

Review

A Comprehensive Review of Secondary Carbon Bio-Carriers for Application in Metallurgical Processes: Utilization of Torrefied Biomass in Steel Production

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Abstract: This review aims to show the significance of the use of secondary carbon bio-carriers for iron and steel production. The term 'secondary carbon bio-carriers' in this review paper refers to biomass, torrefied biomass, biochar, charcoal, or biocoke. The main focus is on torrefied biomass, which can act as a carbon source for partial or complete replacement of fossil fuel in various metallurgical processes. The material requirements for the use of secondary carbon bio-carriers in different metallurgical processes are systematized, and pathways for the use of secondary carbon bio-carriers in four main routes of steel production are described; namely, blast furnace/basic oxygen furnace (BF/BOF), melting of scrap in electric arc furnace (scrap/EAF), direct reduced iron/electric arc furnace (DRI/EAF), and smelting reduction/basic oxygen furnace (SR/BOF). In addition, there is also a focus on the use of secondary carbon bio-carriers in a submerged arc furnace (SAF) for ferroalloy production. The issue of using secondary carbon bio-carriers is specific and individual, depending on the chosen process. However, the most promising ways to use secondary carbon bio-carriers are determined in scrap/EAF, DRI/EAF, SR/BOF, and SAF. Finally, the main priority of future research is the establishment of optimal parameters, material quantities, and qualities for using secondary carbon bio-carriers in metallurgical processes.

Keywords: secondary carbon bio-carriers; biomass; torrefaction; biocoke; iron and steel industry; ferroalloys

1. Introduction

Biomass is considered a valuable renewable energy source [1]. Given that the iron and steel industry is one of the most energy- and emission-intensive industrial sectors, the use of substitutes for conventional fossil fuels is an extremely attractive option. The iron and steel industry is responsible for approximately 1.83 tons of CO₂ per ton of crude steel (for BF/BOF route), with major amounts from the blast furnace (BFs), cokemaking ovens, sintering, pelletizing, iron alloy furnaces, and other processes [2–4]. To reduce the negative impact on the environment [5–7], to reduce CO₂ emissions by 50% until 2030, and reach climate neutrality (zero net CO₂ emissions by 2050) [8], as well as to reduce the use of critical materials, such as coal [9–11], a considerable amount of research has been

carried out on the use of carbon-bearing substitute materials. For instance, biomass has promising potential as a fuel and reductant, but its application in the metallurgical industry has limitations. Numerous studies have concluded that biomass utilization has good potential for the partial replacement of fossil fuels and reducing agents in metallurgical coke production [12–20], as carbonaceous fuel in iron ore sintering [21–24], in iron ore pellet production [25], pulverized injection into the BF [26–28], in EAF [29,30], in the reduction of iron [31–33], and in ferroalloy production in a submerged arc furnace (SAF) [34–36].

It is worth noting that raw biomass can have several disadvantages [37], such as high moisture content, low calorific value, hygroscopic nature, low bulk density, and high content of oxygenated volatile matters (VM). According to [38], the FC content of raw biomass typically ranges from 9–25 wt.%, while VM can range from 63–88 wt.%.

Therefore, in most cases, pre-treatment is inevitable in order to obtain bio-substitutes with properties allowing a partial or complete replacement of fossil fuels in metallurgical processes. Improving the properties of raw biomass can be achieved via thermal treatment (e.g., torrefaction [38], hydrothermal processing [39], gasification [40], combustion [41], pyrolysis [42], etc.). The advantages of thermal biomass treatment include reduced moisture and oxygen content, while increasing the carbon fraction [43,44] and the calorific value of the solid product [45], making it more suitable for use in various metallurgical processes. However, after heat treatment, there is an increase in ash content and a decrease in the mechanical strength of the biochar [46–48]. Many studies have focused on using biochars for metallurgical purposes after pyrolysis from approximately 350 °C to 1100 °C [25,49,50]. The disadvantage of pyrolysis at high temperatures is a reduction of the solid product, which is the most valuable for its further use in metallurgical processes. In this regard, the most attractive way to improve the properties of biomass is torrefaction at 200–300 °C [51], which is also referred to as a mild pyrolysis process. The biomass torrefaction process can be carried out at temperatures of 200–235 °C (light torrefaction), 235–275 °C (medium torrefaction), or 275–300 °C (severe torrefaction) [37] under an inert atmosphere for minutes to hours. Compared to pyrolysis, it is a less violent heat treatment process that improves the properties of biomass without affecting the high molecular compounds.

Additionally, torrefied biomass has less ash than biochar after pyrolysis. Moreover, the biomass weight can be reduced by 30–70%, and torrefied biomass can store 90% of its energy after the torrefaction [52]. Furthermore, torrefaction can reduce CO₂ emissions by 50 kg/t steel [53]. It is worth noting that the torrefaction process changes the distribution of biomass components. Decomposition of cellulose and hemicelluloses occurs at temperatures from 200–400 °C [54], while lignin decomposes slowly at higher temperatures of 200–900 °C. Torrefaction reduces the hemicellulose content from 22% to 4.6% at 300 °C, while the cellulose slowly decomposes and the lignin content increases [55]. During torrefaction, the biomass dries up, slowly decomposes, and simultaneously releases about 20% of CO and about 80% of CO₂ [56], H₂O, and a small amount of volatile organic compounds. As a result, the carbon content of the torrefied biomass increases, while the hydrogen and, especially, the oxygen content decreases. Torrefied biomass has the following properties:

- Fixed carbon (FC) varies from 10–50 wt.% [57], the VM varies from 34–85 wt.%, and ash varies from 9.20 wt.% to 15.04 wt.% [58];
- Higher calorific value from 16–29 MJ kg⁻¹ or energy density [37];
- Lower O/C and H/C atomic ratios [59,60].

After torrefaction, the content of FC can reach 50 wt.%. The greater the severity of the torrefaction process, the greater the value of FC will be obtained. The effect of torrefaction can greatly vary, depending on the type of biomass subjected to heat treatment. Torrefaction is the only heat treatment method in which the yield of solid residue is a maximum and is in the range of 75–90% [61] at a heating rate of 1–10 °C/min and a residence time of 10–60 min [62].

Moreover, torrgas can be used for drying the biomass by reusing the waste heat, according to [63], but before reusing, it should be normally de-dusted using a cyclone.

Torrefied biomass is a good option for partial or complete replacement in processes that require coal [64]. However, the properties of torrefied biomass are limiting in some metallurgical processes that use only coke as a source for carburizing or as a fuel and reducing agent [65]. They should be improved by compaction [65,66] or by adding them to the coal blend to obtain biocoke.

As for the industrial use of torrefied biomass in practice, there is already an active project, TORERO (Horizon 2020 Project, 2017–2024, Grant Agreement No. 745810), coordinated by Arcelor Mittal Belgium NV [67]. This project considers using torrefied biomass for injection into the BF to replace fossil coal. In addition, the POLTORR system has been developed by ThyssenKrupp for drying and torrefying biomass to replace fossil fuels [68].

Many researchers have published several reviews on the application of biomass in selected iron- and steelmaking processes. Additionally, all the papers have focused on using biomass, either in its original state or after pyrolysis. This review paper aims to suggest and discuss the pathways for the integrated use of secondary carbon bio-carriers in four steelmaking methods, as well as ferroalloy production. The paper is mainly focused on the use of torrefied biomass. However, it is worth noting that this paper is not focused on a specific type of biomass, but biomass is instead considered in general as it is a promising carbon source. The systematization of requirements for fuel and reducing agents for different metallurgical consumers is the focus of this review.

ESTEP and Clean Steel Partnership to Decarbonize the EU Steel Sector

The steel industry is an important engine for sustainable growth, adding value and high-quality employment within the European Union. As mentioned above, it is committed to reducing CO₂ emissions by developing and upscaling technologies. The Clean Steel Partnership (CSP, a public-private partnership fostering the decarbonization of the European steel sector), which is led by the European Steel Association (EUROFER) and the European Steel Technology Platform (ESTEP), is focused on research and development to accelerate the implementation of technological CO₂ mitigation pathways comprising Carbon Direct Avoidance (CDA), Smart Carbon Usage (SCU), and a circular economy (CE). The targets of CSP are integrated into a balanced set of Key Performance Indicators (KPI), which contribute to reaching a technological readiness level (TRL) 8 (system or process complete and qualified) to reduce CO₂ emissions stemming from EU steel production by 80–95% compared to 1990s levels, ultimately leading to climate neutrality [69].

ESTEP, the main coordinator of CSP, is a non-profit organization according to Belgian law (international ASBL) [70]. The mission of ESTEP is to engage in collaborative EU actions and projects using technologies that tackle EU challenges (notably on renewable energy, climate change, i.e., low-carbon emissions, and CE) to create a sustainable EU steel industry. Figure 1 shows the organizational structure of ESTEP [70].

A Board of Directors governs ESTEP. The steering group pilots the overall ESTEP research program. Additionally, the implementation group deals with all issues regarding the CSP. It reviews the activities of the seven focus groups (FG). Two of these FGs, which are low carbon and energy efficiency and circular economy, deal with steel production. The former works on developing safe, clean, energy-efficient, and innovative technologies, while the latter deals with innovative solutions to increase the circularity of steel. The major concerns here are reducing CO₂ emissions, conserving resources, and boosting waste recovery. Three FGs cover steel applications: steel solutions for transport and mobility, steel solutions for construction and infrastructure, and steel solutions for energy markets, including engineering. The FG People deals with activities for attracting people to the steel industry, skills development, education and training programs, and occupational safety. The FG Smart Factory covers issues for intelligent and integrated manufacturing, applying developments in the field of information and communication techniques [70]. The CSP and its main strategic foci are explained in further detail in the next subsection.

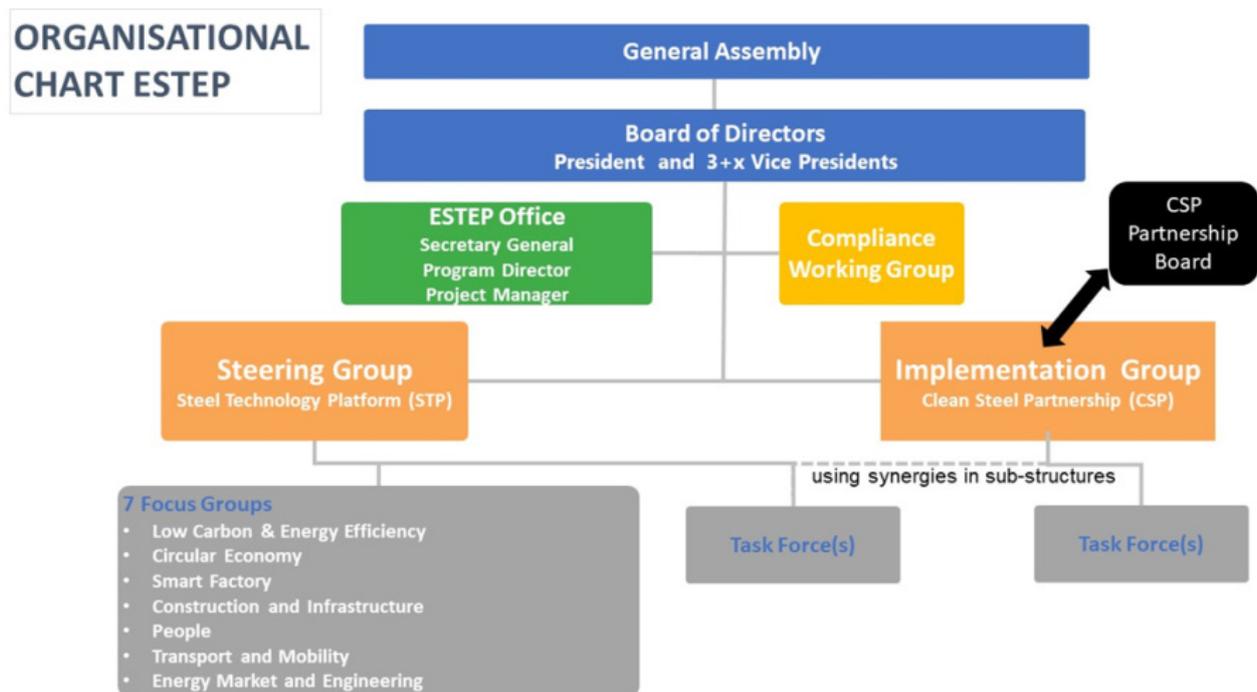


Figure 1. Organizational structure of ESTEP [70].

All R&D&I activities supporting the achievement of the CSP's objectives are classified in the Strategic Research and Innovation Agenda (SRIA, also called roadmap) according to six areas of intervention (AoIs) (see Figure 2 [69]).

The aforementioned technological pathways comprising CDA, SCU, and CE represent four of the six AoIs. CDA means steel production using hydrogen or renewable "green" electricity. SCU is separated into two sub-parts: CCUS (carbon capture, utilization, storage) and PI (process integration). CCU (carbon capture, utilization) encompasses technologies that use CO and CO₂ in steel plant gasses or fumes as raw materials for production or integration into valuable products. PI allows for the reduction of fossil fuels (coal, natural gas, etc.) that are used in both BF-BOF and EAF steel production to reduce the CO₂ emissions generated by the steel industry. In addition to the CE, enablers are another AoI. This field includes integrating technologies, such as artificial intelligence and digital solutions, into industrial production. The development of new measurement techniques and digital tools for monitoring and control in the new steel production processes, new predictive and dynamic models, and strategic scheduling tools are examples of enablers that will ensure the planning, assessment, and optimization of the industrial transition process toward a climate-neutral steel sector [71,72]. The last AoI (denoted as "combination" in Figure 2 above) defines research initiatives in which the different pathways interact with each other [69].

The use of secondary carbon bio-carriers for iron and steelmaking processes clearly addresses the CSP roadmap justified by the following facts, also mentioned in the roadmap ([69]):

- The decarbonization pathway SCU-PI is addressed by (i) the integration of carbonization, pyrolysis, and gasification processes for using secondary carbon bio-carriers as a substitute for fossil sources in existing iron and steelmaking process chains; (ii) the adaptation of grinding, drying, and pneumatic injection technologies to torrefied/carbonized bio-based sources in the BF and EAF; (iii) the design of new solid raw material injectors to use alternative material (i.e., the substitution of coal); (iv) use of auxiliary reducing agents and slag foaming materials (e.g., polymers from waste plastics, rubber from tires, biochar from agricultural/food residues).
- The decarbonization pathway CDA is addressed by (i) replacing traditional carbons and hydrocarbons with secondary carbon bio-carriers in existing melting processes;

(ii) preheating processes implementing multi-fuel burners for primary and secondary metallurgy with the use of secondary carbon bio-carriers as fuels.

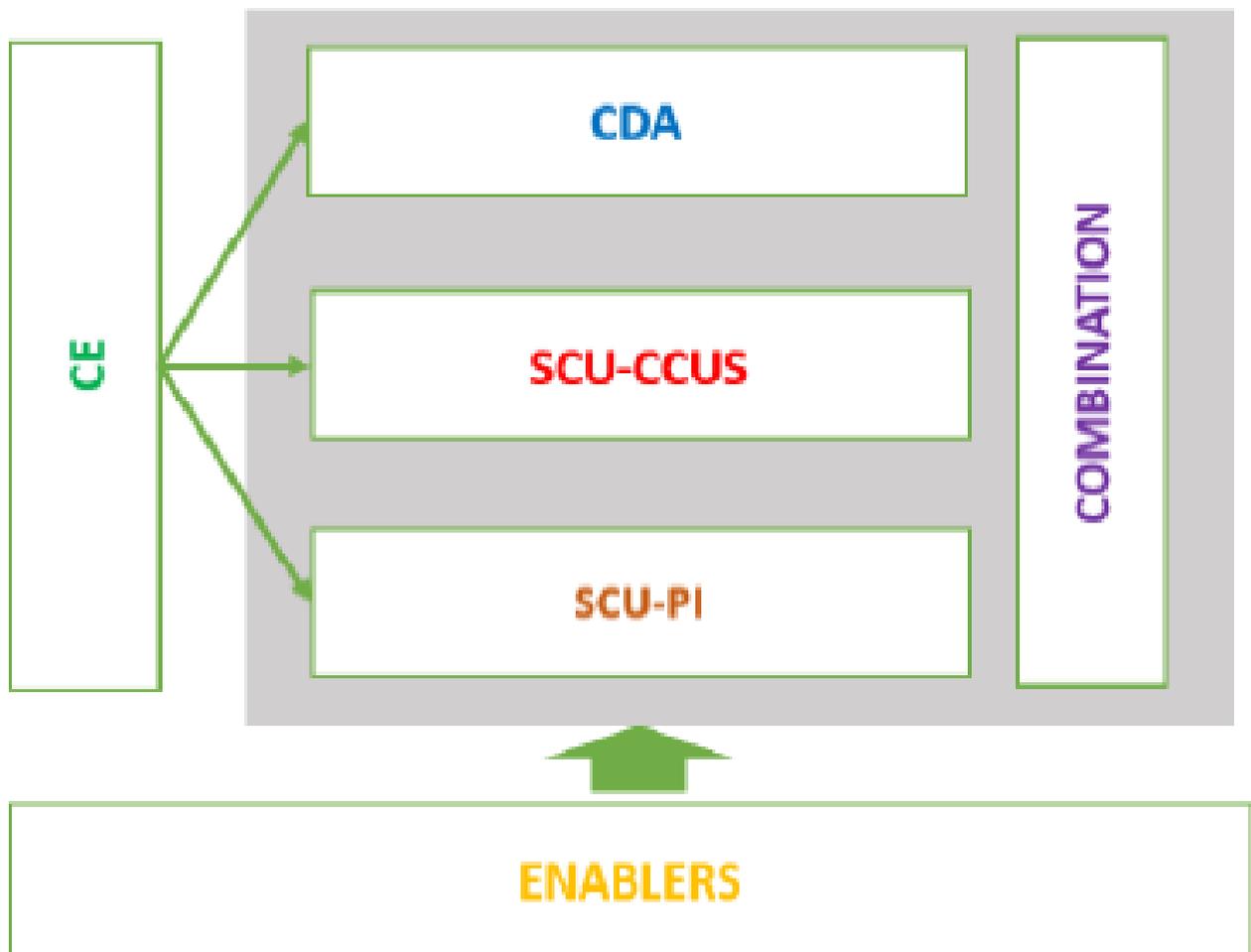


Figure 2. Areas of interventions and their interactions.

2. Pathways for the Use of Secondary Carbon Bio-Carriers in Metallurgical Processes

Iron and steelmaking can be principally conducted by four routes: BF/BOF, scrap/EAF, DRI/EAF, and SR/BOF [69,73]. The BF/BOF route includes cokemaking, iron ore sintering, iron ore pelletizing, BF-based ironmaking, casting, rolling, and power stations [74]. Current BFs operate with 70–80% sinter, 20–30% pellets, and 10–20% lump iron ore [75]. Figure 3 shows the four main iron and steelmaking routes using coal or coke that can be considered for the integrated use of secondary carbon bio-carriers.

As shown in Figure 3, torrefaction (light, medium, or severe, depending on the desired final properties of the solid product) can be used to improve the properties of the raw biomass. The torrefied biomass can either be directly used in cokemaking, sintering, and carbon composite agglomerates (CCAs) production, or it can be injected into the BF. It can be subjected to a further modification of properties through carbonization and compaction beneficiation by removing ash or adding minerals. Once the properties have been modified, secondary carbon bio-carriers can be directed to biocoke production. During cokemaking, the torrefied biomass can be used in a wide range from 3 to 50 wt.% of the feed mixture, depending on the requirements for the carbon-bearing material in a particular process. The biocoke obtained can be directed to:

- Sintering of iron ores to act as fuel;
- BF to carry out functions as a fuel and reducing agent (delivers chemical energy to melt the burden and contributes to the reduction of iron oxide to metallic iron), as a filter

for entrained particles from the raceway, and provides the carbon for the carburization (saturate hot metal with carbon);

- EAF to enable carburizing and slag foaming;
- Melter gasifier to generate heat, to act as a reducing agent, to produce a reducing gas, to ensure the permeability of the burden, and to carburize the hot metal.

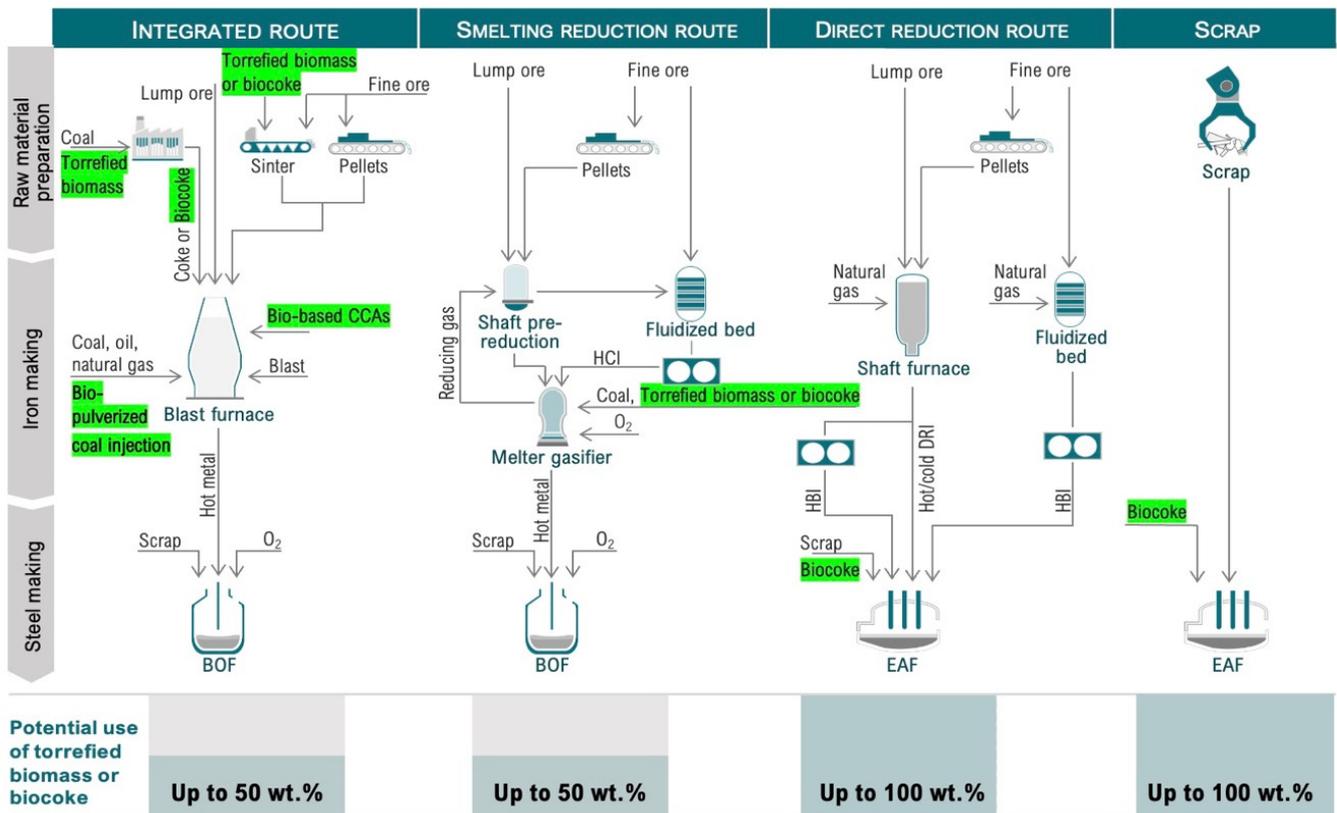


Figure 3. Main pathways for using secondary carbon bio-carriers in iron and steelmaking units.

For each metallurgical route, the carbon-bearing material requirements and the possibility of using secondary carbon bio-carriers will be discussed in detail.

2.1. Cokemaking

2.1.1. Features of the Process and Requirements for the Carbon-Bearing Material

During the cokemaking process, coking coal undergoes several chemical and physical changes, including softening, swelling, shrinkage, and re-solidification, which are requirements for forming a strong coke structure. The coke quality should meet strict requirements for the application in the BF because it is the main consumer. Biocoke, in turn, should also meet these requirements, but they are more challenging to achieve, as part of the coking coal has been replaced by secondary carbon bio-carriers. Table 1 shows the main characteristics of conventional coke.

Table 1. Main properties required for conventional coke.

Parameters	Conventional Coke	References
Ash, wt. %	<11	[76]
Volatile matters, wt. %	<1.1	[76,77]
Moisture by dry quenching, wt. %	<0.7	[76]
Moisture by wet quenching, wt. %	<5	[76]
C, wt. %	96.5–97.5	[76]
Fixed carbon, wt. %	88.8	[77]
H, wt. %	<0.8	[76]
O, wt. %	<0.4	[76]
N, wt. %	<1.3	[76]
S, wt. %	0.5–1.2	[76]
Coke reactivity index, wt. %	<30	[76]
Coke strength after reaction with CO ₂ , wt. %	<65	[76]
Structural strength, wt. %	<80	[78]
Size distribution, mm	40–80	[76]
Bulk density, kg/m ³	430–500	[76]
Porosity, %	45.0–55.0	[76]
Electric resistivity, mΩ·m	10–12	[78]
Calorific value (MJ/kg)	app. 29.0	[79]

Table 2 compares the properties of torrefied biomass and biocoke. Biocoke is a coke in which part of the coal in the coal blend is replaced by biomass (biomass can be used in its original state or after heat treatment) and obtained at a temperature of 1100 °C like conventional coke. The values for biocoke (mentioned in Table 2) can be within a very wide range, as they depend on the type of biomass used, the amount of coal substituted, and the conditions under which the biocoke is produced. The use of torrefied biomass in cokemaking plants is limited because it adversely affects the coke quality. After all, biocoke increases the porosity, the coke reactivity index (CRI), and reduces strength after a reaction with CO₂ (CSR). Increased CRI and porosity can be advantageous for some metallurgical processes, such as for injection in EAF. The low abrasion resistance and the chemical composition of the ash, which can accelerate its reactivity with CO₂ in the BF, are limiting factors for the use of torrefied biomass [80].

Table 2. Comparison of the properties of torrefied biomass and biocoke [16,78,79,81–84].

Parameters	Torrefied Biomass	Biocoke
Moisture, wt. %	4.8	0.65 or 1.35
Volatile matters, wt. %	34–85	1.4–2.7
Ash, wt. %	0.4	5.8–10.8
Fixed carbon, wt. %	13–45	87.8–92.4
C, wt. %	45–68	86.38–91.65
S, wt. %	traces	0.22–0.23
Coke reactivity index, wt. %	n/a	app. 25–50
Strength after reaction with CO ₂ , wt. %	n/a	app. 65–20
Calorific value, (MJ/kg)	16–29	app. 18–32

n/a is not available.

Usually, biochar is characterized by a lower amount of ash and sulfur, which, compared to biocoke, has an advantage for use in metallurgical processes. However, biocoke has a sufficiently high FC and a low VM. It is worth noting that, compared to conventional coke, biocoke has a lower value of ash and sulfur due to the replacement of coal within the blend.

It should be noted that the pre-treatment of secondary carbon bio-carriers before adding them to the coal blend contributes to an increase in its amount. Thus, raw biomass can be added to the coal blend only in a small amount of up to 3 wt.%, which does not adversely affect the properties of the coke [85]. However, after preliminary heat treatment of the biomass, its use can be increased by up to 10% [86]. Further increase in torrefied biomass does not allow biocoke with the requirements necessary for use in a BF to be obtained. The torrefied biomass in the coal blend acts as an inert material, reducing the caking ability of the blend [87]. In addition, the size of the torrefied biomass is important for the process of coal caking. Thus, a smaller particle size reduces fluidity to a greater extent than larger particles [75]. Therefore, using the process of compaction of torrefied biomass can improve its properties and minimize the impact on the quality of the final product [78,82]. Comparing the results of various studies on CRI and CSR, it can be concluded that biocoke with the addition of charcoal is more reactive compared to biocoke from bio-briquettes. This is because, in the case of charcoal, there is a more active biomass structure within the coke.

Kudo et al. [88] carried out briquetting of solid biomass (bamboo, larch, and ground wood) at a temperature and high mechanical pressure of 130–200 °C and 114 MPa, respectively, with subsequent carbonization at 900 °C. As a result of the research, the authors obtained coke with a tensile strength (TS) of 5–19 MPa.

Castro-Díaz et al. [89] performed carbonization tests with hydrochars obtained after the hydrous pyrolysis at 350 °C for 6 h using pine kraft lignin, torrefied lignin, and a mixture of initial and torrefied lignins with a ratio of 50:50 wt.%/wt.%. The amount of ash was less than that of good coking coal. However, the reactivity of the obtained biocoke was high compared to coke from good coking coal, and the mechanical strength of biocoke was significantly lower than that of coke.

Kim et al. [73] studied the TS of cokes and their reactivity using ash-free coal (AFC) as a binder and added torrefied biomass. The TS of the coke containing the torrefied fuel slightly decreased. The reactivity of the coke containing AFC and torrefied fuel was higher than that of the coke containing only AFC.

Castro-Díaz et al. [80] found that blends containing 70 wt.% low-rank coal, 24 wt.% torrefied lignin (before or after demineralization), and 6 wt.% phenolic resin produced biocokes with a suitable mechanical strength. However, reactivity was higher compared to coke.

Table 3 provides a comparative analysis of the required amount of raw biomass and torrefied biomass to replace conventional coke in a blast furnace under the conditions of Lorraine, Saint-Gobain PAM plant [90]. It can be concluded that the torrefaction process allows for improving the properties of biomass and reducing its quantity to replace conventional coke.

Table 3. Amount of raw biomass and torrefied biomass required to substitute conventional coke in BF on the example of Lorraine, Saint-Gobain PAM plant [90].

Source	Amount of Required Biomass (kt/Year)	
	20 wt.%	50 wt.%
Raw biomass	192.5	481.3
Torrefied biomass	77.0	192.5

The use of torrefied biomass in the BF can be the most environmentally friendly option, with 14.7 % CO₂-equivalent reduction, followed closely by pulverized biomass

char injection and charcoal lumps loaded at the top of the furnace, with 14.5 and 14.4 % CO₂-equivalent reduction, respectively [90].

2.1.2. Recommendations for the Use of Secondary Carbon Bio-Carriers

It can be concluded that, according to some research groups, secondary carbon bio-carriers can be considered an alternative to conventional metallurgical coke when finding the optimal conditions for obtaining biocoke. To mitigate the negative impact of torrefied biomass additives, the best way is to use biomass after torrefaction at the maximum possible temperature of 300 °C and in a compressed form, which will facilitate their local arrangement within the blend volume, and often not as uniform as when using the initial biomass. However, the use of compressed torrefied biomass in the coal blend may allow the use of a higher amount to replace coal without drastically degrading the properties of the biocoke. Compared to the existing conventional coke, the advantage of biocoke is reduced ash and sulfur. The amount of torrefied biomass may vary depending on the further purposes of using the biocoke and may reach 50 wt.%.

2.2. Iron Ore Sintering

2.2.1. Features of the Process and Requirements for the Carbon-Bearing Material

Sintering is the most economical and widely used process for preparing fine iron ore for use in a BF. Compared to pellets, sinter production is cheaper, and compared to lump ore, fluxed sinter is often more reducible with better softening characteristics [91]. At the same time, the sintering process accounts for about 10% of CO₂ emissions from the entire metallurgical industry [92].

Sintering occurs at temperatures of 1200–1400 °C, during which a mixture of iron ore fines and other materials (e.g., sinter return fines, limestone) is used [93]. Coke breeze or coal with low volatiles are used as fuel for sintering in the amount of 3–5 wt.% [94]. Table 4 shows the main properties of coke breeze for iron ore sintering. For iron ore sintering, the fuel should have a low VM of <3 wt.%, a high density of >700 kg/m³, a small size of <0.3–3.0 mm, and an FC content of more than 76 wt.%.

Table 4. Main properties of coke breeze for iron ore sintering.

Parameters	Values	References
Moisture, wt.%	<15	[50,95]
Volatile matters, wt.%	<3	[96]
Ash, wt.%	<12	[50,95]
Density, kg/m ³	>700	[96]
Size, mm	0.3–3	[96]
Total sulfur, wt.%	<2	[50,95]
Fixed carbon, wt.%	<76	[97]

There are few studies in the literature [61,98,99] that have analyzed the substitution of coke breeze with 10–25% of raw biomass in the process of iron ore sintering. It has been found that adding biomass can lead to some adverse effects, such as a decrease in productivity, an increase in the total fuel consumption (coke breeze and biomass), which negatively affects the economics and environment, and a decrease in the strength of the sinter. The use of highly reactive charcoal can also increase sintering velocity.

When using renewable fuel in iron ore sintering, it is essential to find the optimal ratio [100] because substitution can deteriorate the strength of the iron ore sinter and reducibility index, and heat treatment of the biomass is also essential to improve its properties as a fuel. This allows fuel requirements for use in iron ore sintering to be met.

Many studies [101–105] have focused on biomass pyrolysis and charcoal after pyrolysis for iron ore sintering. Generally, all research results were based on using biochars after

pyrolysis at 400–1000 °C. These studies found that, when using biochar with a relatively high FC content in the sintering process, a similar sinter yield and productivity to those obtained by using coke breeze can be achieved. Additionally, the application of biomass char in a sintering plant allows for a reduction of 6.7 % CO₂-equivalent compared to the use of anthracite [90].

2.2.2. Recommendations for the Use of Secondary Carbon Bio-Carriers

Biomass, after severe torrefaction, does not gain the necessary properties to completely replace the coke breeze. Biomass torrefaction may allow partial replacement of coke breeze and/or anthracite at 20–25% [99,106] without degrading the properties of the iron ore sinter. Moreover, the use of torrefied biomass in a compressed form can be considered.

The use of biocoke produced using torrefied biomass up to 50 wt.% may allow the 50 wt.% replacement of conventional coke breeze. Generally, the advantage of using biocoke compared to coke breeze is that the ash content is much lower, which guarantees a smaller particulate matter content in the flue gas.

2.3. Bio-Based Carbon Composite Agglomerates (CCAs)

2.3.1. Features of the Process and Requirements for the Carbon-Bearing Material

CCAs are mainly used in the BF and the direct reduction process [107]. Conventional CCAs are produced as pellets by cold bonding with or without a binder or briquettes by hot or cold pressing. Special studies are needed on the production aspects of these pellets, especially since their use in a BF requires higher qualities in terms of strength. CCAs can be referred to as new raw materials for iron production when consisting of carbon-bearing biomaterial powder, iron ore powder, and a small amount of binder materials. Carbon-bearing biomaterials used in pellets can be used in the raw state or after heat treatment. However, there are several requirements for this type of CCA. For example, top-loaded CCAs should meet the minimum mechanical strength requirements for a BF. Otherwise, they can worsen the efficiency of the process [108]. In addition, carbon-bearing biomaterials directly affect the mechanisms of mass and heat transfer, temperature profile, and gas distribution inside the BF.

According to Ahmed et al. [109], the ash content should not increase when using new carbon-bearing components. In this regard, the use of torrefied biomass is a promising approach. Furthermore, agglomerates should have an FC content in a range to ensure the iron carburization process. The reactivity requirements for carbonaceous materials are not very stringent. Nevertheless, it is important that the carbon in the CCAs does not participate in any chemical reactions below the set temperature of the heat reserve zone, as this can reduce the efficiency of the process. One of the most important quality parameters is the strength of composite pellets. Chemical reactions lead to the formation of gasses within the pellet, increasing its porosity [109], and it has been reported by Mousa et al. [108] that the main disadvantage of CCAs is their low crushing strength.

According to Khanna et al. and Ueki et al. [96,110], up to 46% of biochar can be used in agglomerates in the direct reduction (DR) process. It has been pointed out that the reduction rate of iron oxide is higher in biochar-based CCAs due to its greater reactivity than in conventional coal or coke-based CCAs. For instance, Hu et al. [111] focused on using only biochar-iron ore composites. It was concluded that pellets with 60 wt.% iron ore content and a temperature higher than 800 °C promoted carbon conversion and iron ore reduction. Praes et al. [112] carried out tests on iron ore pellets firing, which consumed natural gas, coal (anthracite fines), and two different eucalyptus charcoal (partially replaced) with two diverse ranges of VM. The first charcoal had a VM range of 20.3–25.98%, and the second varied from 9.4% to 11.1%. It was concluded that replacing 7.5% anthracite fines with the two eucalyptus charcoal is possible; 10% anthracite fines replacement is possible with the charcoal with the lower VM.

In another research work [113], the effect of using palm kernel shells as a reducing agent was studied. Iron oxide in iron ore can be completely reduced to magnetite and

partially reduced to wustite when up to 30 wt.% palm kernel shells are present in the blend. In addition, the degree of reduction increases with increasing temperature up to 900 °C, as evidenced by the mass loss of the composite pellet and the mass of oxygen removal.

The level of metallization of the reduced pellets is also an important factor. Srivastava et al. [114] studied the effect of 20 wt.% fine wood on the quality of the resulting pellets. Pellets were fired at different temperatures, and residence times were also studied. In most cases, the total iron loss in the slag from the original pellets was less than 1% by weight. Pellets that contained 97% Fe on average were obtained, and at the highest firing temperature, the pellets contained 98.10% Fe.

Han et al. [31] studied the application of bamboo char, charcoal, and straw fiber to produce DRI. The carbon content was 87.5%, 68.5%, and 20.89% for bamboo char, charcoal, and straw fiber, respectively. The research results showed that the metallization level increased with increasing temperature and, as a result, reached 91%. Furthermore, one of the interesting results was that, despite the low FC content in straw fiber, the rate of metallization of the pellets was higher than that of charcoal and bamboo charcoal pellets due to the increased amount of carbohydrates. Regarding the compressive strength of the pellets, it is possible to achieve production requirements, namely >1800 N, only when using a high firing temperature.

2.3.2. Recommendations for the Use of Secondary Carbon Bio-Carriers

Based on the above and the properties of torrefied biomass, torrefied biomass can be used after the maximum possible torrefaction temperature. This allows the maximum possible values of FC to be reached, which is important for ensuring the carburization process. As the VM of the fuel increases, the possibility of thermal decomposition becomes more likely. This means that secondary carbon bio-carriers with a relatively low VM are less likely to decompose at lower temperatures. It can be concluded that torrefied biomass has the potential to completely replace coal in the production of CCAs and to achieve the necessary production requirements, but finding the optimal technological parameters is also required.

2.4. Injection of Pulverized Secondary Carbon Bio-Carriers

In conventional pulverized coal injection (PCI) technology, non-coking or weakly coking coals are injected into the raceways of BFs to partially replace the coke [115]. This technology is the most efficient method of replacing non-renewable fuels in the BF with different secondary carbon carriers. For example, there is a practice of injecting about 20 kg/tHM of waste plastics at Voestalpine Stahl BF A [116].

Table 5 shows the selected properties of conventional pulverized coal.

Table 5. Selected parameters of conventional pulverized coal [26,117].

Component (wt.%)	C	H	O	N	S	Ash	Volatile Matters	Moisture
	80.6	4.35	5.35	1.65	0.45	10.89	19.50	0.01
References	[26]	[26]	[26]	[26]	[26]	[26]	[117]	[117]

The use of biomass in its raw state after torrefaction, as well as after pyrolysis, in PCI has been well studied [28,75,118–122], and the use of secondary carbon bio-carriers in this technology is proven. The papers mentioned above revealed the possibility of using 20–40% biomass injection, or even up to 100% replacement of injected coal. However, it should be noted that for the purposes of PCI, the secondary carbon bio-carriers should be evaluated through several properties, such as the fuel ratio, ignition temperature, and burnout [123].

Phanphanich et al. [124] reported that proximate and elemental compositions of torrefied biomass could be improved after torrefaction at temperatures ranging from 225 °C to 300 °C, and were comparable to coal.

Chen et al. [125] studied the effect of torrefaction on improving the physical and chemical properties of pulverized biomass for use in a BF. The authors concluded that the calorific value could be improved by subsequent compaction.

In another paper by Chen et al. [126], the torrefaction and burning characteristics of bamboo, oil palm, rice husk, bagasse, and Madagascar almonds were studied and compared to high-volatile bituminous coal. As a result, the authors emphasized that a torrefaction temperature of 300 °C is suitable for converting the initial biomass into biochar, which can subsequently be used for injection into a BF. These results are consistent with the results of studies by Du et al. [123], who reported that biomass torrefied at 300 °C or carbonized at temperatures below 500 °C could be applied with coals for PCI. However, torrefied biomass can only partially replace coal to keep a good burnout in raceways.

Recommendations for the Use of Secondary Carbon Bio-Carriers

The main limitation of the widespread use of torrefied biomass is its high yield of VM. Therefore, the partial replacement of coal from 20–50% with biomass after severe torrefaction can be considered. For a complete replacement of coal, it is possible to consider the option of using a blend of torrefied biomass at 300 °C and biochar obtained after carbonization of torrefied biomass at a ratio of 50:50.

2.5. Blast Furnace Process

2.5.1. Features of the Process and Requirements for the Carbon-Bearing Material

The BF is currently the most predominant technology to produce iron for steelmaking. The principle of the process is the conversion of iron oxides to iron using carbon-based reducing agents. The BF is a large countercurrent metallurgical shaft furnace in which iron oxides and coke fed into the furnace from above move downwards, and the reducing gasses move upwards [127]. The reducing conditions in the furnace are created by top-charged coke and tuyere-injected reducing agents; for instance, pulverized coal (PC). Using carbon-bearing materials is essential to operate a BF, and the requirements are strict [128].

Two of the most important parameters for using metallurgical coke in a BF are the CRI and CSR. According to Alvarez et al. [129], the industrial quality requirements for coke are a CRI under 30% and a CSR above 55%; according to Babich et al. [130], CRI and CSR requirements in European BFs are 23% and 65%, respectively. In addition to these two parameters, the coke should have good mechanical strength; M40 should be >88%, M25 should be >90%, and M10 should be <6% [50]. These indices represent the percentage of material grain sizes remaining > 40 mm, >25 mm, and >10 mm after mechanical treatment (100 revolutions in a drum) according to the Micum drum test [50]. All of this limits the use of secondary carbon bio-carriers for producing coke for BF purposes.

There is a current practice of using charcoal or a mixture of charcoal and PC in mini BFs with a production capacity of 40,000–350,000 t/year [131]. The advantages of the mini BF technology are low emissions, low sulfur content in the iron, and low slag volumes. The carbonization temperature for charcoal can range from 300–700 °C, depending on the quality requirements. For example, a relatively high VM can be useful in PCI technology.

Another study on the mini BF technology was carried out by de Castro et al. [132]. In this work, various scenarios for using charcoal and hydrogen-rich fuel gas were simulated. Some scenarios have shown that it is possible to increase productivity and, at the same time, reduce carbon consumption.

The use of charcoal has also demonstrated the potential to reduce CO₂ emissions in steel production. However, according to Hanrot et al. [133], the successful use of charcoal can be implemented if local conditions and quality criteria permit, such as the availability of biomass cultivation and the production of charcoal in a sustainable manner.

2.5.2. Recommendations for the Use of Secondary Carbon Bio-Carriers

The main pathways for secondary carbon bio-carriers in the BF/BOF route are shown in Figure 4.

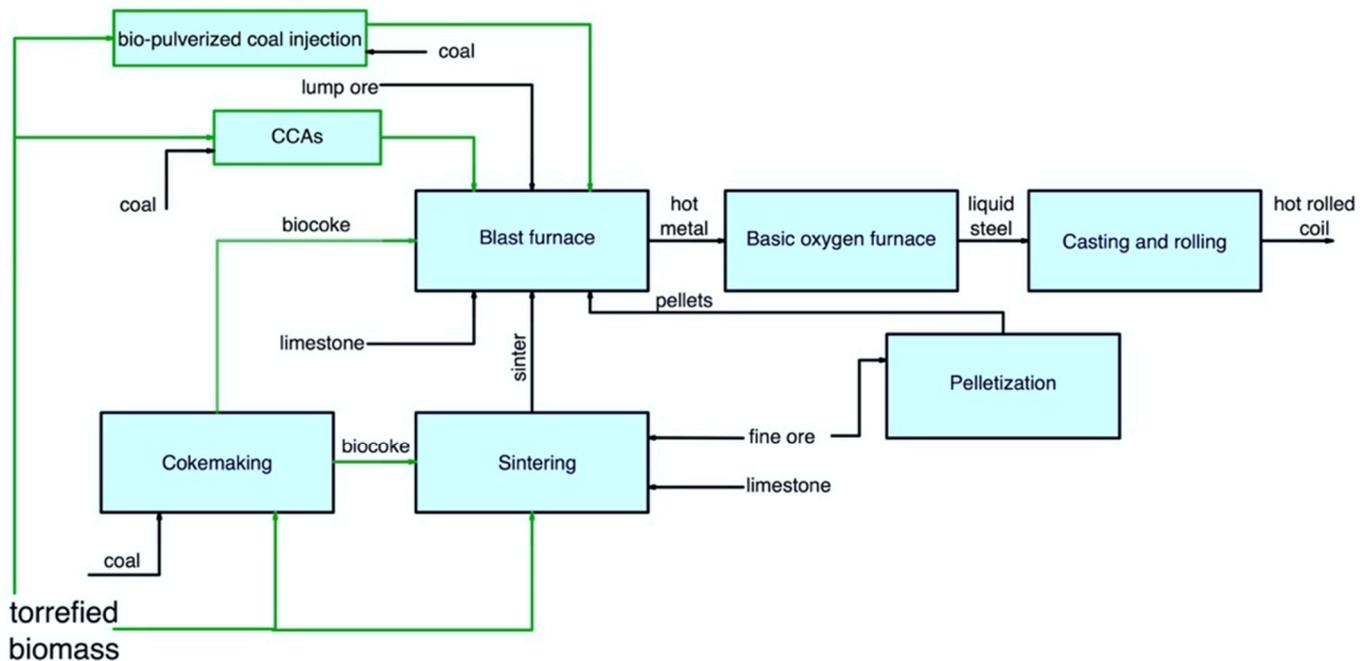


Figure 4. Main pathways for using secondary carbon bio-carriers in the BF/BOF route.

In a BF, the following ways of using secondary carbon bio-carriers can be considered:

- The use of biocoke produced with the addition of torrefied biomass, as discussed earlier in Section 2.1 Cokemaking;
- The use of torrefied biomass or biocoke to produce sinter, which is afterwards used in the BF;
- The use of bio-pulverized coal injection technology with partial replacement of coal with up to 50% torrefied biomass or full replacement of coal with a mixture of torrefied biomass and torrefied biomass after carbonization;
- The use of torrefied biomass to produce CCAs, which are afterward used in the BF.

2.6. Electric Arc Furnace

2.6.1. Features of the Process and Requirements for the Carbon-Bearing Material

EAF-based steel production accounts for 28% of global output (~42% in the EU), according to the World Steel Association [134]. EAFs mainly use electricity with a small amount of carbon-bearing material [135]. Carbon-bearing material is added to the EAF route to perform the following functions: (a) charge carbon, with the main aim of adding chemical energy and creating a reducing atmosphere during smelting that minimizes the oxidation of alloys and metals; (b) injected carbon, also known as slag foaming carbon, where slag foaming technology in the EAF is used to increase energy efficiency and productivity, reduce operating costs, and improve the quality of steel produced [119]; and (c) afterward as a carburizer carbon in the ladle furnace for the carburizing process.

Norgate et al. [119] have shown that replacing a conventional carbon source from 50% to 100% is possible with charcoal after pyrolysis; also under life cycle assessment was charcoal production from Mallee eucalypt biomass. Yunos et al. [136] investigated the possibility of using biomass in the EAF; using palm shell char to partially replace coke in a laboratory-scale reactor at 1550 °C using the sessile-drop approach in an argon atmosphere. The test results showed an improved interaction with EAF slag compared to conventional coke.

In contrast, Huang et al. [137] concluded that the interaction between biochars and slag was weak compared to other carbon-bearing materials. The authors studied five carbon-bearing samples to replace conventional fuels: biochar obtained from wood biomass by slow pyrolysis at 900 °C, biochar obtained from wood biomass by fast pyrolysis at 400 °C, technical graphite, metallurgical coke, and semicoke obtained from waste tire pyrolysis at 700 °C.

Another study was carried out as part of the GreenEAF project (funded by the framework of the Research Fund for Coal and Steel, RFCS, 2009–2012, RFSR-CT-2009-00004). Bianco et al. [30] suggested a 1:1 substitution of coal (anthracite) and charcoal used in the EAF on an energy basis, assuming that charcoal is similar to or higher quality than coal and charcoal. The tests showed that charcoal could be used for both charge and slag foaming. Additionally, to achieve good foaming, the authors suggested several process approaches, such as improving the wettability of charcoal and slag, and the charcoal should be injected under the slag. Additionally, Fidalgo et al. [138] studied two biochars obtained from agricultural residues, grape seed and pumpkin seed chars, for EAF steelmaking. Hard coal and three types of anthracites were also used to compare the results. Biochars were obtained during the GreenEAF project for test runs. The temperatures used to produce biochar were 500 °C and 600 °C. A lower pyrolysis temperature of 500 °C was applied to obtain injected carbon with a higher VM to positively affect the foaming behavior. A pyrolysis temperature of 600 °C was applied to obtain charge carbon, for which it is more important to have a lower VM. The authors found that the biochar used in the project could replace coal with regard to reactivity. Furthermore, it was noted that the high VM of biochar is an adequate stimulation for slag foaming.

As a follow-up to the project mentioned above, Meier et al. [139] performed test runs with different carbon carriers in a dynamic process simulation model to investigate their application in an EAF within the framework of the GreenEAF2 project (RFCS, 2014–2017, RFSP-CT-2014-00003). Within this project, charcoal obtained from pyrolysis and torrefaction and virgin ligneous biomass (palm kernel shells) were used. The results using biomass showed a different behavior of the two materials studied; namely, anthracite and palm kernel shells. The mass fraction of waste gasses increased in the case of palm kernel shells, while melting the first portion of scrap because they have a higher VM content and are a more reactive material. It was concluded that it is possible to increase the use of post-combustion oxygen early in the process for palm kernel shells. It may subsequently lead to higher energy releases and increased melting rates.

Nwachukwu et al. [140] presented a model for the application of biofuels in steel production. According to the scheme, the amount of conventional fuel substitution ranged from 0% to 100%. However, it is worth noting that the model focused on using charcoal and bio-gas products.

Furthermore, Echterhof [29] presented a review of the utilization of alternative carbon sources by the EAF steel production route. The review showed that the use of alternative carbon sources in the EAF is required to produce fully environmentally friendly and carbon-neutral steel. Many research results have shown that it is fundamentally possible to use such substitutes.

2.6.2. Recommendations for the Use of Secondary Carbon Bio-Carriers

Figures 5 and 6 show the pathways for secondary carbon bio-carriers in the EAF, where scrap is used as the main raw material, in the subsequent ladle furnace, and by DRI-EAF routes.

There are several possible ways to apply secondary carbon bio-carriers (biocoke):

- a charge carbon in an EAF;
- an injected carbon in an EAF;
- a carburizer source in a ladle furnace.

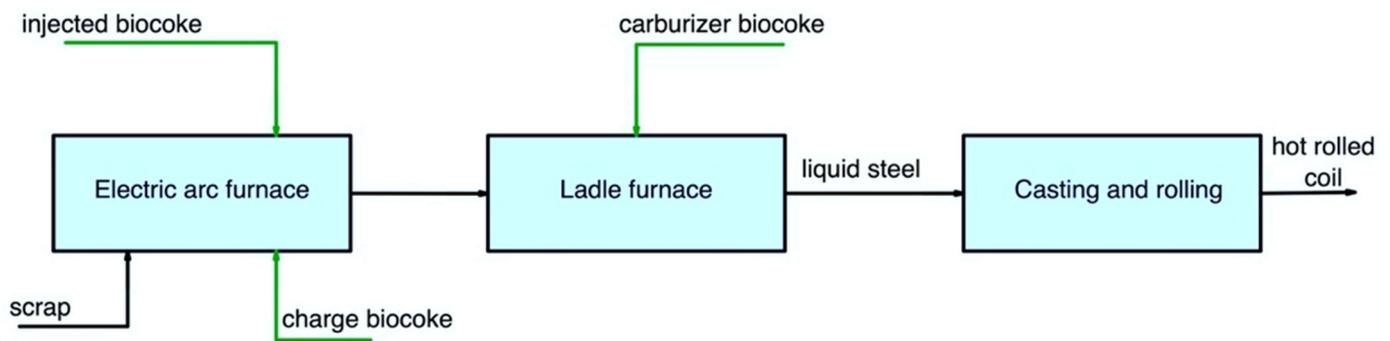


Figure 5. Main pathways for using secondary carbon bio-carriers in the EAF, where scrap is used as the main raw material.

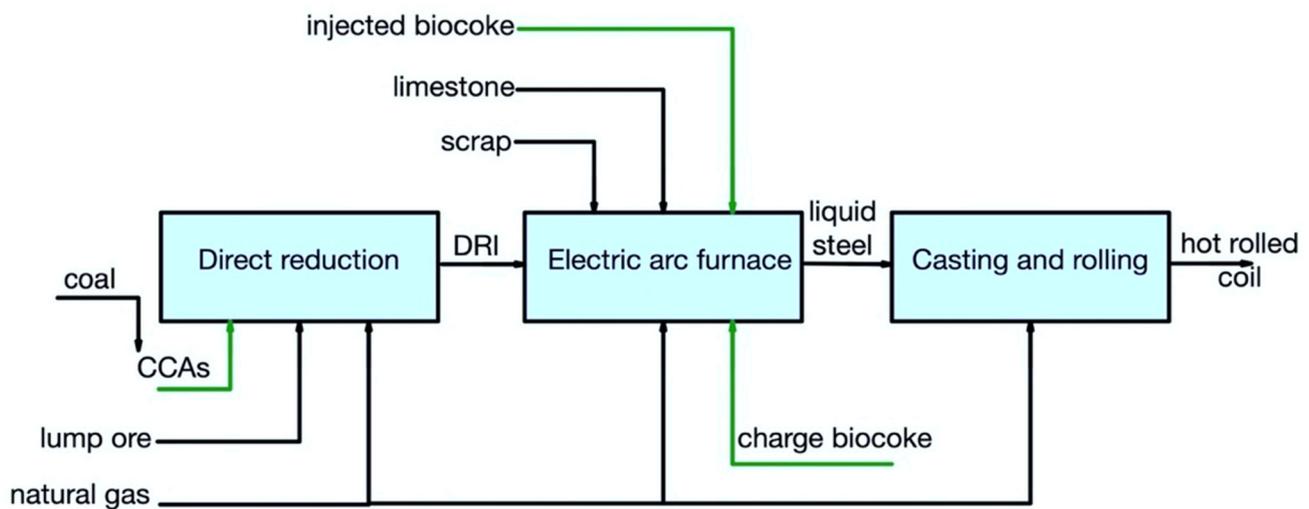


Figure 6. Main pathways for using secondary carbon bio-carriers in the DRI/EAF route.

It should be noted that, in the DRI/EAF route, it is also possible to consider using CCAs obtained using torrefied biomass.

Based on the above requirements, it can be concluded that the use of torrefied biomass is practically limited. However, the use of biocoke up to 100% as a carbon source is possible even with a high additive amount of torrefied biomass up to 50% within coal blend because it can meet the requirements for this process in terms of the VM and has a sufficient amount of FC > 85% for carburizing the steel or creating foaming slag to improve the energy efficiency of the melting process. Additionally, it is important to mention that there are no strict requirements for the strength of the carbon source for use in an EAF because of the features of the furnace [119]. Therefore, using biocoke with a high amount of torrefied biomass is a promising pathway for future research.

2.7. Smelting Reduction Processes

There are mainly two smelting reduction processes that are commercially proven, COREX and FINEX. Iron ores are heated and pre-reduced to DRI within these processes by the off-gas coming from the melter gasifier. The pre-reduction step could be implemented in a reduction shaft (COREX) or a fluidized bed reactor (FINEX). Pre-reduced iron ores are then melted in the melter gasifier. The melter gasifier uses oxygen and coal as a reducing agent. Subsequently, the hot metal is fed to the BOF for steelmaking [141–143]. These processes generally use non-coking coal as a fuel source, with the main requirements of FC > 40% and VM < 34%. Considering these requirements, secondary carbon bio-carriers can be used after torrefaction to the highest possible temperature, thus obtaining biochar with the highest possible values for FC and the lowest VM. Another option is to use biocoke,

whereby it is possible to consider using biocoke obtained with a high amount of torrefied biomass of up to 50% in this route. An additional benefit of biocoke is that sulfur-containing compounds and ash formation are minimized.

2.7.1. COREX Process

COREX is a process that produces hot metal out of lumpy iron carriers (mainly pellets, but also lump ore and sinter). The main reducing agent is briquetted coal. The process mainly consists of two reactors; i.e., a reduction shaft and a melting gasifier [144]. For the COREX process, the most suitable conventional carbon source is non-coking coal with 55–70 wt.% FC content. There are also a number of requirements for the ash content and moisture content. The ash content should be lower than 12 wt.%, as a higher ash content increases the slag volume, resulting in high specific fuel consumption, poor drainage through the coal bed, and reduced productivity [145]. The moisture content should be as low as possible. The main requirements for the properties of the carbon-bearing material are given in Table 6.

Table 6. Main requirements for non-coking coal for COREX [145].

Parameters	Values
Moisture, wt.%	<4
Ash, wt.%	<12
Volatile matters, wt.%	25–27
Sulfur, wt.%	<0.6
Fixed carbon, wt.%	55–70
Calorific value, kJ kg ⁻¹	>27,000

Although a significant amount of coal is used in the COREX process, 10–20% of metallurgical coke is required for heat generation, reducing gas production, and maintaining char bed permeability. The coke quality required for the COREX process is shown in Table 7.

Table 7. Main requirements for coke for COREX [141,146].

Parameters	Values
Coke reactivity index, wt.%	<35
Coke strength after reaction, wt.%	>55
Volatile matters, wt.%	app. 25
Ash, wt.%	<15
Sulfur, wt.%	<1
Grain size, mm	10–15

Several studies have investigated the use of torrefied biomass for the COREX ironmaking route. Adeleke et al. [147] investigated using coal briquettes and pre-treated biomass for use in COREX ironmaking processes. The initial biomass was ground to <2 mm and subjected to a torrefaction process at a temperature of 260 °C and a residence time of 60 min. Carbon fines of 95 wt.%, torrefied biomass of 5 wt.%, and binder were homogeneously mixed, followed by the addition of water and proper mixing to activate the binder for agglomeration. The authors concluded that the coal fines-torrefied biomass briquettes satisfactorily met the required physical properties for the COREX ironmaking process.

Moreover, according to the scheme of mass, iron, and carbon balance for the Bio-COREX/BOF case by Yang et al. [148], the biochar substitution rate can be as high as 45 %LHV.

Figure 7 shows the main pathway for using secondary carbon bio-carriers in the COREX/BOF route. This layout can consider using the following:

- Biomass torrefied at the highest possible temperature can partially replace coal;
- Biocoke for complete replacement of the conventional coke. At the same time, it is possible to consider using biocoke with a high amount of torrefied biomass as a substitute for coal.

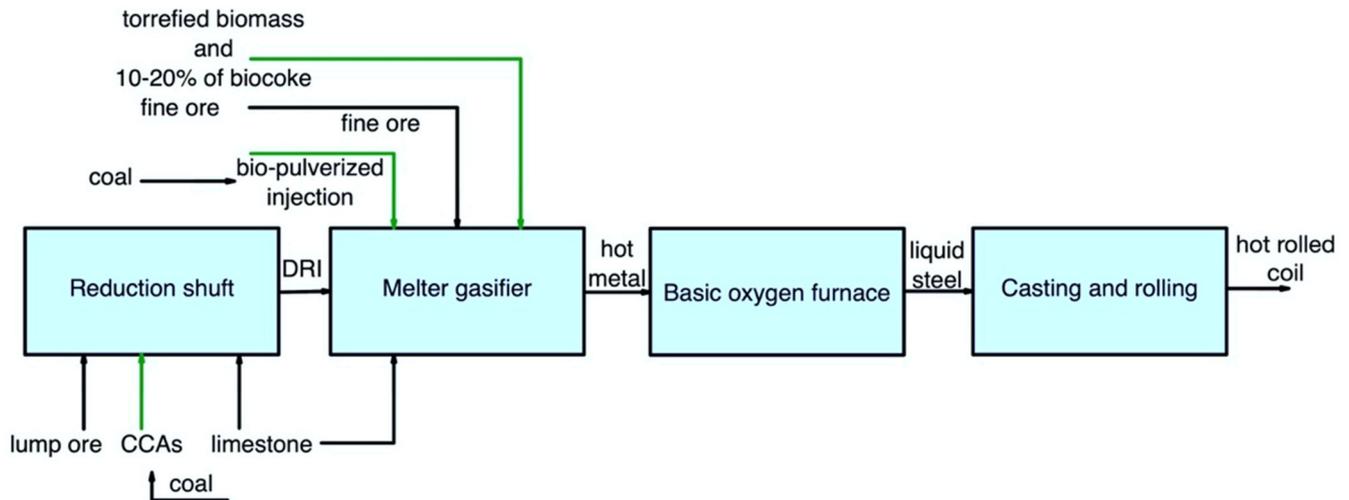


Figure 7. Main pathways for using secondary carbon bio-carriers in the COREX/BOF route.

In addition, the use of bio-pulverized injection and CCAs should be considered possible options for this route.

2.7.2. FINEX Process

The FINEX smelting-reduction process is based on the direct use of non-coking coal and fine ore. The major difference between the COREX and FINEX processes is that the FINEX process can directly use sinter feed iron ore without an agglomeration [146]. The main FINEX process consists of a melter-gasifier and a series of fluidized bed reactors, forming a countercurrent system in which fine ore is reduced to DRI in three or four stages. The fine DRI is then compacted and loaded as hot compacted iron (HCI) into a gasifier melting unit. The HCI is then reduced and melted. The heat required for reduction and melting is provided by coal gasification. The reducing gas, also from coal gasification, passes through fluidized-bed reactors [146]. From the point of view of the fuel route, non-coking coals and coal briquettes are directly loaded into the melter-gasifier unit. The main fuel quality requirements for the FINEX process are shown in Table 8.

Table 8. Main requirements for fuel for FINEX.

Fixed Carbon, wt.%	Ash, wt.%	Volatile Matters, wt.%	Sulfur, wt.%	Reference
min. 55	up to 25	<35	<1	[149]

Figure 8 shows the use of secondary carbon bio-carriers in the FINEX/BOF route.

It is important to note that the use of secondary carbon bio-carriers in this scheme does not differ much from the COREX/BOF route. It is possible to partially replace coal briquettes using biomass torrefied at the highest possible temperature and subsequent compaction. The use of lumpy biocoke can be considered a complete replacement for coal. At the same time, it is also possible to consider the use of biocoke obtained with a high amount of torrefied biomass. Bio-pulverized injection and CCAs can be considered for using secondary carbon bio-carriers.

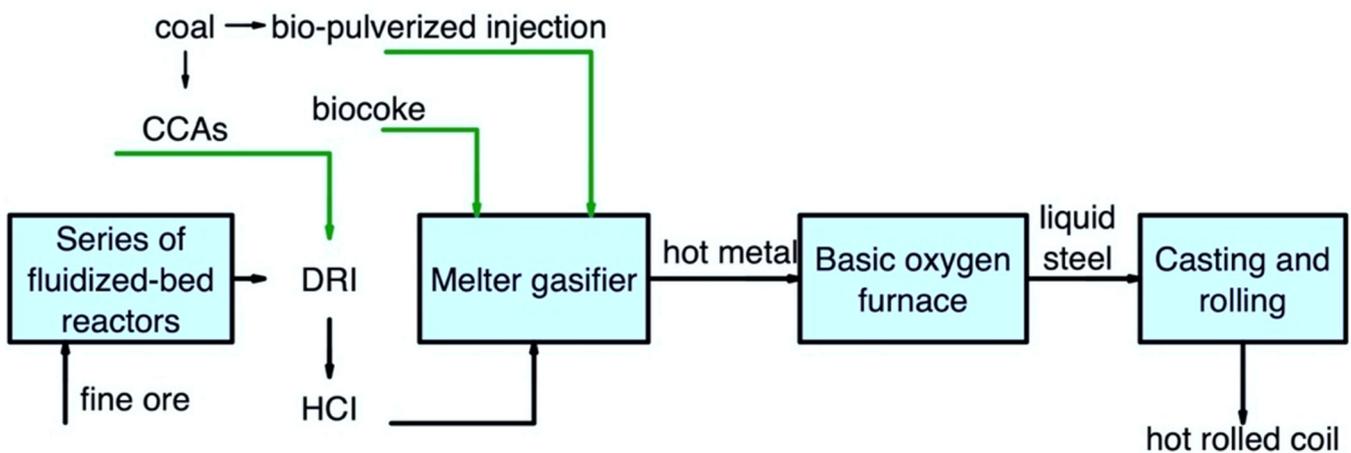


Figure 8. Main pathways for using secondary carbon bio-carriers in the FINEX/BOF route.

2.7.3. Hisarna and Hismelt Processes

Hisarna is a melt-in-bath technology that combines coal preheating and partial pyrolysis in a reactor [150]. This technology uses a melting vessel for the final reduction of ore and a melting cyclone for ore melting. Reduced CO₂ emissions are enabled due to the absence of sintering and coking processes. The Hisarna technology reduces CO₂ emissions by almost 70% by using biomass or natural gas instead of coal, flue gas treatment, CO₂ storage, and thermal energy reuse [151]. Pulverized coal [152] and biomass [151] can be used as fuel in this process. Khasraw et al. [153] studied the properties of two samples of charcoal (birch wood and grass) compared to thermal coal. It was observed that chars showed a faster reaction compared to thermal coal. According to another paper by Khasraw et al. [150], torrefied grass contains a large amount of water and CO₂ that is released at a very low temperature. Therefore, pre-treatment to approximately 400 °C is essential to obtain biochar with properties similar to the coal introduced into Hisarna.

Htet et al. [154] studied the properties of charcoal, thermal coal, and carbon black as reducing agents for the Hisarna process, and also studied their properties to understand how these materials can affect the process. In the case of using substitutes, the important parameters are the alkalinity index, VM content, and its amount, as well as the amount of ash.

Figure 9 shows the use of secondary carbon bio-carriers in the Hisarna/BOF route.

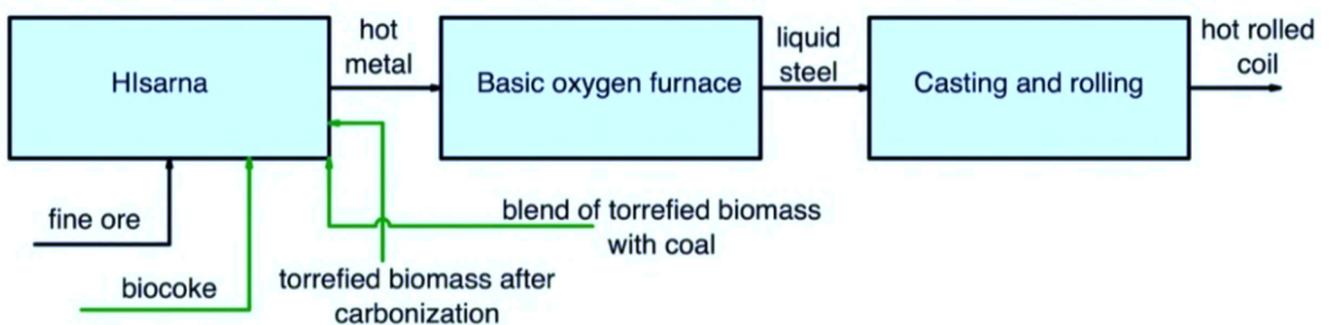


Figure 9. Main pathways for using secondary carbon bio-carriers in the Hisarna/BOF route.

Based on the analysis of the results, it is challenging to use torrefied biomass even at the highest possible temperature due to limitations in its properties. However, the first option of using torrefied biomass after carbonization can be considered for improving the properties. Secondly, a blend of coal with torrefied biomass (up to the highest possible torrefaction temperature) can be used. For further research, it could be of interest to replace coal with up to 50 wt.%. Additionally, the third option of using biocoke obtained using torrefied biomass is viable. At the same time, the amount of torrefied biomass in biocoke

can reach up to 50 wt.% because the VM and FC will be at the required level even with such an amount of a substitute.

A similar recommendation for using biomass to replace pulverized coal with a particle size of <3 mm can be applied to the Hismelt process, which uses a two-stage rotary kiln process to preheat and pre-reduce iron-bearing raw materials (particle size < 6 mm) at 750 °C.

2.8. Ferroalloy Industry

2.8.1. Submerged Arc Furnace

The ferroalloy industry refers to iron alloys with a high proportion of additional elements, such as chromium, manganese, silicon, aluminum, and other elements. They are generally produced in a SAF at a temperature of >1500 °C. A three-phase electrode (AC power supply) is inserted into a mixture of ferroalloys and carbon-bearing reductants [155]. Carbon-bearing materials (coke or anthracite) are used to produce ferroalloys through a carbothermic reduction, which acts as a reducing agent. Biobased reductants can potentially replace fossil-based ones, mitigating anthropogenic CO₂ and GHG emissions and increasing the efficiency of the smelting process. This leads to a search for new ways to produce and use alternative bioreductants to produce ferroalloys. The most important properties required for carbonaceous reducing agents are high reactivity, electrical resistance, high conversion rates, low sulfur content, high bulk density, and specific energy. Table 9 gives some of the important properties of conventional carbonaceous materials for use in ferroalloy production.

Table 9. Required properties for conventional coke in ferroalloy production [35,156].

Parameters	Conventional Coke
Fixed carbon, wt.%	86–88
Volatile matter, wt.%	≤1
Ash, wt.%	10–12
Reactivity with CO ₂ at 1060 °C, %C/s	(0.2–0.5)10 ^{−2}
Thermal cohesion strength, %	93–97
Thermal abrasion strength, %	82–89
Electrical resistance for carbon material with size, mm:	10–20
Electrical resistance at 1000 °C, U·m	0.003–0.008
Electrical resistance at 1400 °C, U·m	0.003–0.009

Surup et al. [157] investigated the pyrolysis treatment of various types of biomass at high temperatures to obtain biochars, which can be subsequently used to produce ferroalloys. It was concluded that with a heat treatment > 2400 °C, it is possible to obtain biochar from renewable sources with a reactivity close to conventional coke. In addition, the co-pyrolysis of biomass with bio-oil was studied, and the prospect of obtaining biochars with a reactivity comparable to metallurgical coke was shown.

Electrical resistance is also an important indicator for carbon-bearing materials. According to another paper by Surup et al. [35], conventional coke used in a SAF is expected to have an electrical resistivity of 7–10 mΩm at room temperature and 1–10 mΩm at 1400 °C for a particle size of 5–20 mm. Coke substitutes, i.e., charcoal, have an electrical resistance of more than 106 mΩ at room temperature, which decreases with increasing temperature. The electrical resistance of charcoal obtained after carbonization at 950 °C was similar to that of coal char, varying from 1.7 mΩm to 3.4 mΩm [35].

Bazaluk et al. [78] investigated the properties of biocoke obtained at different carbonization temperatures and with varying amounts of biomass pellets for use in BFs and non-BFs. It was found that the electrical resistance of carbon-bearing materials decreases

with an increase in the carbonization temperature, which is associated with the formation and/or increase of carbon crystallites. The electrical resistance was in the range of 12.0–15.9 m Ω m for 950 °C and 10.3–13.8 m Ω m for 1100 °C.

The selected obtained results [12,34] are the basis for the approach to use biocoke as a reductant to produce ferroalloys, and from the point of view of reducing the dependence on fossil fuel and mitigating emissions associated with the metallurgical industry, in particular the production of ferroalloys. Biocoke is also suitable for use in terms of such indicators as the amount of FC of more than 85% and the VM content.

According to Surup et al. [158], charcoal can replace conventional carbon-bearing reductants by more than 40% in the SAF, while complete replacement requires an additional heat treatment of charcoal.

2.8.2. Recommendations for the Use of Secondary Carbon Bio-Carriers

In ferroalloy production, the application of torrefied biomass is challenging because it does not achieve the required properties due to the low torrefaction temperature. However, biocoke has good potential for use in a SAF. Figure 10 is a layout of the main pathway for the use of secondary carbon bio-carriers in ferroalloy production.

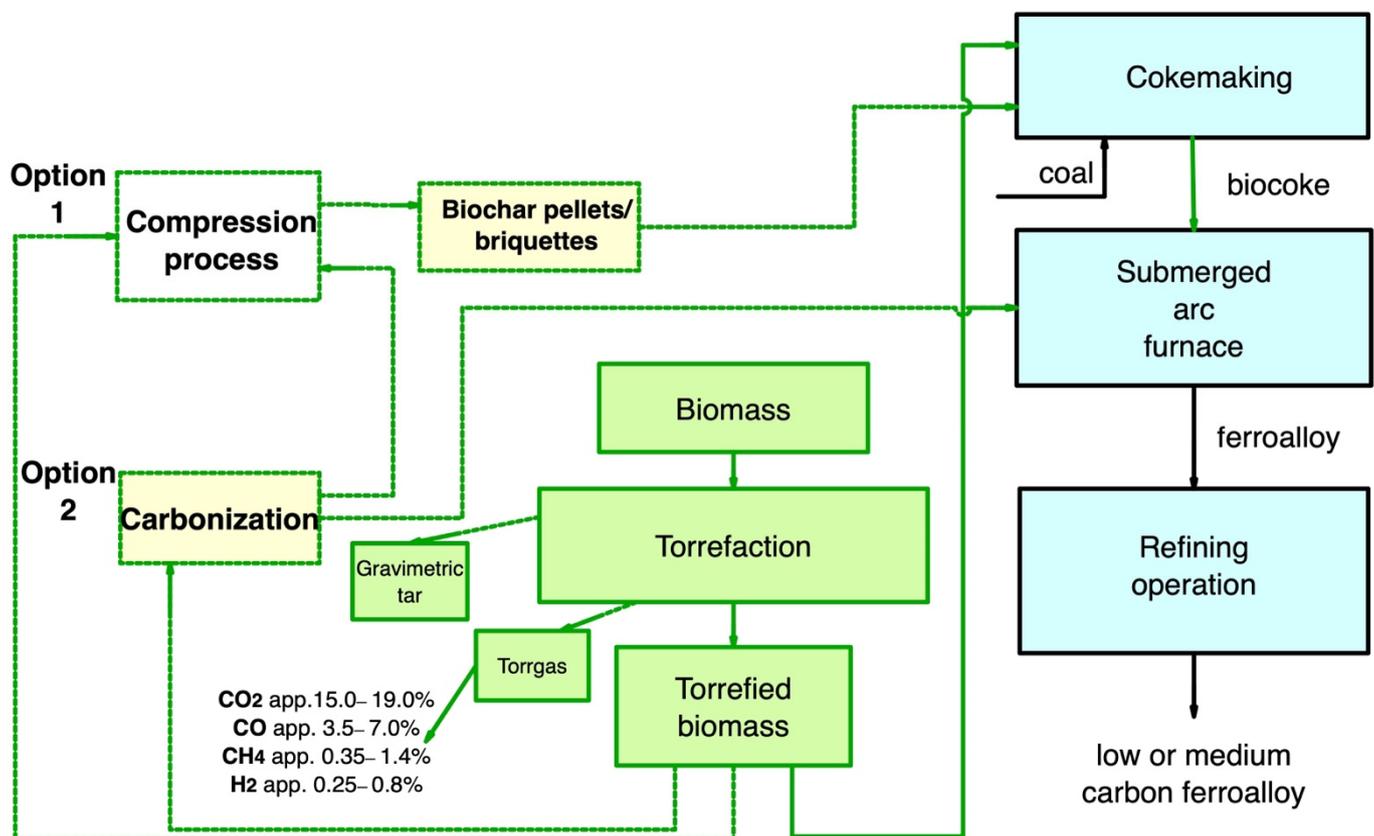


Figure 10. Main pathway for using secondary carbon bio-carriers in ferroalloy production.

There are several ways to use secondary carbon bio-carriers:

- Torrefied biomass to produce biocoke and further use of biocoke to produce ferroalloys. At the same time, it is of interest to replace up to 50% of coal within the coal blend;
- Subject torrefied biomass to carbonization to increase FC, reduce VM yield, and achieve the required electrical resistance values close to that of conventional fuel. Furthermore, after carbonization, secondary carbon bio-carriers can be used in the SAF;
- Torrefied biomass, also after carbonization, can be subjected to subsequent compaction, and then the resulting briquettes can be used to produce biocoke.

3. Modification of the Properties of Secondary Carbon Bio-Carriers

The following section gives an overview of treatment methods to enhance the properties of secondary carbon bio-carriers for subsequent use in metallurgical processes.

3.1. Thermal Carbonization after Torrefaction

Carbonization is a slow pyrolysis process that occurs under an inert atmosphere with temperatures > 400 °C, heating rates < 80 °C/min, and residence times of hours to days. The carbonization of biomass after its torrefaction is less intense, making this process less violent. This is explained by the fact that the main thermochemical conversion of biomass occurs during torrefaction. As the temperature of biomass torrefaction increases and after its subsequent carbonization, the yield of bio-oil and tar decreases. However, this does not significantly affect the yield of the torrgas [159,160]. Carbonization of torrefied biomass at a higher temperature is the most useful option. It achieves the best values for the conversion process, efficiency, and quality of the final products. It should be noted that despite the improvement in the properties of the final products, with increasing temperature, the yield of solids decreases, and the yield of bio-oil from both non-torrefied and torrefied biomass increases [160].

Li et al. [161] studied the effect of different atmospheres, such as N_2 , CO_2 , 14% O_2 , or NH_3 , during torrefaction on the elemental distribution, as well as the subsequent impact on the pyrolysis process. The research showed that using CO_2 as a torrefaction atmosphere has several advantages; for example, increasing the carbon content and reusing CO_2 , which is a GHG.

Louwes et al. [162] investigated the differences between the fast pyrolysis of raw and torrefied biomass. One of the findings was that torrefaction before fast pyrolysis could be beneficial from an energy point of view, as well as having a higher solids yield and a reduced bio-oil yield. The two-stage heat treatment proposed by the authors can be of interest when the targeted product is solid.

3.2. Compaction

The compaction of biomass (also called granulation) involves the application of a mechanical force to compact residues or waste biomass (sawdust, shavings) into uniformly sized solid particles, such as pellets and briquettes. The goals of biomass compaction are to: increase the volumetric energy density and the amount of carbon per unit volume, facilitate storage and handling, reduce transport costs, and give the material a particular shape and porosity [37,163]. Increasing the total energy density of torrefied biomass by compaction is an important process for modifying its properties, because torrefaction of the raw biomass results in mass loss and void formation.

There are two options for applying the compaction process [164] in industry; namely, torrefaction before compaction (TOP) [165,166] and torrefaction after compaction (TAP) [167].

The compaction temperature and compaction pressure are important when pressing torrefied biomass because the compaction of torrefied biomass is a more complex process than the compaction of raw biomass. The choice of the binder for compaction is no less important. There have been many studies about the influence of binder systems on the quality of the resulting torrefied pellets. Regarding the use of the binder, organic binders are of more interest compared to inorganic binders [168].

As for the study of the influence of parameters such as compaction temperature or compaction pressure, Matsumura et al. [169] reported that, compared to untreated wood, wood biomass under pressure to a size of at least 10 mm allows an increase in the addition rate of up to 1.5% while preventing a decrease in the coke strength. Moreover, hot compaction at a temperature of 200–350 °C, at which pyrolysis of wood biomass occurs, prevents a drop in the coke strength. As a result of hot compaction at 200 °C, the density of the pellets that were obtained was more than 60% higher than that of the pellets at room temperature.

Peng et al. [165] studied the effect of temperature and pressure on the quality of the obtained torrefied pellets. The research results showed that a die temperature of 260 °C with a compaction pressure of 187 MPa makes the torrefied pellets 1.24 times stronger than the reference pellets.

Li et al. [170] studied the influence of the degree of torrefaction and compaction temperature on the energy intensity and properties of the pellets. To obtain strong pellets, the die temperature was raised to 170 °C with a residence time of 30 s. The research results showed that it is necessary to use a high compaction pressure or high die temperature to obtain a good density of pellets.

Chen et al. [37] comprehensively reviewed torrefaction and compaction processes. Moreover, it was noted that torrefied pellets have good potential to replace coal in the energy and metallurgical sectors.

Manouchehrinejad et al. [171] performed a technical and economic analysis of the production of torrefied pellets using integrated torrefaction and compaction systems. This paper considered both TOP and TAP options, and a comparison with conventional wood pellets was made. The authors concluded that torrefied wood pellets could partially achieve the necessary properties to replace coal.

3.3. Beneficiation of Secondary Carbon Bio-Carriers by Ash Removal

In addition to the carbonization or compaction of torrefied biomass, its modification by ash removal is also beneficial for improving its properties. Charcoal is the most abundant raw material for use in metallurgy. However, its highly porous structure, as well as its content of alkali and alkaline earth metals, leads to an increase in reactivity, which makes its use challenging.

There are several ways to achieve ash removal; for example, physical beneficiation methods can be efficient, but to a limited extent [172]. Another way is to use acids, alkalis, leachates, oxidants, and various alkalis and acid combinations. According to Dhawan et al. [173] 80–90% demineralization and desulfurization can be achieved.

Iniesta et al. [174] studied different processing options for almond shells with acid and basic solutions at room temperature at various times. It should be noted that the lowest ash content and relatively small weight loss were achieved after treatment with H₂SO₄ for 24 h and 3 h, as well as after treatment with 3 h with sodium hydroxide (NaOH) and 3 h with sulfuric acid (H₂SO₄).

Das et al. [175] conducted three different pre-treatment processes of bagasse (fibrous material that remains after crushing sugarcane or sorghum stalks) used for deashing water leaching, mild acid treatment with hydrochloric acid (HCl), and mild acid treatment with hydrofluoric acid (HF). It was observed that the pre-treatment of bagasse led to changes in the distribution of pyrolysis products due to a combination of changing organic components and selective removal of inorganic ash elements. Mild acid treatment with HF effectively reduces the ash content of biomass to minor levels.

Hussein et al. [176] studied the effect of heat treatment and acid washing on the reactivity of charcoal. Charcoal samples were washed using various concentrations of HCl to determine the optimal leaching conditions. As a result of the treatment, a significant reduction in the reactivity was achieved due to a decrease in the content of inorganic minerals, as well as an improvement in the carbon structure after subsequent calcination.

Oudenhoven et al. [177] investigated the removal of alkali and alkaline earth metals from biomass by leaching with pyrolytic acids. The purpose of the research was to assess the conditions of acid leaching of pine wood, bagasse, and straw that improve the technical and economic indicators of the pyrolysis process. The ash removal process affects the yield of the end products.

In addition, several studies have been dedicated to removing harmful metals by washing them with water. For instance, Vamvuka and Sfakiotakis [178] investigated the effect of washing with water on the thermal decomposition characteristics, reactivity, and

kinetics of the three energy crops. Afterward, the potassium, phosphorus, sulfur, and chlorine content in the ash decreased.

Deng et al. [179] washed six biomass types (wheat straw, rice straw, corn stalk, cotton stalk, candlenut wood, and rice hull) with deionized water at different temperatures. The results showed that potassium, sulfur, and chlorine contained in the biomass could be effectively removed by washing. As the water temperature increases, the removal efficiencies of potassium, amorphous silica, and ash increase for all six biomass types.

3.4. Utilization of Mineral Additives for Secondary Carbon Bio-Carriers

Compared to ash removal, the opposite method is the addition of mineral additives during the compaction of torrefied biomass.

Because mineral substances have an important influence on the activation energy of chemical reactions, they can change the reactivity of the secondary carbon bio-carriers and the kinetic and thermodynamic parameters of metallurgical processes. For example, with an increase in the content of positively charged catalytic oxides or salts (Fe, Ca, Mg, Cu, Ba, Mn), the initial reaction temperature and the reaction activation energy decrease. With an increase in the content of negatively charged catalytic oxides or salts (Si, Al, Ti), the initial temperature of the reaction and the activation energy of the reaction increase. Zinc chloride ($ZnCl_2$) has been used to increase the porosity, specific surface area, and adsorption capacity of biochar [180]. However, Mu et al. [181] investigated the effect of Zn on the reactivity and strength of coke by means of Zn vapor adsorption. The results showed that Zn could increase the CRI and decrease the CSR. These results are also consistent with the conclusions made by Li et al. [182], that the use of certain mineral additives, i.e., compounds with Zn, has harmful effects on the many operations of metallurgical furnaces and, therefore, cannot be recommended for application.

For some metallurgical processes, an increased CRI is not a disadvantage. In this case, applying catalytic gasification can lower the initial gasification temperature and increase the CRI, but the CSR is often reduced [183]. CRI can be increased, the activation energy can be reduced, and the gasification rate can be increased by using alkali vapors due to the catalytic effect [184]. At a low CRI, the catalytic effect is a strong and slight effect when using highly reactive coke, as well as with increasing temperature.

Fe and Ca are promising catalysts for increasing the CRI in the conditions of the thermal reserve zone of a BF [185]. There are several ways to process coke [186–188]. The choice of a suitable processing method can change the reaction regime to a more homogeneous one at a lower reaction temperature, increasing the CSR.

The use of metal salts or metal oxides to modify the properties of biochar is a relevant issue for research. With this modification method, the key biochar properties can be changed, and as a result, its characteristics, including the adsorption capacity, catalysis strength, and magnetism, can be improved. Consequently, it is possible to directly influence the kinetic and thermodynamic parameters of reactions occurring in metallurgical processes by using mineral additives. In this approach, the mineral catalytic index [189] can be used as an indicator to measure and characterize the effect of mineral additives on the reactivity of biochar briquettes, as well as on the kinetic and thermodynamic parameters of metallurgical processes when using biochar briquettes in an EAF, SAF, iron ore sintering, and SR. Industrial wastes are of particular interest as mineral additives.

Table 10 summarizes some effects of different modification techniques on the example of different types of carbon sources and demonstrates the possibility of using this approach to modify the properties of secondary carbon bio-carriers. It can be concluded that further carbonization of the torrefied biomass improves its properties, making it more suitable for use in certain metallurgical processes. The last three techniques allow changing the properties depending on the requirements of the metallurgical process in which secondary carbon bio-carriers can be used.

Table 10. Effect of different modification techniques on the example of different types of carbon sources.

Parameters	Sources										
	CWT	CWC	TCR (Before Compaction)	TCR (After Compaction)	Bch285 (WAT), [174]	Bch285 (AAT), [174]	Switchgrass (Unwashed), [178]	Switchgrass (Washed), [178]	Coke	CRC10	CRC20
Carbonization [190]			Compaction [43]		Beneficiation				Mineral additives [186]		
C (wt.%)	72.85	84.74	48.3	42.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
H (wt.%)	4.56	3.18	5.5	5.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
N (wt.%)	0.27	0.39	2.3	2.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
S (wt.%)	0.14	0.1	1.0	0.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
O (wt.%)	18.95	9.45	33.0	38.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Ash (wt.%)	0.4	0.7	9.9	9.6	n.a.	n.a.	8.5	2.9	n.a.	n.a.	n.a.
HHV (MJ/kg)	28.83	32.32	n.a.	19.3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
R	n.a.	n.a.	n.a.	n.a.	4.9	2.0	n.a.	n.a.	n.a.	n.a.	n.a.
DI ¹⁵⁰ ₁₅	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	84.5	84.0	81.8
CRI, %	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	23.3	24.8	33.2
CSR, %	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	66.8	68.0	58.6
JIS R _e I	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	6.6	39.0	41.8
Inorganics (%):											
K ₂ O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	11.9	0.86	n.a.	n.a.	n.a.
P ₂ O ₅	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.5	1.0	n.a.	n.a.	n.a.
SO ₃	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.17	0.11	n.a.	n.a.	n.a.
Cl (ppm)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	70	18	n.a.	n.a.	n.a.

n.a. is not available; CWT is cedar wood torrefied at 300 °C; CWC is cedar wood carbonized at 450 °C; TCR is torrefied Canola residue; Bch285 (WAT) is biochar obtained after heat treatment at 285 °C (without acid treatment); Bch285 (AAT) is biochar obtained after heat treatment at 285 °C (after acid treatment); CRC10 is calcium-rich coke (10 wt.%); CRC20 is calcium-rich coke (20 wt.%); R is reactivity (normalized weight loss percentage min⁻¹); C is carbon; H is hydrogen; N is nitrogen; S is sulfur; O is oxygen.

4. Research Activities within EU Projects for the Use of Secondary Carbon Bio-Carriers in Iron and Steelmaking

Some funded research projects within the EU, such as TORERO, GreenEAF, and GreenEAF2, and their results have already been mentioned in this review. However, some projects that are still being finished or currently being carried out should also be addressed, as they focus on using secondary carbon bio-carriers in metallurgical processes. Their use is considered only for selected processes within EU-funded projects. Nevertheless, these projects are of great importance, as they lead not only to the development of breakthrough technologies that can mitigate the impact on the environment, but also show the need to find new ways to use secondary carbon bio-carriers.

As part of the project “Ultra-low CO₂ steelmaking” (ULCOS, 2004–2010, Grant Agreement No. 515960) [191], the development of several technologies was planned; namely, (a) blast furnace with top gas recycling; (b) new smelting reduction process (HIsarna); (c) advanced direct reduction; (d) electrolysis of iron ores; (e) carbon capture and storage; and (f) H₂ reduction. These technologies should reduce CO₂ emissions by at least 50% per ton of steel. Figure 11 provides a layout of the technologies within ULCOS. Some developed technologies, such as top gas recycling and direct reduction, have been commercially introduced.

Within the ULCOS project, the possibility of using sustainable biomass was also considered. According to its properties, charcoal is a promising reducing agent with a lower amount of sulfur and ash than conventional agents. One of the tasks was to find ways to optimize the work of new technologies within ULCOS using charcoal. According

to Quader et al. [151], the use of sustainable biomass has not been developed within the framework of this project and is of interest for further research on the use of secondary carbon bio-carriers in steelmaking. However, in [121], it was noted that 15% of theoretical biomass potential is desirable to meet the biomass demand of only 30 plants across Europe, which will have a negative effect. Therefore, the issue of using sustainable biomass requires further work to solve the problem of the strategic use of biomass in Europe.

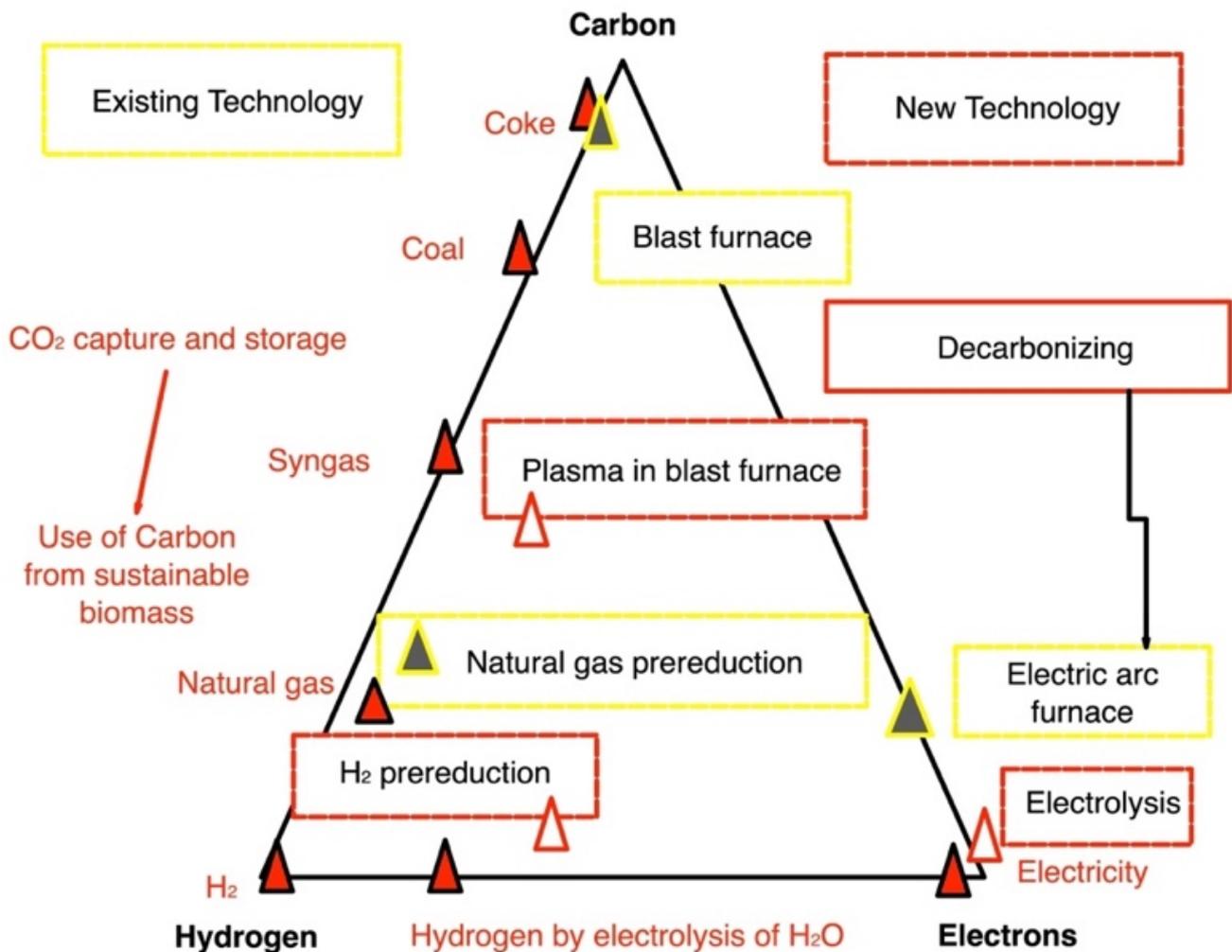


Figure 11. Layout of ULCOs breakthrough technologies for reducing CO₂ emissions [192].

Another project entitled “Development of a Low CO₂ Iron and Steelmaking Integrated Process Route for a Sustainable European Steel Industry” (LoCO₂Fe, RFCS project, 2015–2018, grant agreement No. 654013) [193] coordinated by Tata Steel Netherland Technology was focused on achieving a decrease in CO₂ emissions by at least 35%. The object of this project was the HIsarna ironmaking technology, which can achieve the necessary reductions in emissions, allowing partial replacement of coal with biomass. Additionally, this technology minimizes the use of coal due to the maximum use of energy in the reactor by balancing the energy between different parts of the reactor. Moreover, when carbon capture and storage (CCS) are used along with HIsarna, CO₂ emissions can be reduced by up to 80%.

Another EU-funded project called SECTOR (production of solid sustainable energy carriers, 2012–2015, grant agreement No. 282826 [194,195]) was coordinated by the German DBFZ (Deutsches Biomasseforschungszentrum gemeinnützige GmbH). It was focused on studying torrefied wood-based, agricultural biomass, or energy crops as sustainable energy carriers. The project included the development of standardized analysis and test-

ing methods to assess the efficiency of transportation, storage, handling, and end-use of torrefied biomass. Compaction options such as pelleting and briquetting were studied. Opportunities for optimization by integrating the torrefaction process into existing production facilities were considered. However, in this project, torrefied biomass was only considered for use in the energy sector in terms of cofiring in coal plants, gasification, and small-scale combustion. One of the findings of this project was that it is feasible for the torrefaction technology to be commercially deployed. However, implementation limits should be overcome to utilize torrefied biomass.

The ongoing project “TORrefying wood with Ethanol as a Renewable Output: large-scale demonstration” (TORERO) (grant agreement No 745810) [67], has already been briefly discussed in the review. It is worth adding that the project’s most important impact is expected to be when the torrefaction plant is launched in July 2022. The production of 80 million liters of biofuel to replace fossil fuels is planned (which allows the reduction of CO₂ emissions by 150,000 tons per year), as well as 50,000 tons of biochar to replace coal for PCI operation at the BF (which allows the reduction of CO₂ emissions by 100,000 tons per year) of the ArcelorMittal site in Ghent (Belgium).

Regarding the PCI technology for BF operation and the replacement of coal with more sustainable carbon carriers, an EU-funded project that was run within the RFCS entitled “Improved coal combustion under variable BF conditions” (IMPCO, 2012–2015 RFSR-CT-2012-00002 [196]) coordinated by the Swedish research center SWERIM (formerly known as SWEREA MEFOS) was focused on this issue. Generally, the IMPCO project aimed to reduce the amount of coke consumption in the BF by increasing the PCI rate by using alternative carbon carriers. Two types of coals, lignite coke, lignite coal, petroleum coke, and torrefied biomass were studied as carbon carriers. It was found that the optimal parameters of the BF operation were maintained when using a blend of 20% torrefied biomass and 80% coal.

Within the framework of the RFCS project “Alternate carbon sources for sintering of iron ore” (ACASOS, 2007–2010, RFSR-CT-2007-00003, [197]) coordinated by the German VDEh Betriebsforschungsinstitut (BFI), attention was focused on the iron ore sintering process and the use of alternative carbon carriers to replace coke breeze. Olive pits, wood pellets, sunflower husks, BF dust and sludge, anthracite, and petroleum coke were chosen, pre-treated, and tested by iron ore sintering during pilot iron ore sinter plant trials. The use of 10% wood pellets and 5–15% crushed olive pits deteriorated the process productivity and quality indicators. The use of up to 30% petroleum coke and up to 20% anthracite had a low impact on the quality indicators of the sinter.

Another project addressing the iron ore sintering process and the use of alternative carbon carriers is an ongoing project entitled “Towards a zero CO₂ Sintering” (TACOS, 2019–2022, RFCS Project No. 843722 [198]) coordinated by the Belgium research center CRM (Centre de Recherches Métallurgiques). The research aims to evaluate solutions that provide significant reductions in CO₂ emissions, as well as reductions in other key pollutants during the sintering process. In this project, one of the methods used to achieve this goal is the use of alternative carbon carriers, namely, biomass with or without pre-treatment. Processes such as gasification, hydrothermal conversion, torrefaction, and pyrolysis are provided as pre-treatment.

The aim of the RFCS project “Recycling of industrial and municipal waste as slag foaming agent in EAF” (RIMFOAM, 2014–2017, RFSR-CT-2014-00008 [199]) coordinated by SWERIM was to evaluate and utilize waste mixtures containing both metal oxides and hydrocarbons as slag foaming agents in an EAF. This project investigated the possibility of replacing conventional carbon sources with 20% substitutes. The biomaterials used in the study were olive kernels and sawdust pellets, which were injected with co-injection at Arcelor Mittal Maizieres Research in France. The best foaming results were obtained with rubber powder and petroleum coke (the other substitutes tested within this project), and good foaming was also observed with sawdust pellets.

In another ongoing project, “Implementation of a smart RETROfitting framework in the process industry towards its operation with variable, biobased and circular FEEDstock”

(RETROFEED, 2019–2023, grant agreement No. 869939 [200]), the main focus is to enable the use of an increasingly variable, bio-based, and circular feedstock in process industries. In the specific case study for EAF steel production, a tailored injection system for biochar has been developed and installed in the steel factory of Ferriere Nord in Italy. In the future, it is planned to evaluate the capability of biochar to promote foaming and to contribute to the energy input of the process.

One project regarding ferroalloy production (specifically Mn-alloys) is concentrated on the use of loose biomass to obtain biocoke. This ongoing Norwegian-funded project is called “BioCoke4FAI-Bio-Coke for Ferroalloys Industry Production” (2021–2023 [201]). The idea of the project is based on the production of a non-conventional reductant using blends of coal and biomass (partial replacement) and testing its suitability on a pilot scale.

5. Aspects Being Considered for Evaluation of the Environmental Impacts Due to Substitution by Biomass

Biomass-based fuels are not always carbon neutral, and they may even show higher greenhouse gas emissions across their life cycle than with respect to fossil fuels [202]. Several studies have documented the potential for a lower carbon footprint associated with biomass-based fuels [64,75]; yet to guarantee an actual reduction of environmental damage across different impact categories, several aspects must be taken into account.

- Firstly, a lifecycle perspective of the assessment should be ensured. This is generally accomplished by using the Life Cycle Assessment (LCA) methodology. Carbon footprints of biomass-based fuels are strongly sensitive to upstream processes: cultivation practices, transports, and further treatments (e.g., compaction, torrefaction, and the addition of mineral additives) [64]. These activities must be optimized as well to ensure a significant abatement of greenhouse gas emissions. In particular, cultivation practices are associated with the consumption of energy and materials (e.g., fertilizers may lead to an additional emission of 0.14–0.55 kg CO₂-eq per kg of biofuel), and they may be associated with land use and carbon stock changes (direct and indirect) which may lead to a drastic increase of greenhouse gas emissions: 0.6–4.0 kg CO₂-eq per kg of biofuel [203]. The production and processing of biomass feedstocks are associated with the variability of LCA results, both considering the only carbon footprint [75,195] and other impact categories [204]. In addition, the final applications of biomass-based fuels in steelmaking plants must be optimized as well, which has been the focus of several studies documented in the present paper. A comprehensive environmental analysis must account for possible adverse effects due to the introduction of biomass-based fuels: productivity decreases and an increase in total fuel consumption, as outlined in Section 2.2.1. These effects mean that a higher quantity of biofuel is necessary to replace 1 kg of fossil fuel. Therefore, a 1:1 substitution ratio should be adjusted according to the actual plant configuration.
- Biomass may be obtained by either agricultural wastes or by cultivations. Norgate et al. [205] clarified that biochar is considered to be renewable due to the much shorter carbon cycle (5–10 years) with respect to fossil fuels (around 100 million years). Still, the biomass carbon cycle is not null; therefore, the availability of biomass needed for steelmaking plants should be considered for a correct evaluation. In addition, to minimize transport, biomass availability should be evaluated for specific regions. Kamal Baharin et al. [14] showed that Malaysia disposes of most of its biomass waste without using it as fuels, fertilizers, or animal feedstock; therefore, there is a potential to convert it into biocoke. National analyses for Sweden [28] and Finland [118] showed sufficient and available resources to cover the national demand for biomass use in steelmaking. Piketty et al. [206] reported that Brazil could be a remarkable actor in feeding the global supply chain for charcoal. Instead, Norgate et al. [119] performed an assessment and concluded that 50–150 Mha of land is required as biomass plantation areas to substitute 47% of the fossil carbon used to produce steel by the integrated route, through the use of charcoal. Comparing this value with the global productive

forest plantation area (264 Mha), it emerges that an appreciable amount of land can be used for biomass cultivation. Finally, Mandova et al. [121] further led this kind of analysis by accounting for both resources and supportive policies to identify where a significant potential to harvest biomass sourced in a sustainable way is present. They found that Canada, Sweden, China, the USA, and France were the most suitable countries. It should be kept in mind that higher demand for crops may lead to indirect land use changes, e.g., deforestation, and intensification, which is linked to additional greenhouse gas emissions [207].

- LCAs should also evaluate different potential impact categories to avoid burden-shifting risk, i.e., decreasing carbon footprint while increasing impacts in other categories. Bio-based processes are generally found to increase eutrophication and acidification impacts due to the agricultural phase [208]. Potential concerns are also related to water use for biomass cultivation [209].
- Finally, linked to the matter of biomass availability, further environmental and societal aspects should be accounted for. If biomass is collected from dedicated cultivations, conflicts on land use for other uses (e.g., food and renewable energy production) should be accounted for [119]. If biomass is collected from agricultural wastes, the alternative fate of the waste is important to determine the net environmental impacts: e.g., if wastes would otherwise have been incinerated with energy recovery or used for landfill with large methane emissions. Consequential LCA approaches can account for counterfactual uses of different inputs from attributional models [210].

A comprehensive LCA of bio-based carbon carriers' integration can outline differences in potential environmental impacts with respect to other improvement measures suggested by the literature; e.g., hydrogen-based options [211].

6. The Role of Digital Tools in Intensifying Use of Secondary Carbon Bio-Carriers

Most processes involved in the metallurgical production chains are very complex and challenging, e.g., in terms of required material volumes, energy demands, environmental conditions, and constraints. Therefore, they come equipped with sophisticated monitoring and control systems, which are the results of a continuous evolution mostly driven by targets related to product quality, energy efficiency, emissions control, and health and safety requirements for personnel. These systems are generally tuned to cope with "standard" input materials with no or minimal usage of secondary carbon bio-carriers; they are surely suitable to ensure safety requirements, as well as emissions control when secondary carbon bio-carriers are used, but further efforts might be required when their use is intensified to pave the way to their optimal exploitation. For instance, a recent study concerning the iron ore sinter process [212] addressed, among other topics, the issues concerning process control implementation when alternative fuels, such as biomass, are adopted with the aim of maximizing sintering performance and minimizing energy consumption and environmental impacts. Advanced process monitoring solutions, such as the ones based on soft sensors enabled by artificial intelligence approaches [213], are envisaged to support process capability to dynamically adapt to the gradual and increased introduction of alternative carbon carriers.

Further support for the intensified use of alternative carbon carriers can be provided by advanced modeling and simulation tools, and approaches that can be used for preliminary techno-economic assessment and selection of the most promising use scenarios. For instance, process models based on mass and energy balances, thermodynamic equilibrium, and involved reactions (e.g., flowsheeting-based models) are already generally used to study the effects and environmental/energy impacts on processes and related products of different operating conditions or process modifications, via the EAF route [214]. However, so far, they have not been applied to investigations of the use of non-fossil fuels and renewable C-sources via the EAF route. Moreover, the unstoppable digitalization process of the steel industry provides a large volume of available process data, which can also be exploited for process modeling and simulation for the abovementioned purposes. In this

sense, promising opportunities are provided by the hybrid Physics-Guided Machine Learning (ML) techniques, which integrate physical knowledge in ML-based models design [215] by merging available process knowledge and purely data-driven ML methods [216].

7. Conclusions and Outlook

This review provides an overview of the use of secondary carbon bio-carriers, i.e., bio-based sustainable resources in metallurgical processes for iron and steelmaking, as well as for ferroalloy production. Despite the many studies on biomass torrefaction, the integration of the use of biomass for many processes in iron and steelmaking remains an open issue. Therefore, this review discusses the application of torrefied biomass as the main carbon source or to produce other secondary carbon bio-carriers. Because torrefied biomass has limitations due to its properties, one of the promising options is to use it in cokemaking for biocoke production. The amount of torrefied biomass used in the coal blend may vary depending on the requirements of the particular route. The production and application of secondary carbon bio-carriers as a partial replacement or the complete replacement of conventional fossil fuels are technologically achievable and can be based on known studies and practices. The use of secondary carbon bio-carriers has been considered for four main pathways: BF/BOF, scrap/EAF, DRI/EAF, and SR/BOF. Despite the most stringent requirements for carbon carriers for BFs, the use of biocoke may have significant future use in scrap/EAF, DRI/EAF, and SR/BOF routes. Furthermore, the use of biocoke is promising in a SAF to produce ferroalloys.

Some methods to modify the properties of secondary carbon bio-carriers, such as carbonization, compaction, beneficiation by ash removal, and utilization of mineral additives for secondary carbon bio-carriers, have also been studied by several research groups. The last two methods are opposites of each other; however, they may impact the kinetic and thermodynamic parameters of reactions occurring in metallurgical processes.

An analysis of fulfilled or ongoing projects within the EU showed that secondary carbon bio-carriers are not only promising substitutes for conventional fuels and reductants in the future, but are have already been proven in some metallurgical processes. Moreover, the discussion of these projects revealed that the integrated use of secondary carbon bio-carriers, namely, torrefied biomass and biocoke, has not been generally suggested and studied for the four steelmaking routes.

In terms of process, the integrated use of secondary carbon bio-carriers is an innovative approach that requires adapting already existing technologies used in metallurgical production. Within the EU steel sector, the use of secondary carbon bio-carriers represents one technological pathway to push the decarbonization of the iron and steelmaking processes to reach the climate goal of zero net emission steelmaking processes by 2050. The efforts to implement secondary carbon bio-carriers are strongly promoted by the Clean Steel Partnership (CSP), a public-private partnership comprising all relevant stakeholders from the EU steel sector and scientific experts related to the field. The CSP is coordinated by the European Steel Technology Platform (ESTEP) and supported by the European Steel Association EUROFER. A roadmap (Strategic Research and Innovation Agenda, SRIA) developed by the CSP considers secondary carbon bio-carriers as one important energy source on the way to a sustainable and decarbonized future steel industry. Based on the SRIA of the CSP, research initiatives (funded and non-funded) will be necessary in the future to increase the quantity and quality of secondary carbon bio-carriers for enhanced use in metallurgical processes.

This review provides a basis for scientific development and future research on integrating biomass in different metallurgical processes. It should be noted that biomass is well researched for use in biocoke production, sintering, CCAs, PCI, and BFs. However, applications in SR processes, EAFs, and SAFs should be further studied to achieve new and optimal results. Additionally, the development and implementation of the use of biomass in steel production are highly dependent on preconditions, such as sufficient, sustainable domestic biomass resources, supply chain features, and supportive national policies.

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