
Land filling should be an intermediate stage, to collect know-how and then recycle unpolluted wood ashes

Requirements according to Landfill Ordinance

If no recycling can be organized for polluted wood gasification coke, it must generally be offered to hazardous waste disposal companies for proper disposal.
Without transport, costs of approx. 500 €/t of original substance are to be expected.
Already this urges on max. carbon use and following coke utilization..

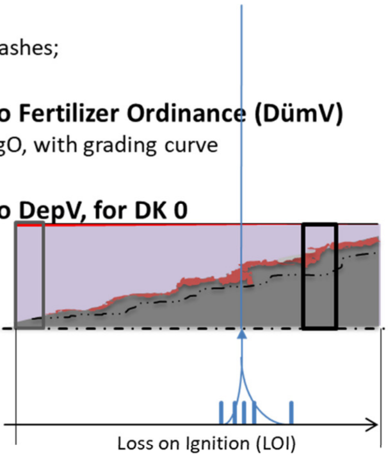
Eliminated coke is a "system" loss.

Fig. 6 Residual materials from thermo-chemical wood gasification - recycling options



Characteristic solid process residue samples from Spanner Re^2 gasification systems for the investigation of exploitation possibilities															
	Sample material										Residue of a fixed-bed gasification system with dry gas cleaning				
								Determination methods							
	Laboratory											eurofins 11603518			HS Zi
			Limit value		Limit Value										
			for hazardous waste		acc. to FO		precautionary values	according to fertilizer ordinance			acc. to FO				
	Parameter		acc. to ELoW			OWO	from		according to landfill ordinance			acc. to LO			
	according to Tab. 2, Annex 3 landfill ordinance	unit					FSPA			others (combustion related characteristics)				others (combustion related characteris	
	blue = regulatory parameters														
	acc. to LO Annex 3														
	red: combustible parameters		solid material	eluate	solid natrial	solid material	solid material				solid material	solid material	eluate	solid materi	solid material
	black: additional specifications													referred to organic substance	
1	organic fractions of the dry residue	%													
	dry matter	%						DIN EN 14346	DIN EN 14346		97,6	97,2			
	water content (or dry matter)	%						DIN EN 14346		DIN 51718	2,4	2,8		3,2	3,4
	ash content 550°C	%													
	loss on ignition of the dry residue acc. to DIN EN 15169	%						DIN EN 15169	DIN EN 15169		80,6	82,5			
	TOC	%							DIN EN 13137			89,8			
	TIC	%								DIN 51726				0,1	
	TC	%								DIN 51732				80,8	
	elemental Carbon	%							DIN 19539 Entw.			0,5			
	Carbonat CO$_2$									DIN 51726				0,52	
	volatile compounds = VOC oder POC	%								DIN 51720				6,1	13,7
	fixed Carbon	%								DIN 51734				78,5	66,9
	ash content	%								DIN 51719				815°C 12,2	15,8
	C	%													
	H	%								DIN 51732				1,34	
	N	%						VDLUFA-Mhb II, 3.5.2.7		DIN 51732	0,4			0,47	
	O	%						DIN EN ISO 11885		DIN 51733				1,8	
	HHV	MJ/kg													?
	LHV	MJ/kg													25
2	criteria for solid materials												µg/l		
	Sum BTEX	mg/kg OS			attention should be payed				DIN 38407-F9-1			3610			
	of which benzene	mg/kg OS	1000		to the fact that				DIN 38407-F9-1			3000			
	Sum of 7 PCB congeners	mg/kg OS	50		input into soil requires		0,05		DIN EN 15308			n.b <0,01			
	(Mineral oil) hydrocarbons	mg/kg OS	8000		a benefit and soil,				DIN EN 14039, LAGA KW 04			< 40			
	Sum of PAH (acc. to EPA) - cold, solvent: acetone	mg/kg OS	1000		environment and humans		3		DIN ISO 18287			1600			
	Benzo-a-pyrene	mg/kg OS	50		must not be harmed		0,3		DIN ISO 18287			26			
	in Bav.: Sum of PAH (acc. to EPA) - hot, solvent: toluen	mg/kg OS	1000				3			analog DIN EN 15527				3430	
	Benzo-a-pyrene	mg/kg OS	50				0,3			analog DIN EN 15527				57	
	PAH (eluate)	µg/l					bei			DIN V19738 vornorm			0,37		
	BaP im Eluat	µg/l					Humusgeh.			DIN V19738 vornorm			< 0,01		
	Acid neutralizing capacity (hazardous waste)	mmol /kg					< 80								
	extractable lipophilic substances	%							LAGA KW/04			0,16			
	VHH per substance or in sum	mg/kg OS	1000											?	
	Fluorosurfactants and PCDD/F			< 0,1 mg/kg ; < 30 ng/kg											
3	elemental contents in solid matter and eluate		mg/kg TR	mg/l	mg/kg TR		mg/kg TR								
	pH *8	_						DIN 38404-C5	DIN 38404-C5		12,3	12,3			
	DOC *9	mg/l							DIN EN 1484			72			
	Phenol(index)	mg/l							DIN EN ISO 14402			0,09			
											mg/kg		mg/l		
	Arsenic			0,2	40			DIN EN ISO 11885	DIN EN ISO 17294-2		28		0,004		
	Lead			1	150	150	70	DIN EN ISO 11885	DIN EN ISO 17294-2		24		< 0,001		
	Cadmium			0,1	1,5	1,5	1	DIN EN ISO 11885	DIN EN ISO 17294-2		3,6		< 0,0003		
	Copper			5	900	100	40	DIN EN ISO 11885	DIN EN ISO 17294-2		430		< 0,005		
	Nickel			1	80	50	50	DIN EN ISO 11885	DIN EN ISO 17294-2		14		< 0,001		
	Mercury			0,02	1	1	0,5	DIN EN ISO 16772	DIN EN ISO 12846		< 0,01		< 0,0002		
	Zinc			5	5000	400	150	DIN EN ISO 11885	DIN EN ISO 17294-2		2000		<0,01		
							for								
	Chloride *12						clay and	DIN EN ISO 10304-0	DIN EN ISO 10304-1				28		
	Sulfate *12						silty		DIN EN ISO 10304-1				3,3		
	Cyanide (easily releasable)						soils		DIN EN ISO 14403				0,017		
	Fluoride			15					DIN EN ISO 10304-1				< 0,2		
	Barium			10					DIN EN ISO 17294-2				0,97		
	Chrome (total)			1	300	100	60	DIN EN ISO 11885	DIN EN ISO 17294-2		73		0,023		
	Chrome VI				2		for	DIN EN 15192	DIN EN ISO 17294-2		2,4				
	Molybdenum			1			clay and		DIN EN ISO 17294-2				0,016		
	Antimony *16			0,07			silty		DIN EN ISO 17294-2				< 0,001		
	Selenium			0,05			soils	DIN EN ISO 17294-2	DIN EN ISO 17294-2		<0,5		0,002		
	Thallium,				1			DIN EN ISO 17294-2			< 0,1				
	Total content of dissolved solids *12	mg/l							DIN EN 15216				2000		
	Electric conductivity	µS/cm						DIN EN 27888					1798		
4	additional regulations										% mg/l	mg/kg	mg/l	mg/l	
	Sum of carbonate resp.														
	Hydrogen carbonate														
	Ca as CaO mineral acid-soluble							VDLUFA-Mhb II, 6.1.1			7				
	Ca water-soluble							VDLUFA-Mhb II, 6.3			0,75				
	basic effective minerals as CaO							VDLUFA-Mhb II 6.3			12	1?			
	K as K$_2$O							DIN EN ISO 11885			0,92				
	Mg as MgO							VDLUFA-Mhb II, 6.1.1			1,1				
	Na							DIN EN ISO 11885			90				
	Fe														
	Al														
	Mn														
	Si														
	B (or)							DIN EN ISO 11885			100				
	Co							DIN EN ISO 11885			2,6				
	N ges (intentionally mentioned twice)							VDLUFA-Mhb II3.5.2.7		DIN 51732	0,4			0,47	
	P als P$_2$O$_5$							DIN EN ISO 11885			0,31				
	S ges							DIN EN ISO 11885		DIN 51724-3	990			990	
	Cl ges									DIN EN ISO 10304-1, DIN 51727				286	
	brown = Values for further characterisation of ash compounds			acc. to											
	respectively for evaluation relating to soil			Annex III											

Tab. 1 Matrix of analysis data as suggestion for the estimation of recycling of solid residues



Analytical steps (read from bottom to top)	**Possible results** a. Potential decisions
5. Proximate analysis firing parameters, e.g. C_{fix}, volatiles, ashes;	5. **Knowledge of thermal behaviour**
4. Analysis package according to Fertilizer Ordinance (DümV) the solids contents e.g. CaO, K_2O, MgO, with grading curve	4. **Knowledge of alkalis**, valuable minerals and to slag-forming agents
3. Analysis package according to DepV, for DK 0 + PAH16 Toluol+ LHC-Value	3. **Knowledge of hazard**, Basis for questioning the ejection, the fuel, the operating mode and the process
2a Selection of typical sample	2a Knowledge of the energy content of the carbon fraction and structure
2. Preliminary Analysis e.g. 5x(TM, GV) 1xTOC of max LOI	2. **Knowledge of the classification** betw. wood ash and gasification coke
1. Own sampling of representative batches in accordance with PN 98	1. Approximation of the equality or fluctuation range of the residual materials

Fig. 7 Staged analysis of solid residues

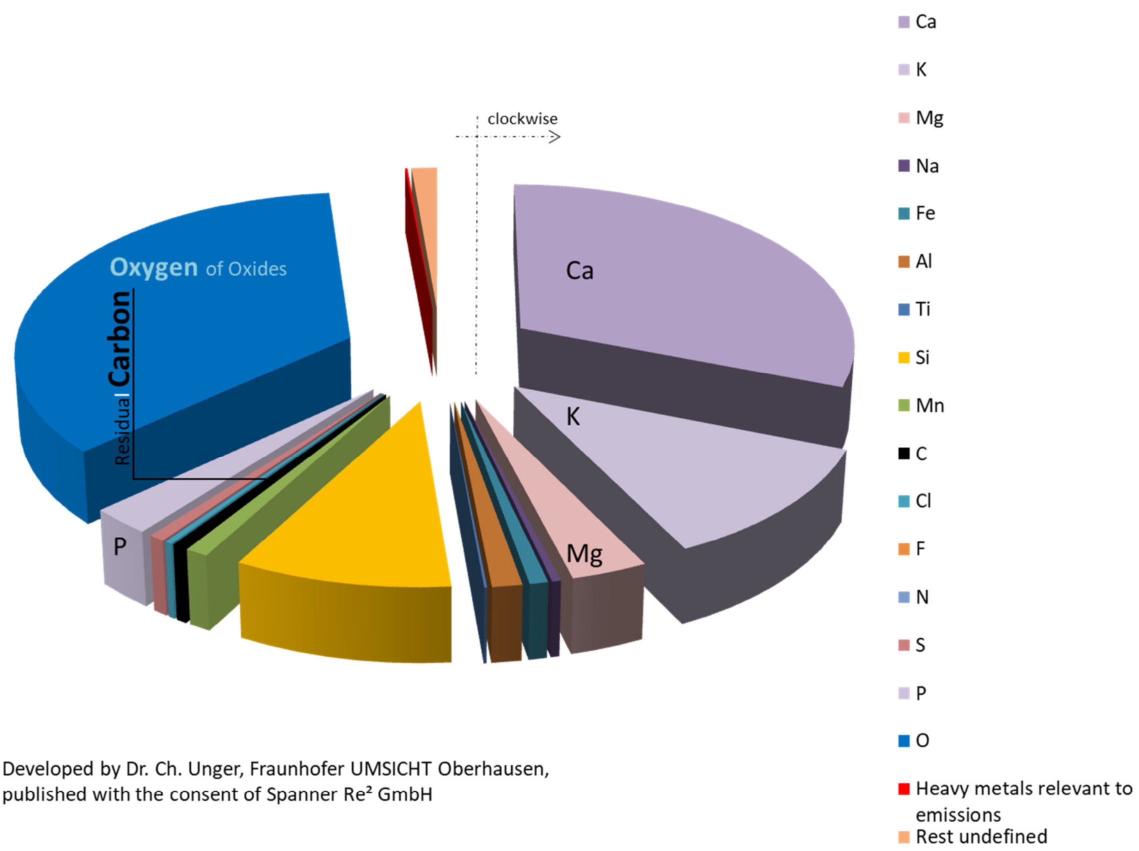


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Fig. 8 Typical composition of a wood ash of a wood gasification plant

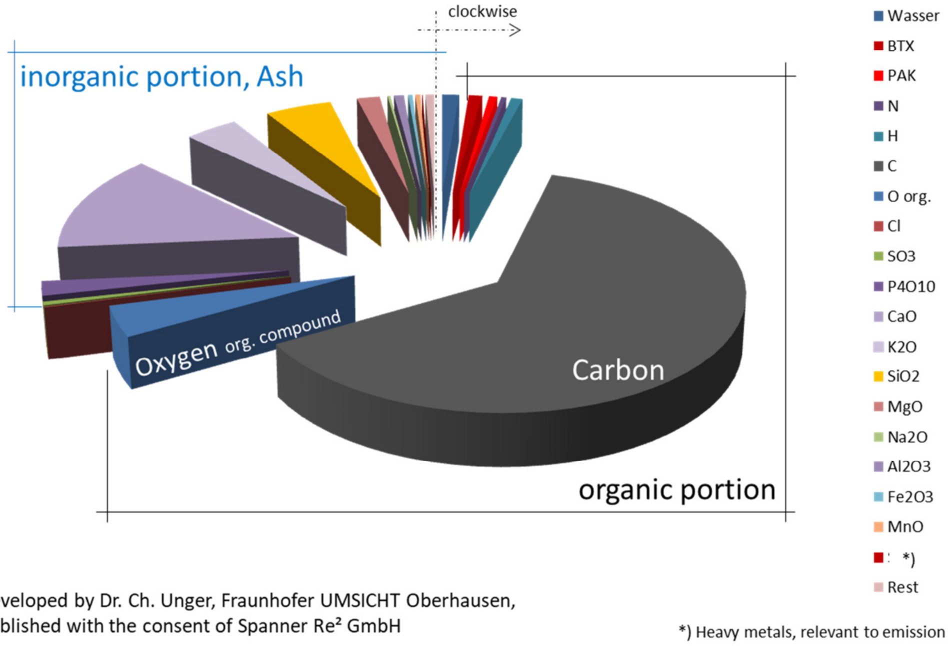

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Fig. 9 Typical composition of wood gasification coke