MUSIC

Market Uptake Support for Intermediate Bioenergy Carriers

WHITE PAPER: BIOCHAR FOR INDUSTRIAL APPLICATIONS

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Contents

List of Acronyms

BFG – Blast Furnace Gas
CMC – Component Material Category
CO_2 - Carbon Dioxide
COG - Coke Oven Gas
CRI Coke Reactivity Index
CSR - Coke Strength after Reaction
EBC – European Biochar Certificate
EC - European Commission
FC – Fixed Carbon
GHG - Greenhouse gases
IBC – Intermediate Bioenergy Carrier
PAHs - polycyclic aromatic hydrocarbons
PC - Pulverized Coal
PCDD/Fs - dioxins
PCI - Pulverized Coal Injection
PFC – Product Function Category
PFRs - persistent free radicals
TC – Total Carbon
VOCs - volatile organic compounds

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1 Introduction

Intermediate bioenergy carriers (IBCs) are biomass that are processed to energetically denser materials, analogous to oil, coal, and gaseous fossil energy carriers. This means they are easier to transport, store and use.

The **EU H2020 MUSIC** project supports the market uptake of Intermediate Bioenergy Carriers (IBCs) by developing feedstock mobilisation strategies, improved cost-effective logistics and trade centres.

IBCs are formed when biomass is processed to energetically denser, storable, and transportable intermediary products analogous to coal, oil and gaseous fossil energy carriers. They can be used directly for heat or power generation or further refined to final bioenergy or bio-based products. IBCs contribute to energy security, reduce greenhouse gas emissions, and provide a sustainable alternative to fossil fuels in Europe.

Biochar is one such IBC; it is the solid carbonaceous material originated from the thermochemical conversion of organic matter via pyrolysis or gasification.

This document provides an overview of biochar **production processes** and **technology status**, biochar **properties** and **industrial applications**, with a focus on possible uses in the **metallurgical industry**. Finally, a section is dedicated to **existing legislation** and to **guidelines** for sustainable production and suitability for specific applications.

2 Biochar production and technology status

Biochar is the solid carbonaceous material originated from the thermochemical conversion of organic matter via pyrolysis or gasification, the other products being permanent gases and condensable vapours. While indeed there are few similarities in the properties of biochar from slow pyrolysis and gasification process, these do not extend to the viability of the processes for their integration in industrial settings where biochar use is pivotal to the large-scale introduction of biogenic and recovered carbon in energy intensive, hard-to-abate industries. This primarily stems from the fact that, while biochar is the intended and optimized product in slow pyrolysis processing, it is only incidentally produced in gasification.

2.1 Pyrolysis

Biomass pyrolysis is a thermochemical process that involves the thermal decomposition of organic material at high temperatures, generally in the absence of oxygen. It involves the breakdown of complex organic molecules into simpler ones, yielding gases, liquids, and a solid product (designated as biochar, charcoal, biocoal) [1].

The pyrolysis process is by far the most common production method to obtain high yield of the desired solid product, besides providing a lower investment cost per unit of capacity against gasification plants.

Unless the recovery of liquid condensate is being pursued, which was not uncommon in the past, it is standard in the industry to recover the energy content of pyrolysis gas to produce process heat, with any excess potentially available to support feedstock drying.

2.2 Gasification

In gasification, the feedstock is heated at elevated temperature (even above 900 °C) under a flow of a gasifying agent. Feedstock conversion is intentionally steered toward the highest possible yield of permanent gases, which would ideally retain most of the chemical energy of the feedstock; in this process, biochar is a co-product, and carbon content in biochar a measure of process conversion (in)efficiency. The produced gas, after being cleaned, is typically sent to an internal combustion engine for electricity production or combine heat and power or is further processed into chemicals or biofuels [2].

2.3 Technology status

Globally, the biochar production encompasses different scales and complexities, from rudimentary batch earth mounds for household needs, to large continuous industrial systems that can match the demand of steel making plants, for example in Brazil.

Mode of operation, construction material, feedstock size, portability, biomass loading mode and heating method are amongst the criteria used to classify biochar production technologies and reactors.

Depending on how energy is supplied to the feedstock, the process can be either allothermal or autothermal. In the allothermal process, an external energy source, usually the combustion of pyrogas (gases and vapors), provides heat to the reactor. In the autothermal process, the energy need is supplied by partially oxidizing the feedstock, typically via air injection.

In general, all commercial processes are operated at ambient pressure to contain costs and limit plant complexity, however the benefit of operating at elevated pressure to move closer to the maximum theoretical yield have been validated in the past up to the pilot scale.

Drawing on reactor technology, one might find the following types of reactors [3], [4]:

- **Kilns,** traditional technology comprising batch autothermal reactors adopted, generally without recovery of pyrolysis gas;
- **Retorts**, mostly allothermal reactors able to convert pile-wood or wood logs over 18 cm in diameter and longer than 30 cm;
- **Converters**, reactors able to convert small-sized feedstock, like wood chips.

2.3.1 Kilns

Earth kilns are the oldest and most rudimental carbonizers and are still adopted in developing countries due to their extreme low cost and simplicity of operation. Typically, wood logs are placed in an earth pit or assembled to form a mound and then covered with soil, which ensure partial biomass oxidation, by preventing air flow; thus, these kilns can be realized in the same location of biomass harvesting, reducing transport costs. However, they require high labor, especially in the preparation of mound kilns, and are characterized by very long production times, even several weeks. During the process, vapors are released to the atmosphere and liquid condensate can easily contaminate the soil, leading to serious environmental issues. The control of the carbonization process is simple and does not require sophisticated technology as it is carried out by observation of the color of vapors [5].

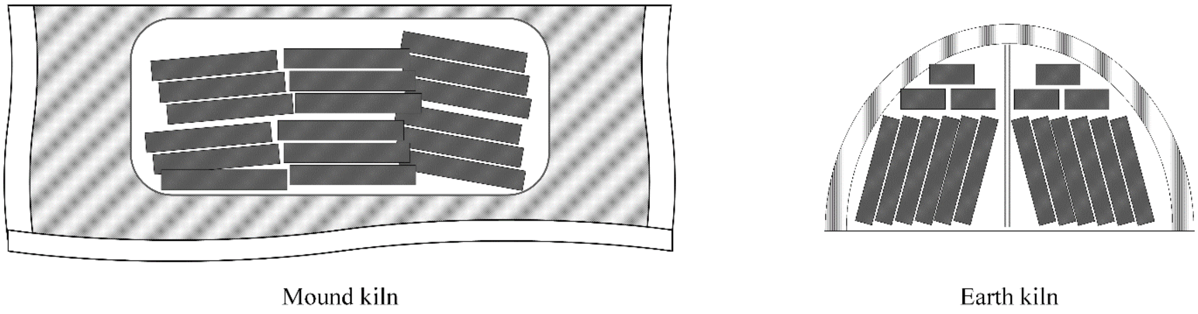


Figure 1: Simplified scheme of mound and earth kiln.

An advance in this technology is essentially represented by an improvement in the construction materials, that is *brick, concrete or metal*, leading to long lifespan, higher char quality and yield. Several types of these kilns have been developed since the 19th Century, with different shape, capacity and enhancements such as external heating chambers or pyrogas afterburners.

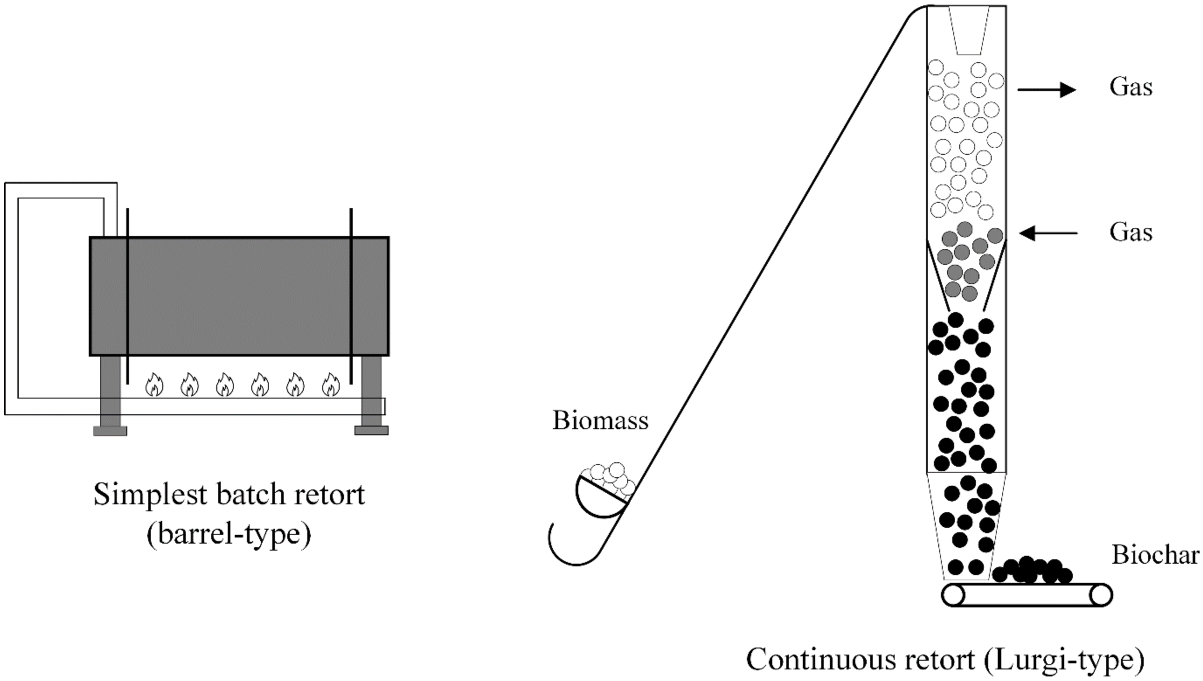
2.3.2 Retorts

Most industrial carbonization units are characterized by an allothermal retort configuration, in which the hot vapors and gases are combusted for producing the heat needed for pyrolysis. In some configurations, pyrolysis vapors are condensed in order to collect a variety of chemicals like methanol and acetic acid, while non-condensable gases are used for heating the process.

The simplest retort carbonizer has an allothermal, indirect heating configuration, typically constituted by a closed metal container (often a barrel) equipped with a pipeline conveying the produced gases and vapors towards the combustion chamber, which can be placed under the reactor or developed around it, in order to maximize the heat transfer [5]. Wood logs are placed in the container, which is then sealed and heated by additional fuel for starting the process. Firstly, and water vapors are produced from biomass drying, then pyrolysis starts and pyrogas is generated, spontaneously moving towards the combustion chamber; the process is therefore self-sustainable. As the reactor is sealed, no oxidation occurs and, consequently, char yield is generally higher with respect to autothermal systems. Several variations have been developed during the decades, including semi-stationary and mobile configurations, semi-batch and continuous operation, with direct heating or partial oxidation, horizontal or vertical reactors, with manual or mechanical feedstock loading and so on.

One of the retorts with the highest throughput (6 kt/y of char) was the *Lambiotte reactor*, which was firstly developed in the 1940s. It consists in a vertical continuous fixed bed retort, in which small wood logs are fed from the top and are forced to pass through different reactor zones by gravity: biomass is subjected to drying, conversion into char and then cooling. The first version of the Lambiotte retort adopted SIFIC technology, where pyrogas combustion was carried out in an external chamber, but an updated version was developed, involving internal combustion and gas recirculation, the so-called CISR Lambiotte. This plant is characterized by a high level of automation, leading to high car yield and quality; its main drawback is that its operability is heavily affected by biomass moisture content.

Another retort operating on the same principle, is the so-called *Lurgi process*: the reactor is equipped with air-locking valve, in order to prevent partial combustion of the biomass bed, and pyrogas combustion occurs in an external chamber.
A very simple, yet smart, retort carbonizer is the *Carbo twin retort*. It is a semi-batch system in which two metal tank reactors are placed in an insulated oven fed by the produced pyrogas and are alternately loaded and unloaded by means of an upper crane on a monorail, ensuring a continuous operation. This system is highly modular and requires minimum labor.



Simplest batch retort (barrel-type)

Continuous retort (Lurgi-type)

Figure 2: Simplified scheme of two retort units.

A similar concept but with continuous operation is the *wagon retort*: wood logs are loaded in wagon cars placed on a track which enter a drying chamber, a furnace chamber heated by pyrogas combustion where the carbonization occurs and then to cooling chambers. Cooling is a critical step due to the risk of accidental char combustion and requires long times.

2.3.3 Converters

Differently from kilns and retorts, converters can process small-sized biomass, like wood chips or straw. Because of this, char is often obtained as powder and further compaction may be required to meet market or technical standards. Most of converters are continuous systems, characterized by inner moving parts which conveys biomass through the reactor [5].

The *rotary kiln* finds ubiquitous applications in waste incineration, cement industry, as dryer or sieve. It basically consists of an inclined cylinder, that rotates to allow biomass to flow through the kiln; the heat for pyrolysis can be supplied by heating the shell from the outside or from the inside by means of hot gas flow, which is generally counter-current with respect to the feedstock. Their main advantages are biomass flexibility, scalability and maturity of the technology.

In *auger converters*, biomass is typically fed to the reactor by a hopper and then is transported throughout the length of the reactor by means of a screw. The reactor can be indirectly heated by pyrogas combustion or internally heated by flue gas injection. Materials like sand and steel/ceramic spheres can be adopted in order to improve the heat transfer, especially when bio-oil is a key co-product.

The *multiple-hearth furnace*, or *Herreshoff furnace*, is one of the oldest converters. It is designed with a vertical layout and cylindrical, insulated steel shell, which contains circular plates. The furnace can process biomass with finely ground particles, such as sawdust. As biomass is fed from the top, a vertical rotating shaft with radial arms moves it through the hearth. Holes in each plate allow the feedstock to descend, while the radial arms enhance contact with the hot gases produced by a burner outside the furnace.
Other converter configurations include the *paddle pyrolysis reactors* and *moving agitated beds*.

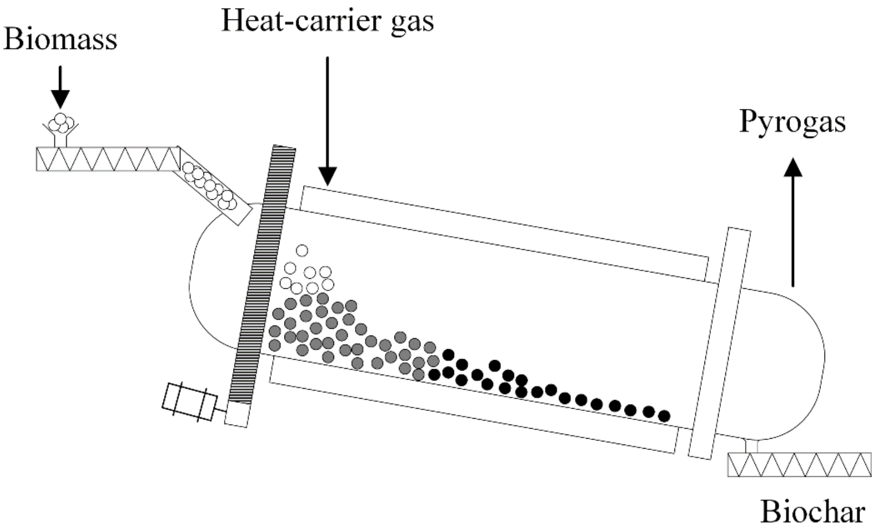


Figure 3: Simplified scheme of a typical rotary drum converter.

Figure 4: Picture of RE-CORD rotary kiln carbonization unit.

3 Biochar properties

A wide variety of factors contribute on the determination of the characteristics of biochar, first and foremost the process adopted for its production and the type of biomass used. These parameters greatly affect the functionality of the obtained biochar, mainly defining its physico-chemical composition and morphological structure.

Figure 5: biochar and the woody biomass from which it is produced.

3.1 Stability

When compared with the starting biomass, biochar is characterized by a higher carbon content and a lower presence of oxygen and hydrogen. These characteristics outline the high levels of both chemical and biological stability of the biochar. This is due also to the nature of the carbon within the biochar chemical structure, which is largely present in the aromatic form and is poorly reactive, biologically recalcitrant, and therefore not subject to mineralization by microorganisms, especially for biochar produced from woody biomass by pyrolysis or gasification [6].

The loss of volatile fractions occurs before the formation of biochar recalcitrant compounds [7], [8]; the greater the degree of formation of aromatic structures, the higher the resistance of the biochar to microbial degradation [9]. The Fixed Carbon content (FC) is a parameter that can be used to evaluate the quality of biochar obtained and also to evaluate the recalcitrant carbon content of the product; indeed, considering only the Total Carbon content (TC) could lead to misinterpretation, because this parameter includes some labile organic carbon [10], [11].

The H:C molar ratio is a key parameter for gauging product stability. Carbon, Hydrogen, and Oxygen are the primary elements of biochar. Materials with low H:C values are like anthracite and graphite and are more stable and resistant to degradation than materials with high H:C values (such as uncharred biomass) [12] For the use in industry sector, the Van Kravelen diagram [13] classifies coals on the base of the H/C and O/C atomic ratio. The "coal like" materials usually have H/C ratio below 1, and O/C ratio not higher than 0.2. To be classified as "anthracite" a biochar must have, according to Van Kravelen, an atomic H/C ratio lower than 0.4 and atomic O/C ratio less than 0.05.

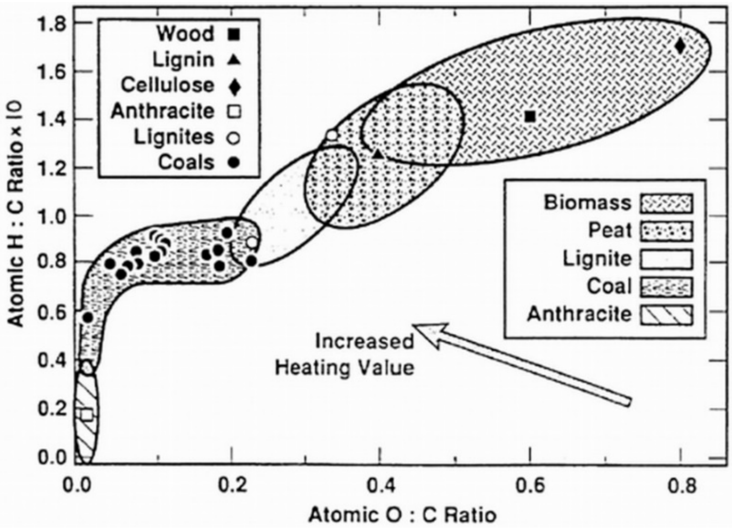


Figure 6. Van Kravelen diagram on coals classification [13]

High H/C ratio and O/C ratio correspond to a high volatiles content, which makes biocoal easier to ignite.

In agriculture, biochar stability allows to use it in the soil for Carbon Capture and Storage actions. The recalcitrancy of the biochar means that the carbon will not be lost in form of carbon dioxide for centuries, minimizing the impact on air pollution; moreover, when the biochar is produced from woody biomass, there is an implicit further advantage, laying on the removal of the atmospheric CO_2 carried out by the plant itself used as feedstock. According to the European Biochar Certificate (EBC) and the International Biochar Institute (IBI), values over 0.7 suggest non-pyrolytic chars or sub-optimal pyrolysis [14], [15]. The H:C ratio is a key factor to identify the Carbon sink value; indeed, Budai et al. [12] stated that a value of 0.4 or lower will ensure at least the 70% of the organic carbon remains in the soil for 100 years with the 95% of confidence [12].

In addition, when used as soil improver for agronomic purposes, the long-lasting residence of biochar in the soil provides a protected habitat for beneficial soil microorganisms, improving the quality of the entire soil microbial community. This is particularly true when another pivotal characteristic of the biochar is considered: its developed porosity, which allows, among many other benefits, to retain water, which is the most important basis for microorganisms' growth and proliferation.

3.2 Porosity

The internal structure of the feedstock, under specific production process condition, determines the porous structure of the biochar after the carbonization, in terms of dimension and distribution of the solid particles size and, hence, in terms of porous network and surface area. In general, biochar can possess a specific surface area on the order of hundreds of m^2/g, and a developed porous structure, ranging from micropores (about 1-2 nm) to macropores, in the order of microns (Figure 7).

The porous structure of the biochar makes it potentially suitable for a range of uses, including - in the industrial sector - acting as an adsorbent against a wide range of compounds, in addition to water. Biochar, in fact, can retain compounds of several nature: gases, i.e. playing an important role in odour filters industry, or polar and non-polar fluids, greatly widening its potential use in several industrial applications, such as in the pharmaceutical field, which is gaining more and more attention from researchers.

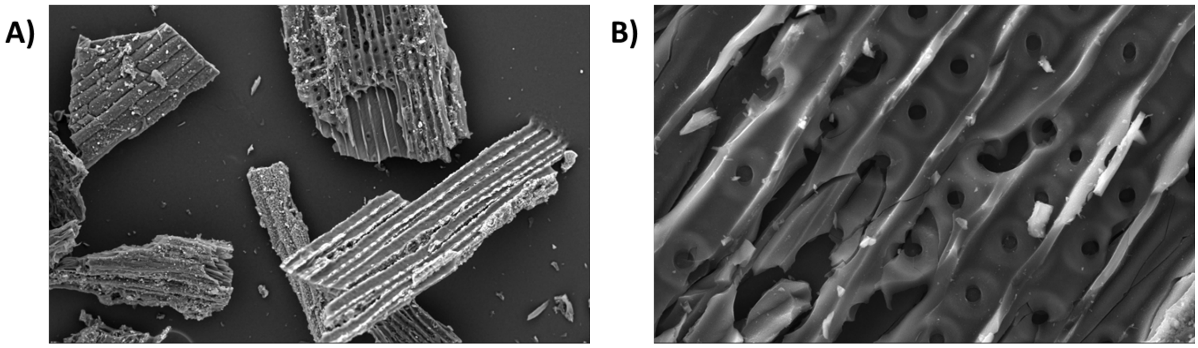


Figure 7: Magnified view of biochar through the Scanning Electron Microscope (SEM). A) 200 µm view. B) 30 µm view

The combination of chemical stability and developed porosity may lead to many other potential uses, especially in contexts where its beneficial impact to the microbiological dynamics could be exploited. In this field, recent research focused on evaluating the effect of using biochar in anaerobic digestion processes for organic waste recover, that aimed to produce compost or digestate as by-product of the biogas production. It has been demonstrated that the biochar provides beneficial effects on both processes, from different points of view (e.g., reducing composting period, accelerating microbiological stabilization, improving biogas yield, reducing pollutants emissions, adsorbing plant-nutrient, and others); such beneficial activities could be mainly related to the adsorbent effect of the biochar and to the improvement of the microbial population involved in relative bioprocesses.

Moreover, due to its high surface area, porosity and mineral content, biochar plays an important role as an adsorbent, to purify air and water from contaminants, or as a catalyst for both tar removal from syngas and for biofuel production. Biochar, indeed, is recognized to be able to adsorb heavy metals, organic contaminants, nitrogen and phosphorus contaminants, and other pollutants from aqueous solutions, with performance often comparable to those of the activated carbons [16]. Moreover, it has been demonstrated that biochar can capture undesired gaseous compound such as low concentrations of formaldehyde in an indoor environment or carbon dioxide (CO_2) through weak bonds on the biochar surface. Lastly, biochar has been used as catalyst in the transesterification and esterification processes for biodiesel production [17], [18].

3.3 Contaminants

In general, thermal processing of biomass concentrates most of the inorganics and metals, including heavy metals, in the solid product. These substances are generally inhibitory or toxic toward microorganisms or living organisms in general [19]; besides, also industrial applications as fossil coal substitute might require to meet specific thresholds on the content of inorganics and metals, thus further processing of char e.g. by leaching might be needed to accommodate the end-user requirements

Other contaminants that might be present in the char include organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), dioxins (PCDD/Fs), volatile organic compounds (VOCs), persistent free radicals (PFRs) and other.

4 Legislation and product quality

Biochar, char, pyrochar, bio-coal, charcoal; there are multiple terms for the same product category. All these terms often cause confusion. In general, **biochar** is defined as a vegetable carbon produced by the carbonization process, but with specific product end-uses. Hagemann and Schmidt distinguished biochar from charcoal in terms of end use: "*Biochar is a porous, carbonaceous material that is produced by pyrolysis of plant biomasses and is applied in such a way that the contained carbon remains stored as a long-term C sink or replaces fossil carbon in industrial manufacturing. It is not made to be burnt for energy generation*" [20]. According to Lehmann and Joseph biochar use is focused on environmental management and carbon sequestration: "*[…] it (ed, biochar) distinguishes itself from charcoal and similar materials […] by the fact that biochar is produced with the intent to be applied to soil as a means of improving soil productivity, carbon (C) storage or filtration of percolating soil water*" [6].

Of course, what is called biochar has also a wide range of different product characteristics (e.g., ash content, porosity structure, stability grade, functional groups in its surface, ion exchange capacity, sorption capacity, etc.) interesting for a lot of potential end uses, different from the classic ones above mentioned. The **European Biochar Certificate** (EBC) has published, and frequently updates, the guidelines for a sustainable production of biochar, defined as "*a porous, carbonaceous material that is produced by pyrolysis of biomass and is applied in such a way that the contained carbon remains stored as a long-term C sink or replaces fossil carbon in industrial manufacturing. It is not made to be burnt for energy generation*".

The EBC recognizes and characterizes 7 categories of biochar, based on its end use, which are subjected to thresholds in order to validate the quality of the product and its suitability according to the requirements and safety regulations of the different applications:

- **EBC-FeedPlus** meets all EU and EFTA regulations relevant for animal feeding and agricultural soil applications;
- **EBC-Feed** meets all requirements of the EU feed regulation but not those of the EU fertilizer product regulation;
- **EBC-AgroOrganic** meets all requirements of the new EU fertilizer product regulation and all the requirements of the EU Commission regulation on organic production;
- **EBC-Agro** meets all requirements of the new EU fertilizer product regulation;
- **EBC-Urban** provides a strong standard for the use of biochar in tree planting, park maintenance, sidewalk embellishments, ornamental plants, and rainwater drainage and filtration and it must not be used as soil amendment for food or feed production;
- **EBC-ConsumerMaterial** biochar can be used in products that may come into direct skin contact with consumers or food-grade products (examples would be takeaway coffee cups, plastic computer cases, toothbrushes, carpets, textiles, flowerpots, freshwater pipes, etc.), excluding medical and healthcare product or food. The biochar must be

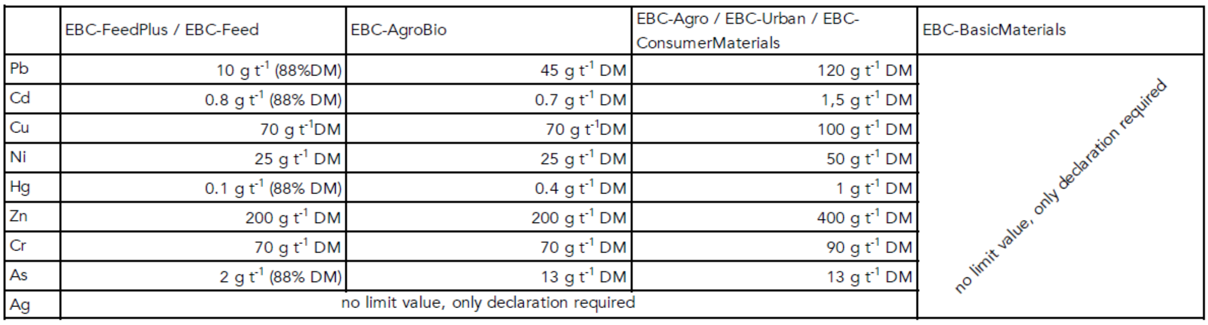
included in the consumer products in such a way that no coal dust is released because of product use;

- **EBC-BasicMaterial** certificate guarantees sustainably produced biochar, which can be used in basic industry such as to produce building materials, road construction asphalt, electronics, sewage drains, and composite materials like skis, boats, cars, rockets without risk to the environment and users. However, precautions in handling, storing, and labeling the materials are required.

Threshold values recognized by the EBC guidelines are increasingly less stringent from the FeedPlus class up to the BasicMaterial class, which is introduced as the basic and fundamental certification class, defining what can be considered biochar or not, according to the EBC, and complies with the EU-REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals).

According to the EBC Guidelines, both EBC-ConsumerMaterials and EBC-BasicMaterial cover all necessary environmental requirements for non-soil applications. Specific industry classes, defining biochar qualities for the use in construction materials, polymers, textiles, and other materials will be developed from 2023 onwards depending on the demand from the respective industries.

The EBC Positive List (Appendix 1) outlines which types of biomass are allowed as feedstock to be converted in biochar for each application class. As an example, the table concerning limit values for heavy metals according to the EBC application classes is presented in Figure 8 below.



	EBC-FeedPlus / 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 8: Limit values for heavy metals according to the EBC application classes [20]

The **EU Regulation 2019/1009** of 5th July 2019 sets the rules for the suitability of the biochar towards the market of fertilising products. The modifications (applied from 16 July 2022) to Annexes II, III and IV of the EU Regulation included the possibility to classify pyrolysis and gasification materials (biochar) as Component Material Category n.14 (CMC 14). Indeed, the regulation includes provisions for EU fertilising products that contain requirements at two levels in accordance with their intended function (‘Product Function Category’, PFC), and for the component materials contained in the EU fertilising product (‘Component Material Categories’, CMC). Specific requirements for CMC 14 (biochar) refer to organic pollutants content, such as PAH-16 (polycyclic aromatic hydrocarbons), PCDD/F (dioxins and furans) and PCB (polychlorinated biphenyls), including also Cl^- (chloride) and Tl (thallium). CMC 14 can be used alone or combined with other CMCs to constitute a PFC. The Product Function Categories n.3A and n.4, for example, permit to characterise a product as soil improver (PFC 3A) or growing medium (PFC 4). These classifications included thresholds for heavy metals content, such as Cd (Cadmium), Cr VI (Hexavalent Chromium), Hg (Mercury), Ni (Nickel), Pb (Lead), As (Inorganic Arsenic), Cu (Copper) and Zn (Zinc).

In conclusion, biochar that complies the EU FPR requirements, is a very clean and safe vegetable carbon to be used for agronomic purposes. The high carbon content, resistant to thermochemical and biological degradation and only marginally subject to mineralisation by microorganisms [6], [21], coupled with the water holding capacity and the nutrient retention ability, provides an interesting solution for the application of the product as an effective soil improver and, at the same time, a potential innovative carbon capture and storage strategic solution (as indicated in the IPCC report released in 2019 [22]) able to persist in soil for a timespan ranging from decades to millennia [14].

5 Biochar industrial applications

The potential industrial applications of biochar strongly depends on the properties imparted by feedstock type and quality. For example, biochar can be used in industrial processes as a catalyst to improve product quality and reduce emissions [23]. By increasing the surface area of the catalyst particles, biochar can speed up chemical reactions and reduce energy requirements for processes such as refining, cracking and distillation.

Biochar is also used as adsorbent for gas, or for water filtration due to its increased sustainability when compared to other adsorbents such as activated carbons [24].

It can also be used to improve the performance of wood-plastic composites (WPCs) by adding biochar to the matrix before moulding or extrusion [25]. The presence of biochar facilitates improved moisture uptake and moisture release, which improves the strength, stiffness, and dimensional stability of the composite.

Biochar can promote the growth of microorganisms, and it can improve the efficiency of biochemical processes, such as anaerobic digestion [26] or composting (Figure 9A) [27].

Additionally, biochar has been increasingly used in various biomedical and pharmaceutical applications due to its ability to improve medicine's efficacy. Biochar can act as a drug delivery (Figure 9B) system and can also be used as a medical scaffold material [28].

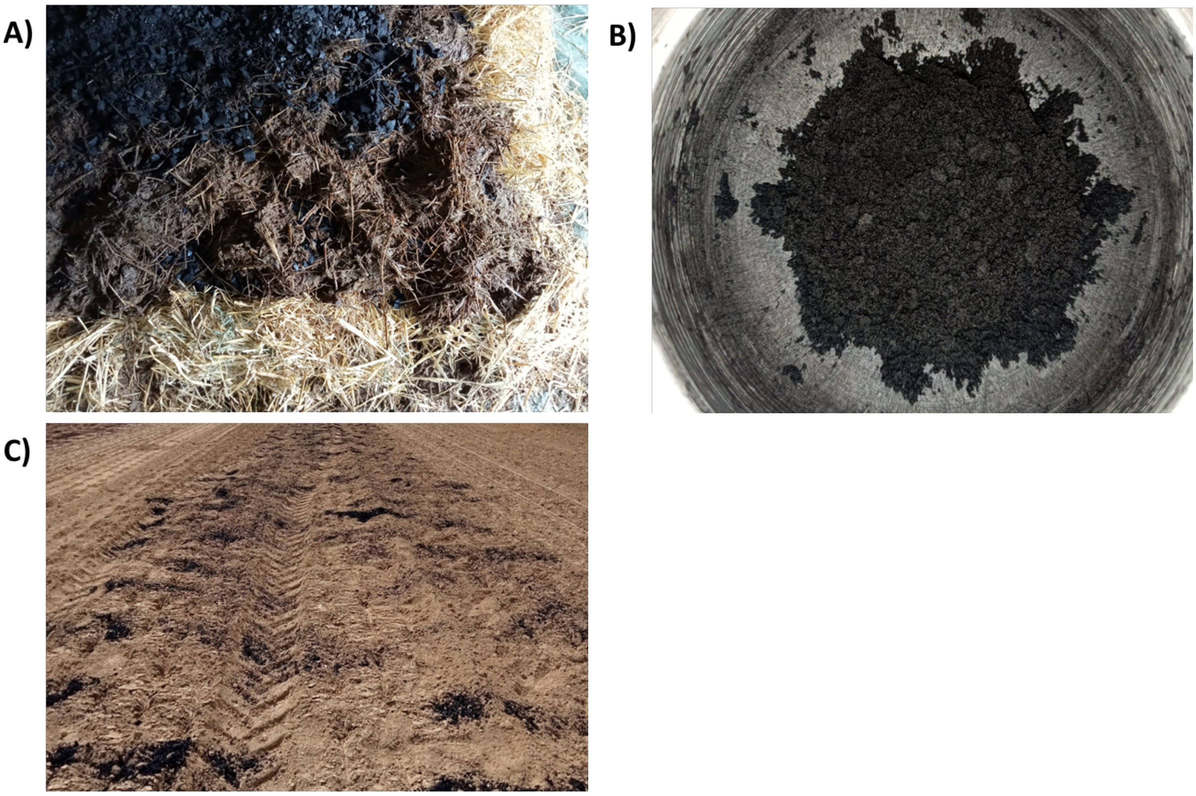


Figure 9: A) Preparation of composting test with biochar as additive. B) Biochar used for the loading of a pharmaceutical active ingredient. C) Biochar used as soil improver.

Its carbon sink potential raised the interest of using biochar not only as soil improver (Figure 9C) for agronomic purposes, but also as additive in building materials, such as cement [29].

Biochar, in fact, can act as a pozzolanic additive, helping to improve the properties of cement by reacting with the calcium hydroxide present in cement, increasing strength and water resistance, while storing organic carbon in the material.

Biochar can also be used as a substitute for fossil carbon in the metallurgical industry for a variety of applications. This includes the uses of biochar as a reducing agent in metallurgical processes replacing fossil coal as source of carbon for the reduction of metal ores into metals. Biochar can also be used as an energy source for metal smelting during the metallurgical processes. Additionally, biochar can be used as a binding material to hold metal particles together during forging or to help create metal cements.

5.1 Biochar in the metallurgy sector

One of the main factors influencing the sustainability of the steel making processes is the intensive use of fossil coal as energy and carbon source. High ranked coals such as anthracite and bituminous coal are used in most of steel production processes. About 200 million tons of coal were consumed in Europe in 2019, before covid pandemic. Of these, around 134 million tons were imported [30].

During the last years, steel industries managed to reduce fossil coal consumption, replacing part of it with gaseous fuels, which are used in the fuel mixtures injected in the furnaces. In 2017, 85 million cubic meters of natural gas have been consumed by steel sector. In summary, 89% of a BF-BOF’s energy input comes from coal, 7% from electricity, 3% from natural gas and 1% from other gases and sources. In the case of the EAF route, the energy input from coal accounts for 11%.

It is for this reason that the application of coal fuels in steel industries, and in particular of biocoal in the EAF processes (fossil coal replacement in Electric Arc Furnaces) have been the subject of a wide number of studies since many years. Coal fuels, gaseous, liquid, or solid, can be used to replace fossil energy carriers in steel sector. In particular, biocoal, or charcoal is currently used in Brazil as a biomass-based reductants in Blast Furnaces and the technical feasibility in EAF has been already demonstrated by multiple industrial tests [31]. Other ways to use bioreductants in industry could include injection of different biofuels, such as ethanol, biodiesel, natural gas.

Different biomass-based products rely on different production processes, such as slow pyrolysis (biocoal) and pyrogas, fast pyrolysis (bio-oil) technologies, but also gasification and anaerobic digestion, as bio-syngas and biomethane producing processes. Natural gas (methane) is already used in both Electric Arc furnaces and Blast furnaces in EU countries.

There are various means by which biochar, as a biomass-based carbon source, can replace fossil coal in metal production and processing. For example, biochar can be used for [32]:

- coke-making for production of bio-coke;
- sintering process for production of bio-sinter;
- pelletizing/briquetting for production of bio-composites and/or bio-briquettes;
- partial or full replacement of coal injected into the blast furnace through Pulverized Coal Injection (PCI);
- partial or full replacement of coal charged in the batch of Electric Arc Furnaces (EAF)
- bio-recarburization of steel in the ladle furnace

Although biocoal contribution to the decarbonisation of steel industry is well known, its industrial application in Europe is still not in place, due to a set of technical, economic, and environmental barriers.

5.1.1 Benefits and barriers to the use of wood-based biocoal in steel sector.

The partial replacement of Pulverized Coal (PC) with biochar in the Pulverized Coal Injection (PCI) in the Blast Furnace represents the technically more straightforward option [33]. In fact, it is proven that biochar could be successfully blended with PC. The same can be stated for the replacement of fossil coal in EAF, which was identified as a promising solution to improve the sustainability of the whole process. The use of biochar in Blast Furnaces and Electric Arc Furnaces leads to a series of benefits, such as:

- **CO_2 reduction:** Given the carbon neutrality of biomass fuel, replacing fossil coal with biobased material would bring to significative CO_2 abatement potential. Wang et al. (2015) [34] estimate that substituting coal with biocoal can reduce on-site emissions by 17– 28%. For Sweden's largest steel mill, located in the northern part of the country, this reduction corresponds to a potential saving of 1.14 million tonnes of fossil-based CO_2.
- **Lower impurity content:** In biocoal the contents of sulphur and phosphorus are substantially lesser than in coke. This low impurity content results into a better quality of the hot metal (HM) and consequently has higher market value (32–45% higher than coke-based HM). In addition, initial low sulphur and phosphorus concentrations in the biocoal imply easier desulphurization and dephosphorization of steel produced by the scrap route, i.e., by the Electric Arc Furnace. This results in a low demand of raw materials (mainly lime) but also in a reduction of the process time, i.e., less oxygen injection during the scrap melting and less Ar stirring during the steel refining in the ladle [35], [36].
- **Ash content:**. The ash in biocoal can be lower than in coke, with a reduced amount of sulphur and phosphorus, so that to bring to the same benefits as above.

Technical barriers

In order to investigate the possibility to replace coal with pyrolyzed biomass, the most crucial parameters have been identified:

- **Fixed C content:** The fixed carbon content represents a crucial quality condition for coal used in EAFs. This parameter strongly influences the fuel behaviour at high temperature, e.g., reactivity and specific heat. The Fixed C value for fossil coal varies from 75 % to 90%.
- **Ash content:** Metallurgical coal used in Electric Arc, always have ash content as a critical aspect to monitor. Industrial plants can tolerate carbon with ash content not higher than 30% and, in most of the cases, 15% is considered as an upper limit.
- **Alkali content:** Alkali are detrimental to the blast furnace operation, as they catalyse the solution loss reaction ($C + CO_2 \rightarrow 2CO$), decreases the coke strength, and condense on the lining of the BFs, forming scaffolds. In electric arc, aluminium and phosphorus are also considered detrimental elements for the application of the coal [31].

In addition to the chemical composition, physical characteristics can be critical if biochar is used to replace coke. The replacement of coke with biochar still faces difficulties because of the quality requirements, including high coke strength after reaction (CSR> 60%) and low coke reactivity index (CRI 20–30%), which are required to ensure sufficient permeability in the upper part of the BF shaft and low-pressure loss in the furnace [37], [38]. For this reason, charcoal-based blast furnaces, widely used in Brazil, are of smaller scale.

5.1.2 Biochar requirements for substitution of coke and coal

Requirement for PCI replacement

Differently from torrefaction, charcoal produced from biomass slow pyrolysis is a coal-like material with high C content and low volatility, able to fully replace fossil coal as PCI in Blast Furnaces. Table 1 below includes the quality of three different coal types used in as PCI, which can be considered as a quality target for the obtained biochar.

Table 1: Element composition of several coal samples

Feature	Anthracite	Australian Coal Sample	North American Coal Sample	Measure Unit
C	77.38	79.22	75.62	$\%wt_{db}$
H	3.61	3.53	3.57	$\%wt_{db}$
O	1.35	3.56	1.60	$\%wt_{db}$
N	0.86	1.66	0.86	$\%wt_{db}$
S	0.90	0.43	0.82	$\%wt_{db}$
Ash content	15.02	9.10	5.08	$\%wt_{db}$
Fixed Carbon	70.93	64.87	67.00	$\%wt_{db}$
Volatile matter	13.21	18.03	19.92	$\%wt_{db}$
Moisture	0.84	8.00	8.00	$\%wt_{db}$

Given the low sulphur content of biomass compared to fossil coals, charcoal obtained from slow pyrolysis is expected to have Sulphur content of less than 0.3% db.

Requirements for Coke replacement

The replacement of coke offers an even larger potential, since currently still coke is used as reductant compared to PCI. There is however a limitation in the physical properties of the coke. Measurement of physical properties aid in determining coke behaviour both inside and outside the blast furnace. In terms of coke strength, the coke stability and Coke Strength After Reaction with CO_2 (CSR) are the most important parameters. The stability measures the ability of coke to withstand breakage at room temperature and reflects coke behaviour outside the blast furnace and in the upper part of the blast furnace. CSR measures the potential of the coke to break into smaller size under a high temperature CO/CO_2 environment that exists throughout the lower two-thirds of the blast furnace. A large mean size with narrow size variations helps maintain a stable void fraction in the blast furnace permitting the upward flow of gases and downward of molten iron and slag thus improving blast furnace productivity.

Charcoal usually exhibits the required chemical properties of both coal and coke; but it difficultly achieves the required coke physical properties, so only small fractions of the coke can be replaced by charcoal.

Quality requirements for a coke to be used in a European blast furnace are following reported in Table 2, data provided by [39].

Table 2: Coke properties for Blast Furnace steelmaking application

Property parameter	Required	Applied
CSR	>65%	60.0 – 68.4
CRI	<23%	20.0 – 31.9
Mean size	50 – 55 mm	47 – 75 mm
Ash	<9%	8.67 – 11.35
S	<0.7%	0.51 – 0.93
P	<0.025	0.02 – 0.06
Alkali	<0.2	0.16 – 0.38
Moisture	<5.0	1.5 – 5.5

Results for analysis on a sample used in a Polish plant is reported in Table **3** below [40].

Table 3: Coke properties for a sample used in a Polish steel-making plant

Property	Value	Measure Unit
Carbon Content	88.83	%wt
Ash Content	10.20	%wt
Volatiles	0.57	%wt
S	0.49	%wt

5.1.3 Valorisation of pyrogas in a pyrolysis - steelmaking integrated process.

Another valuable energy stream from a slow pyrolysis plant integrated within a steel-making plant is represented by the **excess pyrogas**; it can be used to replace a share of fossil energy coming from either Natural Gas or Coke Oven Gas (COG) and Blast Furnace Gas (BFG), but it necessarily has to be maintained at high temperature in order to avoid condensing of its tar and moisture content. The organic condensable fraction, in particular tars, condensate at temperatures below 300 °C, creating fouling and clogging in pipelines and injection systems. Water content can create problems during gas injection. These two main barriers can be avoided if pyrogas can be directly reused next to the pyrolysis plant, avoiding condensation. Otherwise, in order to use the pyrogas i.e. in the power plant, it is necessary to separate the tars and the condensable hydrocarbons from the pyrogas. To do so a dedicated pyrogas cleaning unit would be needed; otherwise, under a further integration perspective, it could be theoretically possible to use the coke oven by-product plant that is located near to the Coke Oven.

Figure 10 provides a simplified process flow description that summarizes the slow pyrolysis plant integration measures within an existing steel-making plant.

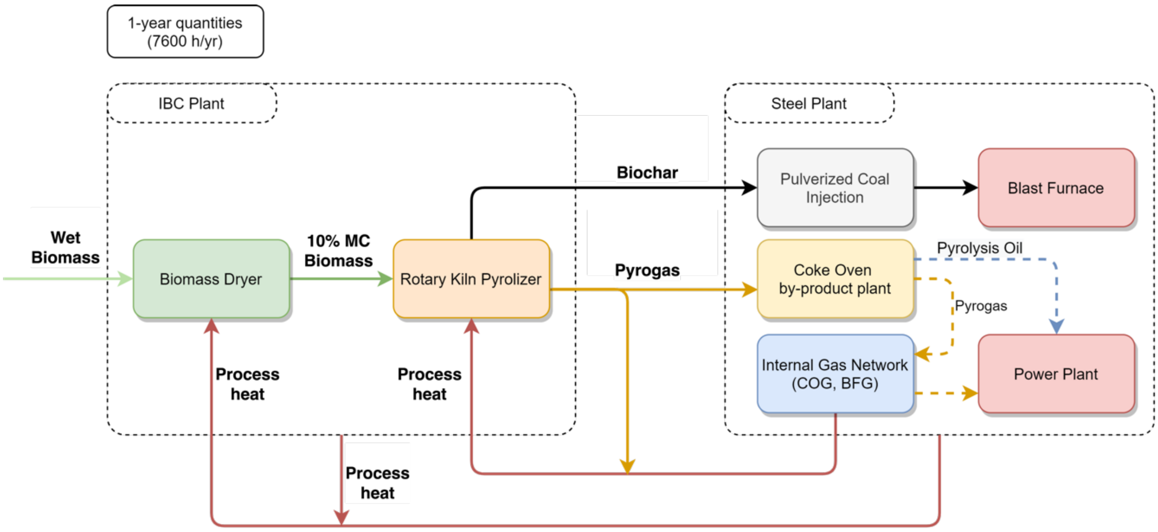


Figure 10: IBC plant mass and energy flows, integrated with steel-making plant.

The **Coke Oven** is an airless kiln for the industrial production of coke from coal; there, the coal is baked temperatures usually around 1,000°C –1,100 °C. This process vaporises or decomposes organic substances in the coal, driving off volatile products, including water, in the form of coal-gas and coal-tar. The non-volatile residue of the decomposition is mostly carbon, in the form of a hard somewhat glassy solid that cements together the original coal particles and minerals. The coke oven by-product plant has the function of recovering chemical by-products from the liquid condensate stream that forms after the raw coke oven gas is cooled, and of conditioning the remaining gas stream into a fuel gas.

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