

## Article

# Life Cycle Based Climate Emissions of Charcoal Conditioning Routes for the Use in the Ferro-Alloy Production

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**Abstract:** Renewable reductants are intended to significantly reduce CO<sub>2</sub> emissions from ferro-alloy production, e.g., by up to 80% in 2050 in Norway. However, charcoals provide inferior properties compared to fossil fuel-based reductants, which can hamper large replacement ratios. Therefore, conditioning routes from coal beneficiation was investigated to improve the inferior properties of charcoal, such as mechanical strength, volatile matter, CO<sub>2</sub> reactivity and mineral matter content. To evaluate the global warming potential of renewable reductants, the CO<sub>2</sub> emissions of upgraded charcoal were estimated by using a simplified life cycle assessment, focusing on the additional emissions by the energy demand, required chemicals and mass loss for each process stage. The combination of ash removal, briquetting and high-temperature treatment can provide a renewable coke with superior properties compared to charcoal, but concomitantly decrease the available biomass potential by up to 40%, increasing the CO<sub>2</sub>-based global warming potential of industrial produced charcoal to  $\approx 500$  kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC. Based on our assumptions, CO<sub>2</sub> emissions from fossil fuel-based reductants can be reduced by up to 85%. A key to minimizing energy or material losses is to combine the pyrolysis and post-treatment processes of renewable reductants to upgrade industrial charcoal on-site at the metallurgical plant. Briquetting showed the largest additional global warming potential from the investigated process routes, whereas the high temperature treatment requires a renewable energy source to be sustainable.

**Keywords:** charcoal; upgrading; renewable reductants; global warming potential; life cycle assessment



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## 1. Introduction

The transition from the fossil fuel-based to a sustainable energy foundation society is one of the greatest challenges for the upcoming few decades. To limit the global temperature increase to 1.5–2 °C in the year 2100 compared to the pre-industrial level, anthropogenic greenhouse gas (GHG) emissions must be eliminated in all sectors, including agriculture, households, transport and industry [1]. To realize this ambitious goal, most countries have committed to the Kyoto Protocol and/or Paris Agreement. Zero emission discharge can be difficult to achieve with current technologies and, thus, new technologies are constantly developed, or renewable substitutes are intended to replace the fossil fuel-based feedstock. This transition can result in a larger demand for special materials and depleting easily accessible sources will further increase the energy demand in the future, e.g., mining [2]. Thus, feedstock supply may require additional governance to ensure sustainability and economic feasibility [3].

An increasing demand for metal alloys from primary metallurgy and its sustainable production are the key challenges to minimize greenhouse gas emissions from metallurgy. Currently,  $\approx 5$ –10% of anthropogenic CO<sub>2</sub> emissions are emitted by the metallurgical

industry [4–6]. In steel industry,  $\approx 98\%$  of greenhouse gas emissions are related to  $\text{CO}_2$  and methane emissions from smelting and coke-making [7], whereas the total emissions from alloying elements production in submerged arc furnaces are highly affected by the indirect emissions from electricity production. Short-term opportunities to decrease greenhouse gas emissions from metallurgy are based on the replacement of fossil fuels, e.g., carbon neutral reductants or blue hydrogen, carbon neutral electricity and carbon capture and storage [8]. Studies have shown that more than 31% of the  $\text{CO}_2$  emissions can be removed in the production of green steel [9], reducing the GWP to 1.6  $\text{kg CO}_2\text{-eq. kg}^{-1}$  of steel. In addition, the use of charcoal can reduce the  $\text{SO}_2$  emissions by more than 75% compared to fossil fuels [10]. Combinations of new processes, bio-reductants and carbon capture and storage have shown that the  $\text{CO}_2$  mitigation potentials can be in the range of 1.4–2.7  $\text{t CO}_2 \text{ t}^{-1}$  steel, corresponding to  $\approx 75\text{--}150\%$  of the current emissions [11].

Norway is a main producer for silico-manganese (SiMn), ferro-manganese (FeMn), silicon (Si) and further alloying elements, which resulted in a total release of  $\approx 9$  million tonnes  $\text{CO}_2$  equivalent [12]. Despite the already low specific greenhouse gas emissions from Norwegian's metallurgical industry, a net zero policy is intended to become a reality by 2050 [13]. A similar roadmap was released for the decarbonization of the steel industry in Europe [14]. Renewable reductants in combination with carbon capture and storage (CCS) shall cover  $\approx 75\%$  of the current emissions and  $\approx 45\%$  of the future emissions [12]. The application of CCS in combination with new technologies, such as sustainable hydrogen, are intended to further reduce and potentially leading to net negative  $\text{CO}_2$  emissions. Biomass and its derivatives are considered as renewable reductants in the metallurgical industry [15,16] and can reduce greenhouse gas emissions by  $\geq 50\%$  [17]. However, the use of reductants with insufficient properties can result in a lower efficiency of the process [18] and consequently higher greenhouse gas emissions.

Classical charcoal provides inferior properties compared to fossil fuel-based reductants used by ferro-alloy production [19,20], possibly resulting in a different process behavior in operation [21]. While a high mechanical stability and low gas reactivity are desirable in conventional large blast furnaces [22,23], mechanical properties are of less importance for small scale blast furnaces, electric arc furnaces (EAF) and submerged arc furnaces (SAF) [24–26]. Closed hearth SAF require a low volatile matter content based on their off-gas system, and specific electrical properties to provide a homogeneous temperature profile in the furnace. Open hearth furnaces, on the other hand, are more flexible to volatile matter content but require properties to ensure a good gas transport in the burden. Thus, multiple parameters must be improved in order to increase the substitution rate of renewable reductants, such as particle size, mechanical and abrasion strengths,  $\text{CO}_2$  reactivity and chemical composition at similar economics [18]. In addition, the economics of renewable substitutes are often inferior, e.g., a lower bulk or energy density, resulting in higher costs in handling, transport and storage to a price increase of  $\approx 2$  [27,28]. Moreover, published data still lack information about the influence of feedstock, production process conditions and upgrading strategies on certain applications on industrial scale [29]. It is assumed that charcoal can replace fuel-based reductants by more than 40% in SAF, whereas larger to fully replacement require additional processing of the charcoal. Full replacement of fossil fuel-based reductants has been carried out in open hearth furnaces in Brazil at the cost of furnace efficiency [30].

A great deal of effort has been undertaken in the past few years to optimize specific properties of biomass and its derivatives for the application in metallurgy, the energy sector and other industries, such as construction, biochemistry or medicine. A multifaceted use of biomass can optimize the sustainable usage biomass by developing plans for a diverse usage [31]. The production of thermochemical and biochemical products have significantly increased in the last few years with a further increase forecasted to  $\approx 25\%$  in 2024 [32]. Thus, industrial processes may compete for the available potential of renewable feedstock. Therefore, conditioning routes for the biomass and its application should be considered regarding the availability of biomass and alternatives. For example, the potential of biomass is not large enough to be considered as a sustainable replacement of fossil fuel

in the power production in addition to other sectors [31]. Renewable energy from solar, wind or hydropower can replace fossil fuels in this sector, whereas no alternatives currently exist to replace carbon in the reduction of manganese(II) oxide to its metallic form.

To reduce metals to its metallic form by renewables, different process routes have been investigated or developed to produce charcoal with specific properties [9,21,29]. New thermochemical conversion processes, such as hydrothermal carbonization (also called wet torrefaction), seem superior to classical dry pyrolysis in producing binderless pellets [33,34], whereas the organic binder can increase the mechanical stability of biomass and charcoal pellets and briquettes [9,26,27,35–37]. The combination of different biomass feedstocks showed an improved mechanical stability compared to their individual counterparts [38]. On the other hand, biomass or charcoal addition to coal blends in metallurgical coke production resulted in inferior mechanical properties at a mass ratios larger than 5–15% [39–41]. Thus, the quality of renewable reductants can partially be designed by the different feedstock materials and processes. However, additional upgrading processes, as well as a concomitant mass loss, will decrease the economic feasibility and usable biomass potential of renewable reductants and reducing its sustainability.

To decrease CO<sub>2</sub> emissions from metallurgy, renewable reductants must remain CO<sub>2</sub> neutral, to a great extent lower than used fossil fuel-based reductants. The higher reactivity of charcoal compared to fossil fuels leads to an average higher CO and CO<sub>2</sub> amount in the off-gas [21]. A higher CO<sub>2</sub> concentration may be favorable for its utilization in consecutive processes, such as carbon capture and storage or carbon capture and utilization [42]. The application of such mainstream technologies can reduce the CO<sub>2</sub> emissions from the iron and steel industry by more than 40% [43].

The aim of this work was to perform a life cycle assessment (LCA) to evaluate the impact of upgraded charcoal manufacturing on the environment in Norway. The objective of this study was to develop a simplified approach based on ISO 14044 aiming to reduce the CO<sub>2</sub> emissions through the replacement of fossil-based metallurgical coke with the bio-based reductants. The GHG emissions from the manufacturing of charcoal were calculated using different scenarios including novel industrial ways to utilize the liquid pyrolysis by-products and various feedstock pre-treatment processes. For the first time, the life cycle analysis of the charcoal manufacturing was performed through inventory of the energy and materials that are required across the metallurgical industry value chain in Norway.

## 2. Methodology

The methodology of the present study suggests the execution of the LCA according to the framework of the ISO 14044. This will allow us to analyze the environmental burdens of the metal reduction process. The goal and scope will be identified using literature data followed by Life Cycle Inventory (LCI), assignment to categories and is finished by the brainstorming and interpretation of the category endpoint. Figure 1 shows the first step with the definition of the aim, objectives, functional unit and system boundaries.

The next step consists of collection, description, verification of inventory regarding process steps, input parameters of water, material, and energy and emissions of the whole charcoal life cycle. The third step is used to quantify parameters based on the inventory analysis that includes selection of impact categories depending on the parameters of goal and scope and assignment of life cycle inventory results to various categories. Normalization and weighting were not performed in a frame of this study. The last step is the interpretation of the results to calculate environmental impacts to describe how environmentally relevant flows will change in response to possible decisions. This impact category for the charcoal manufacturing was divided according to CO<sub>2</sub> emissions released into the air, water and landfill. Each category formed from the life cycle inventory analysis represent a sequence of effects that can cause a certain level of damage to the environment based on the used pre-treatment method, e.g., alkali leaching, heat treatment or briquetting. This type of method generates a simplified and narrowed picture of the ecological impacts of charcoal integration into metallurgical industry. The results of an LCA are not

absolute values and therefore cannot serve as a certification on itself. Calculations were carried out with SimaPro software (Version 9, PRé Sustainability B.V.) for each individual process step. Compared to a full life cycle analysis, where also toxicity, eutrophication and further impacts are considered, the scope of this study was limited to the evaluation of the CO<sub>2</sub> emissions.

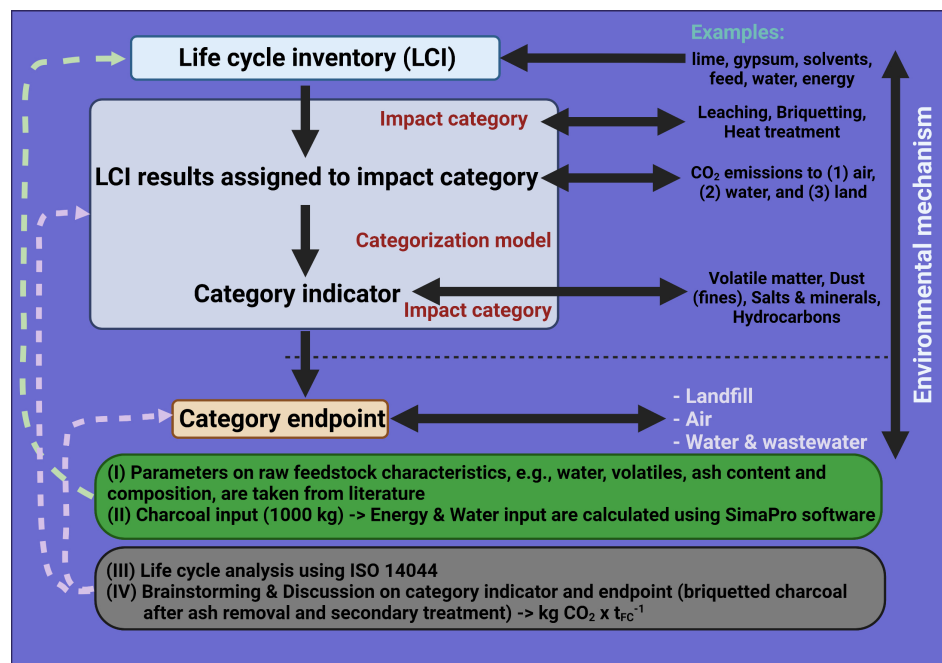


Figure 1. Schematic presentation of the used methodology based on ISO 14044:2006.

The input parameter of 1000 kg of charcoal was used in all LCA calculation. Tables 1 and 2 provide the data on the raw feedstock characteristics such as water, volatiles, inorganics contents and composition, etc. Tables 3–9 show the results of estimated input and output parameters based on the literature and LCA calculation to determine the CO<sub>2</sub> emissions for the entire charcoal life cycle. The CO<sub>2</sub> calculations of the charcoal manufacturing will be compared with the emissions from the life cycle assessment of fossil-based metallurgical coke. The results will not guarantee the sustainability of a product, but these are valuable for the comparison of different products and process steps. The local impacts on the charcoal manufacturing in Norway are of importance to link these results with environmental damage on global scale.

### 3. Charcoal State-of-the-Art

#### 3.1. Charcoal Properties

Bio-reductants (wood chips and charcoal) are currently used in Norwegian silicon production to about 50% based on the required fixed carbon input, and up to 100% for silicon (Si) production in Brazil [44] and ferrosilicon (FeSi) production in Paraguay [45]. An advantage of charcoal usage in Si and FeSi production is the lower energy consumption and greater silicon yield due to the higher porosity and SiO reactivity of charcoal [46], and a lower specific energy consumption in electric arc furnaces by the combustion of the higher content volatile matter in renewable reductants [21]. However, it is assumed that the mechanical and physicochemical properties of classical charcoal are insufficient to be applied in large quantities in closed hearth SAF [19,20]. Charcoal properties should match the properties of currently used fossil fuel-based reductants to fully replace those in metallurgical industry.

The properties of classical charcoal, industrial charcoal (produced in a retort) and metallurgical coke are summarized in Table 1 with respect to their proximate analysis, bulk density, mechanical stability and ash composition. It is obvious that volatile matter content,

bulk density and mechanical strength of charcoal are inferior to those of metallurgical coke. Wood charcoal has a volatile matter content  $\geq 10\%$  and a bulk density less than  $300 \text{ kg m}^{-3}$ , while sulfur content, ash content and fusion temperature are at lower range [47]. In addition, ash analysis of industrial charcoal exhibits a much larger CaO, MgO and  $\text{K}_2\text{O}$  content than metallurgical coke [19,20], affecting the  $\text{CO}_2$  reactivity of the carbon reductants. The removal of alkali and alkali earth metals decreases  $\text{CO}_2$  reactivity of the reductants [48,49]. The removal of potassium from biomass may decrease the solid yield at high heating rates [50,51], whereas the breakdown of lignocellulosic compounds is recommended to produce biochar [52].

The  $\text{CO}_2$  reactivity at  $1000\text{--}1100 \text{ }^\circ\text{C}$  of industrial charcoal is  $\approx 10$  times larger than that of metallurgical coke [20,53]. Pyrolysis temperatures larger  $1300 \text{ }^\circ\text{C}$  improve the carbon ordering, further reducing the  $\text{CO}_2$  reactivity similar to that of metallurgical coke [53–55]. Bio-oil conditioning can partially convert liquid pyrolysis by-products to a secondary char [9,27,56–58], concomitantly increasing the density of the charcoal fraction. Recent investigations have shown that the density of charcoal can be increased by methane decomposition at elevated temperature [59].

Furthermore, the low mechanical strength and durability of charcoal can lead to the formation of up to 20% of fines, which are not suitable for direct application in SAF and may affect the global warming potential by additional dust warming effects. Briquetting and pelleting can be used to utilize fine material and provide reductants with specific size and shape. Organic binders, such as lignin, starch or bio-oil, can improve the mechanical properties to provide a reductant approaching the mechanical strength of fossil fuel-based reductants [36–38,58,60–62]. The electrical resistivity of charcoal in the coke bed ( $1400\text{--}1600 \text{ }^\circ\text{C}$ ) is two to four times larger than that of metallurgical coke [63,64].

**Table 1.** Typical properties of charcoal and metallurgical coke [19,20,47,64].

Property	Unit	Classical Charcoal	Retort Charcoal	Metallurgical Coke
Moisture	%,ar	5–10	5–10	$\leq 3$
Fixed carbon	%,db	65–85	84–90	86–88
Volatile matter	%,db	15–35	12–16	$\approx 1$
Ash	%,db	0.4–4	$\leq 4$	10–12
Bulk density	$\text{kg m}^{-3}$	180–350	250–350	500–600
Compression strength	$\frac{\text{kg}}{\text{cm}^{-2}}$		20–60	$\geq 100$
Durability	%	90–94	90–94	$\geq 99$
Electrical resistivity *	$\text{m}\Omega \text{ m}$	9–18	8–16	3–9
Ash composition (% of ash):				
$\text{SiO}_2$		5–25	5–10	25–55
$\text{Fe}_2\text{O}_3$		1–13	3–7	5–45
$\text{Al}_2\text{O}_3$		2–12	1–2	13–30
$\text{P}_2\text{O}_5$		4–12	n.d.	0.4–0.8
CaO		20–60	50–65	3–6
MgO		5–12	5–12	1–5
$\text{K}_2\text{O}$		7–35	6–15	1–4

\* heat-treated at  $1400$  and  $1600 \text{ }^\circ\text{C}$ .

Charcoal's properties can be improved by post-treatment processes, which are known from coal beneficiation and special applications. The  $\text{CO}_2$  reactivity can be adjusted by the removal of inorganic elements catalyzing the Boudouard reaction [65] and by increased structural ordering of the carbon structure at elevated temperature [53,55]. The catalytic effect of alkali and alkali earth metals on the Boudouard reaction can be ranked in the order  $\text{K} > \text{Na} > \text{Ca} > \text{Fe} > \text{Mg}$  [66,67] and, thus, should be removed on basis of importance and concentration. Briquettes can be formed from charcoal fines by the addition of organic binder, resulting in an increasing usable charcoal yield, and renewable reductants with specific shape and size. The mechanical properties of heat treated charcoal pellets produced

with bio-oil binder [60,68] seem to be suitable for application in SAF. Heat-treated briquettes produced after hydrothermal carbonization (HTC) fulfilled the European standards for barbecue briquettes and showed improved mechanical properties [35]. However, the limited availability of HTC products currently inhibits a large scale application in metallurgy. Composite briquettes of biomass, charcoal and fossil fuels, as well as bio-coke can be additional alternatives to reduce CO<sub>2</sub> emissions [21,27,69].

### 3.2. Reductants

To replace a significant fraction of fossil fuels in ferro-alloy production, renewable reductants should provide similar physical, mechanical and electrical properties to continuously ensure stable operation of SAF and be suitable as drop-in reductant. Required properties reported in literature are summarized in Table 2 for pig iron production in blast furnaces and silicon and manganese-alloy production in SAF [16]. In addition to the technical issues related to implementation of renewable reductants, challenges such as availability, upgrading technologies and high market competition with fossil fuels can inhibit an efficient application of renewable reductants [18].

**Table 2.** Desired properties of carbon reductant in ferro and ferro-alloy industry [24,70–76].

Property	Unit	Ferro	Silicon	Ferro-Alloy
		Blast Furnace		Manganese
Moisture	%	1–6	≤6	≤6
Fixed carbon	%	≥85	≥84	≥85
Volatile matter	%	≤1.5	≤9.5	≤3
Ash	%	≤12	≤12	≤12
Phosphorous	%	≤0.06	≤0.02	≤0.02
Sulfur	%	≤0.9%	≤0.6	≤0.6
Size	mm	47–70 mm	5–40	5–40
Bulk density	kg m <sup>-3</sup>		400–500	400–500
Ash fusion temperature	°C		1250–1450	1250–1450
CSR	%	≥60	-	-
CRI	%	20–30	-	-

### 3.3. Charcoal Production

The previous research identified a need in the new manufacturing routes for renewable reductants with properties similar to those of fossil fuel-based reductants, especially metallurgical coke. In addition to new technologies, charcoal properties can be improved by post-treatment processes [9] and process stages which can be adopted from coal beneficiation. These processes should increase the mechanical properties and decrease the volatile matter content and CO<sub>2</sub> reactivity compared to classical and industrial charcoal. However, additional processes will also increase greenhouse gas emissions by additional energy and chemical demands, as well as decreasing the usable charcoal yield based on its conversion efficiency. On the other hand, briquetting or pelleting can increase the usable charcoal yield by upgrading fines.

A sustainable biomass potential is limited by its growth rate, which can be stated to 0.4–3.6 t<sub>carbon</sub> ha<sup>-1</sup> a<sup>-1</sup> of Norway spruce and up to 31.5 t<sub>carbon</sub> ha<sup>-1</sup> a<sup>-1</sup> for tropical forests [77,78]. Waste materials, such as lignin from second generation biofuels or agricultural waste can increase this potential and optimize the multifaceted use of biomass [9,31,37]. The main key strategies for the application of biomaterials were summarized to: (1) ensure the use of biomaterials to mitigate climate change; (2) avoid the direct and indirect land use change; (3) minimize biodiversity impacts; (4) ensure biomass multifaceted usage; and (5) discourage trade barriers of biomass world widely [31]. Approximately 20–50% of the carbon is recovered in classical charcoal production; more than 50% is released as bio-oil or pyrolysis gas, such as CO, CO<sub>2</sub> or CH<sub>4</sub>. This volatile matter is utilized in industrial retorts to provide the required heat, or post-processed to a value-added by-product. Several

studies have shown that a decomposition of bio-oils can enhance the yield and properties of the charcoal [56,65,68,79,80].

However, only 1% of charcoal is produced in Europe [81], decreasing the local availability and thus, also minimizing chances of bio-oil utilization or post upgrading to renewable coke. In addition, the increased demand and upgrading of classical produced charcoal increases the risk of deforestation without securing a sustainable biomass production. Charcoal production and upgrading processes should therefore be selected on chemical and energy demands, and carbon losses or their sustainability. On-site upgrading can reduce or eliminate the additional losses and energy demand.

### 3.3.1. New Production Processes

Charcoal is mainly produced in industrial kilns and retorts at a conversion efficiency of 20–35% [16]. The main greenhouse gas emissions occur by the incomplete combustion of volatile matter, and by unsustainable biomass production, e.g., deforestation. Furthermore, a low conversion efficiency reduces the available biomass potential and increases the required area to harvest biomass for the renewable reductants. Industrial retorts with a conversion efficiency  $\geq 30\%$  are mainly used in Europe and North America, using similar process technologies and process conditions since decades. Laboratory scale to pilot scale experiments have shown, that increased pressure or a multi-stage pyrolysis can increase the charcoal yield [82]. For example, ThyssenKrupp and Arcelor Mittal have introduced torrefaction and pyrolysis plants for the biocarbon production for the steel industry [9].

Properties such as charcoal yield, fixed carbon content, bulk density, crushing strength and reactivity can be correlated to the process conditions of the pyrolysis [83]. While no clear tendency was observed for the friability of charcoal, the grindability improves by flash pressurized pyrolysis [65]. An increased pyrolysis pressure improves the bio-oil decomposition inside the particles and concomitant increase final charcoal yield. However, the secondary char can exhibit different properties compared to classical charcoal, such as CO<sub>2</sub> reactivity or elemental composition [65,84,85]. One of the major disadvantages of the bio-oil decomposition by primary pyrolysis is an increased oxygen content and lower carbon content of the charcoal [79], which can also result in an increased volatile matter content.

The main difference between industrial charcoal production in retorts and new processes is a pressurized vessel, multiple heating zones or an increased pyrolysis temperature. Intense process conditions require an increased wall thickness, different materials and a higher energy input. Based on the reviewed literature, it is not stated if an additional energy source is required. High temperatures postulate mechanical and temperature-resistant materials, which require more energy and resources in the production process. However, the share of greenhouse gas emissions for construction and maintenance is generally small, for example less than 1% for coal fired power plants [86]. In addition, new processes can be optimized to handle a wider range of biomass at greater conversion efficiency. For example, elephant grass can be milled, heat treated and densified by briquetting with a likelihood of larger 84% being profitable within 10 years [87]. However, charcoal's properties and the energy demand for new processes are unknown and are therefore not considered in this study.

### 3.3.2. Ash Removal

The mineral matter of charcoal can be removed prior to primary pyrolysis or as post-treatment process before further application. The former would be carried out decentralized on small-scale and can increase the suitable biomass availability or homogenize the biomass properties. However, the removal of mineral matter can also affect the product distribution (solid, liquid, gaseous products) [88] and require multiple small units, which hamper the recovery of energy or used chemicals. Post treatment of charcoal can be executed in centralized large-scale systems, for example at harbor or on-site the metallurgical plant. In this study, only the centralized pathway is considered to neglect changes in transport and handling of the process chain. Since information of ash removal (AR) of charcoal on industrial scale are scarce, knowledge from coal beneficiation is adopted as reference.

Moreover, studies have shown that the removal of mineral matter by leaching before pyrolysis can be economically feasible [88]. To meet future demands of high-quality charcoal, emphasis is set on the proper utilization of classical and industrial charcoal. In addition, upgrading of classical charcoal is economically favorable due to the availability of charcoal and the lower CAPEX and OPEX of large-scale systems.

Ash removal can be carried out by physical methods, such as floatation, ultrasound treatment, or chemical processes, e.g., chemical leaching and solvent extraction [89]. From process perspective, ash removal and organic recovery are process variables that must be considered to evaluate additional emissions. Physical methods remove mainly extraneous mineral matter, which occurs as a contamination by harvesting and handling. Conventional physical beneficiation methods do not remove mineral matter from the carbon matrix [90] and are suitable only for inorganic sulfur. Chemical methods on the other hand are suitable to remove mineral matter from the organic structure of biomass, charcoal or coal [90]. Physical separation methods have a high organic recovery of the organics. For ultrasound separation, an organic recovery of 97.6 to 99.8% with a ash removal of 11.6 to 31.1% was reported, about 10% better than that of conventional flotation [89]. Other researcher reported a removal of  $\approx 7\%$  alkali and alkali–earth metals for biomass [91]. Organic solvent extraction of coal at ambient pressure conditions showed an extraction of 25–30% [92], in which the extraction efficiency is affected by the ash composition. The extraction can be further increased by increasing temperature and pressure but may concurrently change the organic structure of the raw feedstock. The most efficient ash removal was reported for alkali–acid leaching, where a demineralization of  $\geq 80\%$  can be realized.

The removal of alkali and alkali–earth metals is crucial to reduce the  $\text{CO}_2$  reactivity of the charcoal in the burden of SAF. Most important is the removal of potassium and calcium, since potassium has largest catalytic effect and both elements are present at a high concentration in most biomass ashes. Si, Al, Fe, and P are dissolved during alkali digestion [93]. It was shown in previous studies that 97.3% of alkali and alkali–earth metals can be removed by dilute-acid leaching [91]. In addition, most of chlorine and phosphorus are removed by washing and acid leaching [94]. However, the removal of potassium and sodium can be limited by the presence of stable minerals and bimetallic oxides [94]. Acid leaching is effective to remove minerals such as carbonates, iron-oxide, and sulfides, whereas clay-bearing minerals are not dissociated [90]. Alkaline leaching is used to remove silica and other impurities and may also dissolve some organic carbon [93]. Temperatures of 200 to 300 °C and leaching under pressure is more effective to remove ash forming minerals from bituminous coals [90].

Most common chemicals in chemical leaching processes are NaOH and KOH for alkali leaching, and HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , HF in acid leaching and NaOH– $\text{H}_2\text{SO}_4$ , NaOH–HCl, KOH– $\text{H}_2\text{SO}_4$ , KOH–HCl in alkali–acid combinations [89].  $\text{Ca}(\text{OH})_2$  and CaO have been used as reagents for coal leaching with favorable effects to the combustion properties [90]. Based on the low energy demand of the process and the improved removal of ash, an alkali–acid combination is selected for this study. The liquid to solid ratio is set to 10:1 with a solvent consumption of 25 kg  $\text{t}^{-1}$  for the optimum case, and 100 kg  $\text{t}^{-1}$  for the standard case. A similar solvent consumption is stated for coal ash leaching [94,95]. NaOH and  $\text{H}_2\text{SO}_4$  are selected at a ratio of 2:3 as solvents for the alkali–acid leaching. While elevated temperatures improve the removal of ash, two cases are considered in this study: (1) a temperature of 25 °C for optimum case, and (2) 60 °C for standard case. In both cases, the charcoal is dried naturally to 15% and further thermally dried to 5%, whereas the solvent is recycled at operating temperature. Additional emissions occur from chemical demand, discharged by-products, and required energy. The process flow sheet of the ash removal is shown in Figure 2.



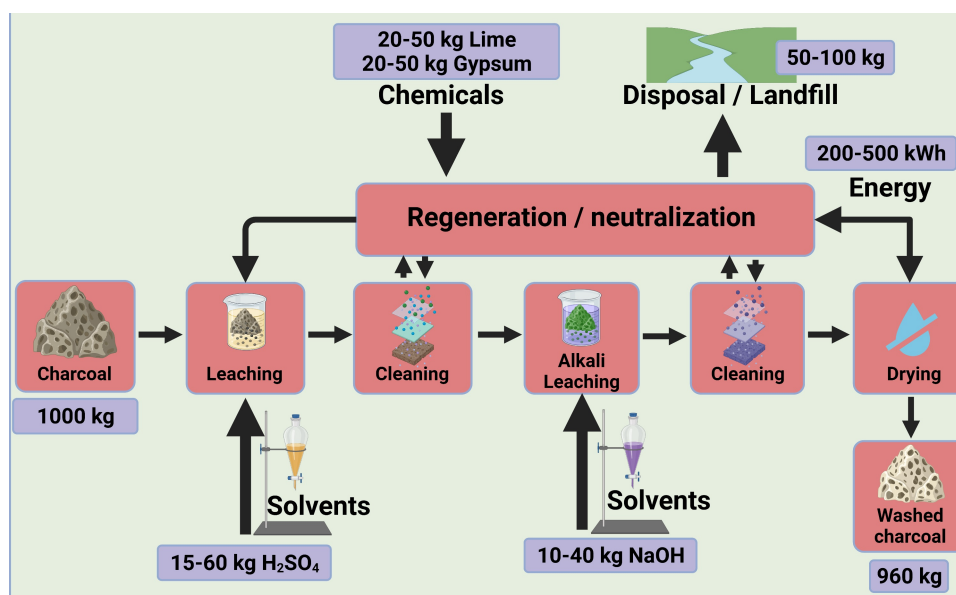


Figure 2. Flowsheet of the ash removal from charcoal.

A theoretical energy demand is calculated based on process temperature and drying, in which the indirect emissions are related to the power consumption covered by the Norwegian energy mix. To minimize the chemical demand for the process, the spent alkali and acid solutions are assumed to be regenerated. It is reported in literature that spent alkali-solution can be partially regenerated with lime, whereas acids can be recovered by the addition of gypsum [90]. For example, potassium can be recovered from precipitated potassium by adding sodium perchlorate and further thermal decomposition to potassium chloride [96]. Reactant and product recovery are important, since the discharge of excess chemicals, such as acids, bases and dissolved minerals in the water phase can be of great environmental concern [92]. A discharge of  $100 \text{ kg t}^{-1}$  of minerals and chemicals is assumed for the standard case, and of  $50 \text{ kg t}^{-1}$  as summarized in Table 3.

Table 3. Input parameter used for ash removal from charcoal.

Variable	Unit	Standard Case	Optimal Case
Input			
Charcoal	kg	1000	1000
Water	$\text{m}^3$	10	10
Energy (heating)	MJ	1890	420
Solvent (acid)	kg	60	15
Solvent (alkali)	kg	40	10
Energy (drying)	MJ	371	322
Solvents (regeneration)	kg	100	40
Output			
Charcoal	kg	960	960
Landfill	kg	100	50

### 3.3.3. Charcoal Compaction

Charcoal fines can be compacted to briquettes or pellets with the addition of binder to produce reductants with specific size and shape, in which briquettes are superior to produce particles of larger lump size by coarse charcoal particles. Largest particle size suitable as feedstock material is  $\approx 12 \text{ mm}$ , with an optimum particle size of 6–8 mm and about 10–20% of fine particles less than 4 mm [97], whereas industrial pellets have generally a diameter less than 10 mm and thus, require a much smaller feedstock material. A random distribution of small to large particle size improves the mechanical properties of briquettes [97]. The mechanical strength at atmospheric and elevated temperatures are important to avoid

fines feeding and formation in SAF, since fines can hamper the gas permeability in the SAF and decrease the value of by-products, such as microsilica in silicon production [98]. Reductant and composite briquettes, which consists of blends of the raw materials, can be produced to feed the materials into SAF to increase the usable yields. Such briquettes can be produced from fines generated by handling or by crushing charcoal lumps, in which the latter will provide a better distribution of particle size required for briquetting. The mechanical stability of composite briquettes is highly affected by the carbon/oxygen ratio, in which furnace dust and other waste streams can be utilized up to 10% [26].

Grinding of biomass and charcoal to fine particles increase the energy demand of the process chain, e.g., by  $750 \text{ kW h t}^{-1}$  for spruce wood or  $850 \text{ kW h t}^{-1}$  for beech wood [99]. The energy demand of milling is decreasing after a thermal heat treatment of biomass. For example, the energy demand for grinding of coarse particles decreases to less than  $100 \text{ kW h t}^{-1}$  for torrefied biomass [99]. Milling of densified biomass pellets in hammer mills results in a specific energy consumption of  $\approx 10\text{--}25 \text{ kW h t}^{-1}$  [100], similar to that of coal [99]. In most cases, biomass pellets are produced by adding water as binding agent. The lower energy consumption of pellet milling compared to the grinding of parental feedstock indicates a lower mechanical stability, and the requirement of additional binder to reduce mechanical fragmentation. Bentonite clay has been used as binding agent for coal briquettes over decades, but the addition of inorganic clay increases the ash content, e.g., sodium or calcium content and  $\text{SO}_x$  and  $\text{NO}_x$  emissions [36]. Calcium compounds ( $\text{CaO}$  and  $\text{Ca(OH)}_2$ ) have been proven to increase the mechanical stability of charcoal pellets [101], but may increase the  $\text{CO}_2$  reactivity of the briquettes.

Organic binders, such as lignin, starch or bio-oil are suitable to produce renewable reductants without increasing the mineral matter in briquettes and pellets [36,38,56,68]. While durability of green briquettes is reported to larger than 99% [35,102], information of the hot strength are scarce. Studies of coal briquettes had shown that organic binder often lack the mechanical stability at high temperatures [103,104], limiting the application in metallurgy as bed material. A combination of multiple binder, e.g., lignin and bituminous binder, can be used to produce briquettes with high mechanical stability [61]. Bio-oil pellets exhibited improved mechanical properties after a secondary heat treatment, which is favorable to reduce fines formation by handling and ensure a high mechanical strength inside SAF. An optimum binder ratio was determined to  $\approx 34\%$  bio-oil [27,60], and 20% bio-oil for optimum heat propagation with low particulate matter release [58].

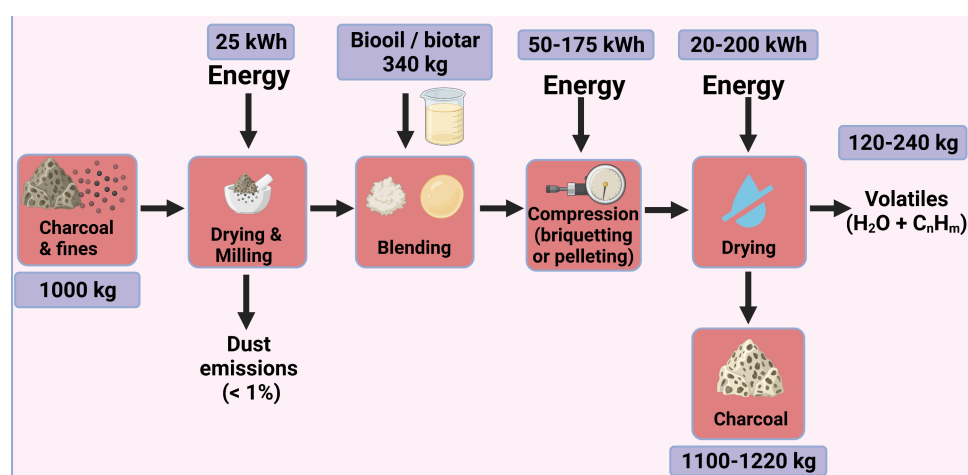
Bio-oil can be supplied by an additional flash-pyrolysis or as pyrolysis by-product, at which a by-product utilization is expected to be limited to the close distance to pyrolysis plants. In addition, volatile by-products are often combusted to provide the required thermal energy for the process. These by-products contain the 15–30% pyrolysis water of the bio-oil, light hydrocarbons and oxygenated organic compounds. The main organic compounds ( $\text{C}_n\text{H}_m$ ) include C1–C4 molecules with a boiling point less  $130 \text{ }^\circ\text{C}$ , such as carboxylic acids, alcohols, furanics, etc. [105,106]. The high binder ratio can be chosen to utilize the heavy fraction of the liquid pyrolysis by-products without previous distillation or extraction. In this study, the utilization of a flash pyrolysis bio-oil is considered for an indigenous feedstock as standard case, whereas the heavy distillate side stream is considered as best case scenario. The separation of the heavy bio-oil fraction from acidic water and light oil fraction reduces the volatile emissions from green briquettes and minimizes the porosity after the heat treatment. The allocated  $\text{CO}_2$ -eq. emissions of bio-oil production are stated in the range of 100 to  $\approx 570 \text{ kg t}^{-1}$  [107,108]. The lower range can be obtained by upgrading bio-oil into biofuel, which is not considering further processes of volatile matter. However, the combustion of bio-oil is generally assumed to be  $\text{CO}_2$  neutral.

Optimum production conditions are depending on the chosen feedstock and binder [27]. For the production of charcoal pellets with bio-oil, process conditions should be set to  $60 \text{ }^\circ\text{C}$  and  $\approx 115 \text{ MPa}$  [60], and  $60 \text{ }^\circ\text{C}$  and  $\approx 20 \text{ MPa}$  for briquettes [97]. The average power consumption of biomass briquetting varies from 160 to  $175 \text{ kW h t}^{-1}$  using both case

scenarios with and biomass pre-heating [109]. Energy consumption for wood briquettes varies from 30 to 150 kW h t<sup>-1</sup> [97,110]. However, pyrolyzed wood pellets have a lower mechanical abrasion strength than the pelletized charcoal counterparts [111]. In total, the total energy demand of charcoal briquettes is in the range of 250–350 kW h t<sup>-1</sup>, similar to that reported in literature [112]. This excludes an additional heat treatment to decompose the bio-oil and form a stable secondary char between the fine particles. The used input parameter and flow sheet for briquetting are summarized in Table 4 and Figure 3.

**Table 4.** Input parameter used for charcoal compaction.

Input	
Charcoal	1000 kg
Energy (crushing)	25 kW·h
Bio-oil (binder)	340 kg
Energy (heating)	75–350 kW·h
Output	
Charcoal	1100–1220 kg
Off-gases	120–240 kg



**Figure 3.** Flowsheet of charcoal briquetting with bio-oil binder.

### 3.3.4. Secondary High Temperature Treatment

A secondary heat treatment (SHT) at elevated temperature can decrease volatile matter content and CO<sub>2</sub> reactivity of charcoal and charcoal briquettes. In this study, the second heat-treatment temperature is set to 1300 °C, similar to the wall temperature in coke oven batteries to produce metallurgical coke [72]. The additional heat treatment results in the release of remaining volatile matter and further carbonization of the carbon matrix, while the temperature remains below the ash melting temperature of most biomass ashes, minimizing the risk of blocking the micropore structure [113]. Charcoal heat treated at 1300 °C has obtained a surface area and electrical resistivity similar that is similar to that of semi-coke [64]. Temperatures above 2000 °C are required to reduce the CO<sub>2</sub> reactivity by thermal treatment to be similar to metallurgical coke [54], which seem not to be economically feasible for low value applications. However, it was shown that the combination of acid leaching and secondary heat treatment can decrease the CO<sub>2</sub> reactivity to the same extend [55].

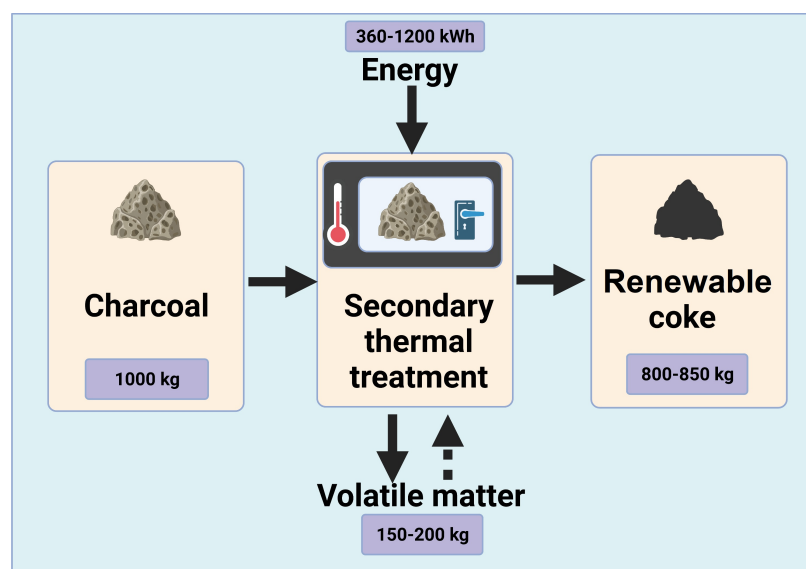
In addition to gas reactivity, surface area and density are affected by the high heat treatment temperature [55], increasing the quality of charcoal reductants in metallurgical industry. For classical charcoal and metallurgical coke production, pyrolysis gases are commonly combusted to supply the thermal energy for the process. The primary pyrolysis can result in a deficit of volatile matter, and lack of heat provided by the combustion of volatile products. A mass loss of 12.8–21.3% was measured for a secondary heat treatment at

1300 °C for oak and spruce charcoal [56]. The calorific value of volatiles was calculated using Boie equation ranging from 1.2 to 4.6 MJ kg<sup>-1</sup><sub>charcoal</sub>. The required energy for the secondary heat treatment can be provided by the oxidation of the volatiles, or additional energy from a renewable source. In addition, furnace gases from SAF can be utilized for an on-site process. The high heat treatment temperature emphasizes the potential for integration of an energy recovery. Metallurgical furnaces are operated over decades and thus, long payback periods of waste heat recovery or side streams utilization units can significantly improve the environmental benefits without negatively impact on economy [114].

High temperature processes are less energy efficient when no heat recovery is coupled. For example, an energy loss of 70% can occur at 1300 °C, at which only 30% are further used in the process [115]. This loss is considered for a heat supply by the combustion of feedstock material for the standard case scenario, whereas an electrical power supply can minimize these losses. In this study, an energy recovery for sensible heat for temperatures larger than 300 °C is assumed for the best case scenario. An energy recovery of 40% is assumed for the standard case, which was reported for gas temperatures of 1200 °C [95]. Energy recovery is utilized by preheating the feedstock materials but can also be used for power production. Pyrolysis of biomass is mainly endothermic at temperatures less than 800 °C due to decomposition reactions and becomes exothermic at temperatures above [116]. Since most of the volatiles have been released in primary pyrolysis, reaction enthalpy is considered as energy neutral in this study. The required thermal energy is calculated based on the heat capacity of the charcoal, which is estimated to 1 kJ kg<sup>-1</sup> K<sup>-1</sup> [117]. However, specific heat capacity can be in the range of 1–2 kJ kg<sup>-1</sup> K<sup>-1</sup> and can further increase to 2.5–4.5 kJ kg<sup>-1</sup> K<sup>-1</sup> at elevated temperatures [116]. The input parameter and flow sheet for the secondary heat treatment are summarized in Table 5 and Figure 4.

**Table 5.** Input parameter used for the secondary heat treatment of charcoal and briquettes.

Variable	Unit		Charcoal	Briquettes
		Input		
Charcoal	kg		1000	1000
Energy (heating)	kW·h		360–1200	500–1600
Bio-oil	kg		-	340
		Output		
Energy (recovery)	kW·h		125–140	125–160
Charcoal	kg		800–850	840–1055
Off-gases	kg		150–200	285–500



**Figure 4.** Flowsheet of the secondary heat treatment.

### 3.4. Life Cycle-Based Global Warming Potential

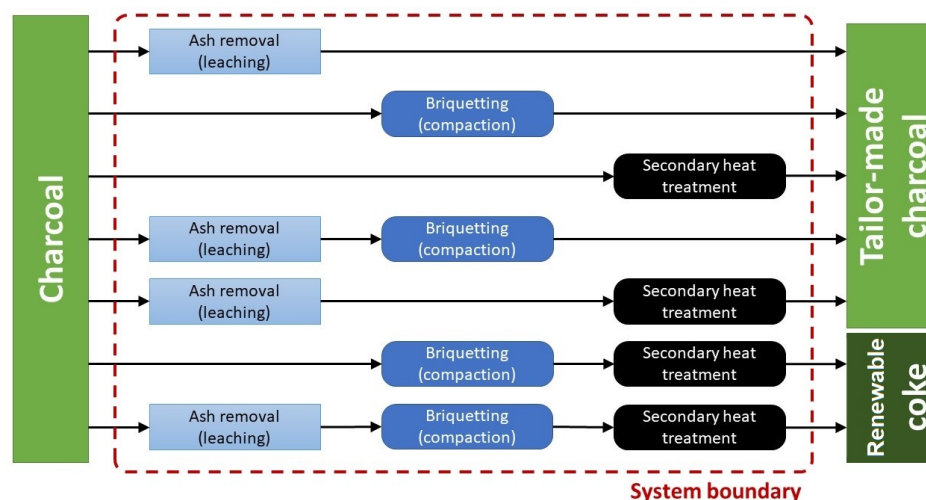
The global warming potential of the above mentioned processes is evaluated individually based on the CO<sub>2</sub> emissions from the energy and chemical demands. Compared to a full life cycle analysis, where also toxicity, eutrophication, and further impacts are considered, the scope of this study is limited to the evaluation of the CO<sub>2</sub> emissions. The global warming potential is part of the life cycle assessment and conducted for the complete life cycle (cradle-to-grave) or for the production route (cradle-to-gate), whereas differences in initial charcoal production routes are taken as uncertainty in this study. Thereby, upgrading processes are individually analyzed and the global warming potential is calculated based on the specific CO<sub>2</sub> emissions, carbon losses, as well as indirect emissions from energy and chemical demands. The total energy and chemical demands are summarized for the process chains in Table 6, in which further emissions, e.g., dust emissions, were disregarded in this simplified approach.

**Table 6.** Mass and energy demand for the different process routes for ash free charcoal, briquettes and renewable coke on the basis of 1 t FC.

Processes	Charcoal	Bio-Oil kg t <sub>FC</sub> <sup>-1</sup>	Acids	Alkalis	Energy /MJ
	Input				
Ash removal (AR)	1240–1390	-	18–75	12–50	920–3140
Briquetting (BR)	1095–1215	370–415	-	-	495–540
Heat treatment (SHT)	1235–1315	-	-	-	1600–5350
AR + BR	1150–1295	375	12–50	17–60	1000–3420
AR + SHT	1300–1550	-	13–50	19–70	2180–8610
BR * + SHT	915–960	345–365	-	-	1920–5700
AR + BR * + SHT	1070–1300	375	14–55	20–80	2390–8640

\* Excludes the additional fines (approx. 10%) for the charcoal demand.

Total CO<sub>2</sub> emissions of process chains including multiple post-treatment steps are calculated based on the accumulated emissions of the individual processes. The target audience is researchers for upgrading processes, policymakers to establish national regulations, and industrial stakeholders to calculate scenarios. System boundaries in this study are defined for each individual process, in which intermediate products are considered in the process chains, schematically shown in Figure 5.



**Figure 5.** Investigated processes and process chains to produce tailor-made charcoal or renewable coke.

Input parameters, such as energy and raw materials are referred to as main input variables, in which changes by origin, production technology, etc., of each variable are

considered as uncertainties. Indirect emissions from power supply are calculated on the energy mix for selected countries, which are selected based on the charcoal production and possible application in SAF. An increase in efficiency, or renewable technologies, can reduce greenhouse gas emissions by  $\approx 3\%$  for each 1% increase in power production [86]. In a full LCA, further uncertainties have to be investigated in a consistency check, such as transport emissions, which are neglected for the centralized or on-site upgrading processes. Reductants are fed in SAF based on the fixed carbon content (FC) of the material, as shown in Table 7.

**Table 7.** Carbon materials in relation to the functional unit (fixed carbon).

	FC kg	Mass $\text{kg}_{\text{charcoal}} \text{t}_{\text{FC}}^{-1}$	Carbon Content $\text{kg}_C \text{t}_{\text{FC}}^{-1}$
Classical charcoal	1000	1200–1650	1100–1250
Industrial charcoal	1000	1075–1250	1050–1150
Renewable coke	1000	1050–1175	1000–1050
Metallurgical coke	1000	1125–1175	1000–1050

Charcoal with an FC larger than 84% is considered metallurgical grade charcoal [82], and an FC larger than 75% is required for barbecue charcoal based on EN 1860-2:2005.

Thus, fixed carbon content is used as the functional unit in this study. Carbon content or reductant weight could be alternative functional units since these are easier accessible from literature. The minimum fixed carbon content from metallurgical coke is standardized and taken as reference. Industrial charcoal with an FC of 84% is used as the parental feedstock for the calculations, whereas an FC of 85, 75 and 95% are assumed for ash free charcoal, briquettes, and renewable coke. The lower FC content for green charcoal briquettes is related to the volatile matter content of bio-oil binder, which can be reduced by the post heat treatment. In addition to the different global warming potential by the feedstock material and production, ash free charcoal, briquettes and renewable coke may result in decreasing greenhouse gas emissions by its consumption, such as  $\text{NO}_x$  and  $\text{SO}_2$  of SAF, improving the benefits of renewable reductants [118–120]. Both  $\text{SO}_x$  and  $\text{NO}_x$  emissions are not considered in this study.

For open hearth furnaces, ash removal and charcoal briquetting may be sufficient to provide renewable reductants with minimum required properties, whereas a secondary heat treatment is compulsory to reduce volatile matter content for closed hearth furnaces. The emissions for industrial charcoal production are considered as input emissions and added to the post-treatment processes. However, it is expected that charcoal is continued to be produced mainly outside Europe, possibly increasing the initial  $\text{CO}_2$  emissions per metric tonne of charcoal. The  $\text{CO}_2$  emissions are compared to those of metallurgical coke, which are stated to  $2300 \text{ kg CO}_2 \text{ t}^{-1}$  [121]. Upgraded charcoal is assumed to be able to substitute between 60 and 100%, in which a greater replacement ratio is assumed to be possible for the complete post-treatment process chain, containing mineral matter removal, fines utilization and a secondary heat-treatment. Methane from waste material utilization may be further considered as an alternative carbon source. This may significantly improve the economics of biogas production, if gas cleaning can be reduced to a minimum.

## 4. Results and Discussion

### 4.1. Life Cycle Inventory Analysis

The summary of the unit processes and the life cycle inventory analysis are summarized in Tables 8 and 9 based on the input parameter from ash removal, briquetting, secondary heat treatment and combinations thereof.

**Table 8.** Data summary of the unit processes.

Material inputs	Units	Quantity	Process unit stage
Acid (solvent)	kg t <sub>FC</sub> <sup>-1</sup>	18–75	Ash removal
Alkali (solvent)	kg t <sub>FC</sub> <sup>-1</sup>	12–50	Ash removal
Solvents (regeneration)	kg t <sub>FC</sub> <sup>-1</sup>	42–120	Ash removal
Charcoal	kg t <sub>FC</sub> <sup>-1</sup>	1240–1390	Ash removal
Charcoal	kg t <sub>FC</sub> <sup>-1</sup>	1100	Briquetting
Bio-oil	kg t <sub>FC</sub> <sup>-1</sup>	375	Briquetting
Charcoal	kg t <sub>FC</sub> <sup>-1</sup>	1240	Secondary heat treatment
Water consumption	Units	Quantity	Process unit stage
Water demand	m <sup>3</sup> t <sub>FC</sub> <sup>-1</sup>	≤14	Ash removal
Water demand	m <sup>3</sup> t <sub>FC</sub> <sup>-1</sup>	≤1	Briquetting
Water demand	m <sup>3</sup> t <sub>FC</sub> <sup>-1</sup>	≤1	Secondary heat treatment
Energy input	Units	Quantity	Process unit stage
Electric energy for heating and pumping	MJ t <sub>FC</sub> <sup>-1</sup>	520–2650	Ash removal
Electric energy for regeneration & drying	MJ t <sub>FC</sub> <sup>-1</sup>	400–515	Ash removal
Electric energy for milling	MJ t <sub>FC</sub> <sup>-1</sup>	90	Briquetting
Electric energy for compaction	MJ t <sub>FC</sub> <sup>-1</sup>	264–925	Briquetting
Electric energy for drying	MJ t <sub>FC</sub> <sup>-1</sup>	132–460	Briquetting
Electric energy for heating	MJ t <sub>FC</sub> <sup>-1</sup>	1600–5350	Secondary heat treatment
Material outputs	Units	Quantity	
Charcoal (ash reduced)	kg t <sub>FC</sub> <sup>-1</sup>	1175	Ash removal
Wastewater	m <sup>3</sup> t <sub>FC</sub> <sup>-1</sup>	≤14	Ash removal
Minerals (landfill)	kg t <sub>FC</sub> <sup>-1</sup>	30–100	Ash removal
Charcoal (compacted)	kg t <sub>FC</sub> <sup>-1</sup>	1300–1450	Briquetting
Volatile matter	kg t <sub>FC</sub> <sup>-1</sup>	130–260	Briquetting
Charcoal (renewable coke)	kg t <sub>FC</sub> <sup>-1</sup>	1050–1100	Secondary heat treatment
Volatile matter	kg t <sub>FC</sub> <sup>-1</sup>	185–250	Secondary heat treatment

The latter contains possible emissions by inappropriate handling, insufficient cleaning or post-treatment of the products, such as the release of volatile matter, the dissolution of condensed tars and oils by leaching and washing, and the evaporation of bio-oil binder. Extracted ash and neutralized solvents are accounted as landfill but may be upgraded to mineral fertilizer or filling material [122]. In addition, dissolved bio-oil species and dissoluble hydrocarbons from charcoal necessitate a wastewater treatment before discharging the water and before water recirculation to the ash removal. Recovery of hydrocarbons by liquid–liquid extraction or thermal separation may provide an additional chemical side stream for further applications. However, the complexity of organic species and their application are currently not considered as a chemical feedstock and no market has been established to the knowledge of the authors.

A large uncertainty occurs by the energy demand of the different processes, especially for the secondary heat treatment at elevated temperatures. An effective energy recovery is assumed for the optimal case, in which losses to the environment are minimized. Biomass or charcoal as energy carrier can substitute the power supply for these processes, but the heat supply by charcoal or biomass will further reduce the available biomass potential, which may be the limiting factor in replacing fossil fuels in the future. In addition, energy losses for high temperature processes increase for processes which are heated by the oxidation of fuel due to the larger off-gas volume flow. Direct heating with combustion gases may increase carbon losses by Boudouard reaction, which occur at temperatures larger than 700 °C. Volatile matter release by bio-oil binder and secondary heat treatment is assumed

to be an energy source to partially provide heat for the individual processes, as shown in Table 9.

**Table 9.** Life cycle inventory analysis for possible additional emissions.

Emissions to air	Units	Quantity	Process
Volatile matter	$\text{kg}_{\text{C}_x\text{H}_y\text{O}_z} \text{t}_{\text{FC}}^{-1}$	0–10	Ash removal
	$\text{kg}_{\text{C}_x\text{H}_y\text{O}_z} \text{t}_{\text{FC}}^{-1}$	0–260	Briquetting
	$\text{kg}_{\text{C}_x\text{H}_y} \text{t}_{\text{FC}}^{-1}$	0–50	Secondary heat treatment
Dust (fines)	$\text{kg} \text{t}_{\text{FC}}^{-1}$	0.1–45	Briquetting
Emissions to water	Units	Quantity	Process
Salts from neutralisation	$\text{kg}_{\text{salt}} \text{t}_{\text{FC}}^{-1}$	0–100	Ash removal
Hydrocarbons (*)	$\text{kg}_{\text{C}_x\text{H}_y\text{O}_z} \text{t}_{\text{FC}}^{-1}$	10–30	Ash removal
Hydrocarbons (*)	$\text{kg}_{\text{C}_x\text{H}_y\text{O}_z} \text{t}_{\text{FC}}^{-1}$	0–50	Briquetting
Emissions to land	Units	Quantity	Process
Minerals & salts	$\text{kg}_{\text{minerals}} \text{t}_{\text{FC}}^{-1}$	0–100	Ash removal

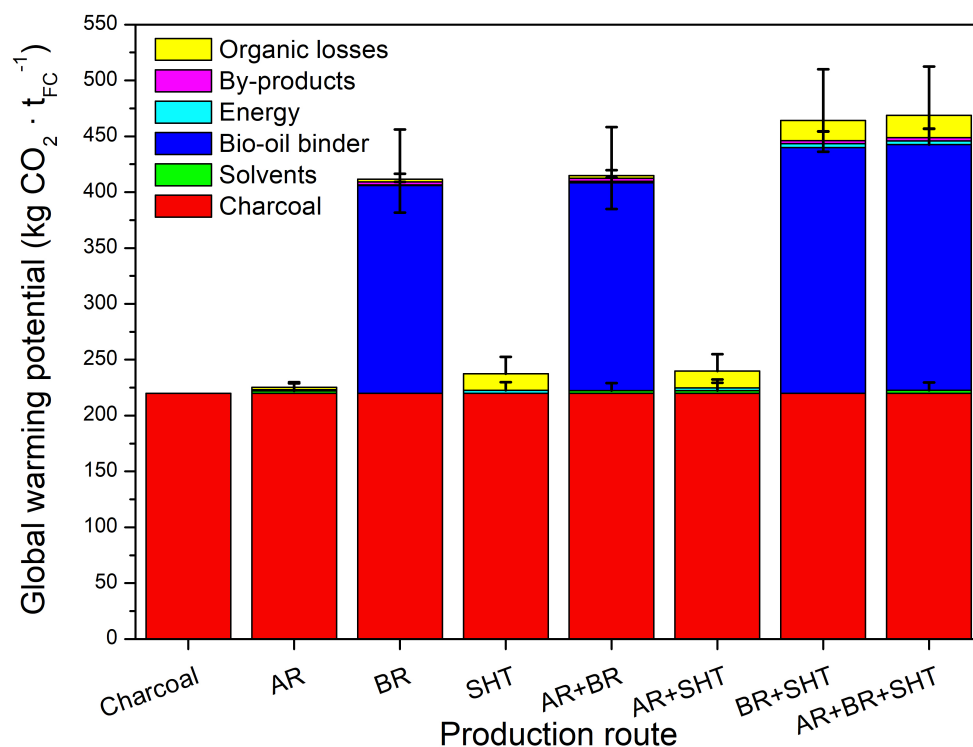
(\*) Hydrocarbons contain organic acids and bio-oil compounds.

However, hydrocarbons with a low boiling point may also be used as renewable energy carrier or as chemical feedstock. Moreover, the removal of volatile species of bio-oil prior to the compaction may improve the mechanical properties of the renewable coke due to the decreasing void fraction by volatile release. Bio-pitch binder would require an increased production of bio-oil, which would result in an increased global warming potential of the process chain under the current conditions.

#### 4.2. Upgraded Charcoal

Upgrading of industrial charcoal by ash removal, briquetting and renewable coke production increases the potential to replace large amounts of fossil fuel-based reductants in SAF. The inferior properties of charcoal can be upgraded individually by existing technologies to fulfill requirements of ferro-alloy production in SAF. Washing and leaching can reduce the ash content of bio-reductants, whereas charcoal fines can be compacted by briquetting to decrease the losses by transport and handling. Organic binders, e.g., bio-oil binder, require a heat treatment to increase the mechanical strength of the briquettes, which can be executed at elevated temperature to further reduce the volatile matter content to the requirements of closed hearth SAF. However, the additional processes to improve charcoal's properties increase the CO<sub>2</sub> emissions per metric tonne of ash free charcoal, briquettes and renewable coke by the additional energy demand, chemicals (e.g., solvents and binder), carbon losses, and by additional by-product streams, as summarized in Figure 6 for a renewable power supply.





**Figure 6.** Global warming potential of ash reduced charcoal, briquettes and renewable coke on basis of renewable energy and sustainable chemical supply. Industrial charcoal is used as reference case.

The centralized upgrading (e.g., at harbor or on-site the SAF) was used to disregard additional transport or handling. Treatment of wastewater to a zero liquid discharge and possible off-gas cleaning were further neglected, which increase the energy demand of the upgrading processes. Ash removal at atmospheric temperature has only a minor effect on additional CO<sub>2</sub> emissions, in which main emissions occur from solvent regeneration and landfill. Thermal drying can further increase the indirect emissions for the ash removed charcoal from fossil power supply. Briquetting showed the largest increase in CO<sub>2</sub>-eq. emissions based on the global warming potential for the bio-oil production. The high global warming potential of bio-oil production nearly doubles the of briquettes and renewable coke, whereas organic losses occur mainly for the secondary heat treatment. The global warming potential increase by organic losses are correlated to the production process of primary charcoal and can increase by charcoal with lower FC content and classical charcoal. However, volatile species contain often oxygenates and permanent gases, e.g., CO<sub>2</sub> and CO, resulting in a lower carbon loss compared to its mass loss. The uncertainty of a lower fixed carbon content between classical and industrial charcoal is negligible compared to the different global warming potential of the production processes. The low conversion efficiency and risk of deforestation by classical charcoal production can increase the global warming potential to a level larger than metallurgical coke.

#### 4.3. Acid and Alkali Leaching

Acid leaching can reduce critical alkali and alkali–earth metals by more than 90%. Most minerals can be removed by a combination of acid and alkali leaching. Single acid leaching of charcoal reduces K and Ca content by 85% and 50% [55]. A significant removal of potassium and calcium prior to the application in SAF is required due to the recirculation and accumulation in the burden [123], and the catalytic effect of these elements on the Boudouard reaction [124]. The low energy demand at low temperature leaching increased the specific CO<sub>2</sub> emissions of renewable fixed carbon (charcoal) by  $\approx 1.9 \text{ kg CO}_2 \text{ t}^{-1}$ , mainly for the production and regeneration of the used chemicals. A partial recovery of the solvents

by gypsum and lime can reduce the emissions per metric tonne of fixed carbon (charcoal) by  $\approx 10\%$  to  $1.7 \text{ kg t}^{-1}$ , but negatively affects the economy of the process. Leaching at elevated temperatures is favorable to remove mineral compounds, but further increase the energy demand for the process. No further thermal decomposition of charcoal is expected at temperatures less than  $300 \text{ }^\circ\text{C}$ . In contrast to coal, charcoal's density is less than that of most solvents and may float in open vessels, increasing the technical challenge of a homogeneous transport for continuous processes or closed batch systems.

Leaching of charcoal may dissolve condensed bio-oil compounds, concomitantly decreasing the solid yield on ash free basis. This mass loss is mainly assumed for charcoal produced in pressurized pyrolysis, whereas only a minor loss of organics is expected for industrial charcoal. An organic mass loss of  $1\%$  is assumed by leaching, which decreases the biomass potential by  $2\text{--}3\%$ . Washing of classical charcoal can result in an organic loss of up to  $1.5\%$  [125]. A larger weight loss of classical charcoal can be related to the lower pyrolysis temperature and the loss of nonpolar functional groups by the release of volatiles [47]. Leaching of raw biomass can result in the removal of extractives and the modification of organic structure, resulting in an organic mass loss of  $2\text{--}30\%$  [126,127], concomitantly increasing the energy density by up to  $25\%$ . Organic losses occurring by leaching stages will increase the need for wastewater treatment and, thus, increase the indirect global warming potential, which are not considered in this study. In addition, untreated solvent discharge or leakages can harm local water reservoirs or pollute soil by acidification and light hydrocarbons dissolved by the solvent [128].

Ash removal at elevated temperature and thermal drying can increase the energy demand by  $\approx 900 \text{ kW}\cdot\text{h t}^{-1}$  FC. Based on the  $\text{CO}_2$ -eq. emissions from the country-specific power supply, the global warming potential increases by up to  $810 \text{ kg CO}_2\text{-eq. t}^{-1}$  FC. The increased ash removal at elevated temperature goes along with increased indirect emissions, which may balance the benefit of the additional removed mineral matter. A major uncertainty is the level of alkali metal removal required to ensure a stable operation of the SAF, due to the possible accumulation of alkali metals and feeding by manganese ores.

#### 4.4. Briquetting

Briquetting and pelleting enable the utilization of charcoal fines and the production of renewable reductants with specific size and shape. Bulk charcoal can be crushed and milled prior to the compaction process to provide a wide particle size range in large quantity. The lower energy demand for charcoal crushing compared to biomass milling decreases the required energy demand by  $\geq 50\%$  to  $\approx 25 \text{ kW}\cdot\text{h}$ . Partial crushing of charcoal prior to briquetting can provide a broader particle size distribution for briquetting, which can improve the mechanical strength of untreated (green) and heat treated (hot) briquettes. The crushing, blending and compaction result in an additional global warming potential per tonne of renewable fixed carbon (charcoal) of  $2.6 \text{ kg CO}_2\text{-eq.}$  for renewable power supply. However, weak binding forces between charcoal particles necessitate the usage of additional binder to ensure a high mechanical abrasion strength of pellets and briquettes, and to withstand the compression force induced by the load.

Organic binder such as starch, lignin, bio-oil or bio-pitch are superior to inorganic binder on basis of ash content and critical elements [129]. Bio-oil binder in combination with a secondary heat-treatment provide a renewable reductant with adequate mechanical properties for metallurgical application in SAF [111]. However, minerals and clay binder can improve the secondary char formation by bio-oil cracking [130], decreasing direct emissions by volatile release and by its mass loss. The limited availability of bio-oil and the additional emission of  $\approx 575 \text{ kg CO}_2\text{-eq. t}^{-1}$  for its current production [107,131] increase the overall emissions of charcoal briquettes by  $\approx 170 \text{ kg CO}_2\text{-eq. t}^{-1}$  FC. These emissions can be reduced by the recovery of bio-oil as a by-product from primary pyrolysis at the cost of additional power supply.

Charcoal milling and handling prior to the briquetting can result in an additional global warming potential of  $\approx 2.5 \text{ kg CO}_2\text{-eq. t}^{-1}$  FC, whereas the utilization of fines and

can decrease the global warming potential by up to 30 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC. Moreover, the bio-oil conditioning of primary pyrolysis can decrease the additional bio-oil demand, replacing the greenhouse gas emissions from bio-oil production by indirect emissions to produce power. The pyrolysis of beech wood results in the formation of ≈12.5% tar [132], which is sufficient to form briquettes from about 50% of the produced charcoal. Thus, on-site briquetting at the pyrolysis plant can minimize the global warming potential from bio-oil demand, which is especially beneficial for renewable coke production, decreasing the GWP to ≈350 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC. For comparison, the GWP of Brazilian charcoal briquettes was reported to 2100 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC [133], and ≈1.1 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC for charcoal pellets [9].

#### 4.5. Secondary Heat Treatment

High temperature treatment of charcoal and charcoal briquettes can reduce the volatile matter content and CO<sub>2</sub> reactivity, approaching those of metallurgical coke [53,56]. In addition, a secondary heat treatment is required for charcoal briquettes produced with bio-oil binder to enhance the mechanical stability [60,68]. Moreover, multiple bio-oil compounds are removed which can be dissolved by rainwater in storage, minimizing the potential risks of groundwater and soil pollution [128]. The high temperature treatment results in a mass loss of 15–20% [56], increasing the global warming potential by 15–30 kg CO<sub>2</sub> t<sup>-1</sup> FC for an additional charcoal production. The minor global warming potential increase is related to the greater FC content of the heat treated charcoal and renewable coke, which increases by ≈10%-points to 95% for wood charcoal.

The combination of acid leaching and secondary heat treatment to reduce the CO<sub>2</sub> reactivity were similar effective as heat treatment temperatures above 2000 °C [54,55]. A secondary heat treatment temperature of 1300 °C reduces the volatile matter content to ≈1.5%, approaching that of metallurgical coke and fulfilling the requirements of closed hearth SAF. While process heat in classical charcoal production can be covered by the combustion of the volatile matter, less than 33% can be covered by the volatile matter in the secondary heat treatment. This energy demand can be provided by electrical power or the combustion of additional feedstock. In the current study, required heat was provided by electrical power, resulting in additional global warming potential of 2 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC for renewable power supply, and 100 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC based on European energy mix. An additional heat recovery or by-product utilization can further decrease the global warming potential for the secondary heat treatment. Best case scenario would be that the hot charcoal is directly fed into the SAF to minimize heat losses and reduce power supply in the metallurgical process.

#### 4.6. Process Chains

The combination of the processes improves the final product quality of the renewable reductant. The removal of alkali and alkali–earth metals by leaching in combination with a secondary heat treatment can decrease the CO<sub>2</sub> reactivity and volatile matter content to a level similar of metallurgical coke [55]. Both properties are critical in closed hearth SAF for FeMn and SiMn production. Accumulation of potassium in the burden of SAF will require an ash removal for all feedstock materials, decreasing the chance of a partial replacement of ash free charcoal and renewable coke. A combination of leaching and briquetting slightly improves the CO<sub>2</sub> reactivity, ash content, charcoal yield and mechanical strength. However, a low mechanical strength of fresh briquettes (also called green briquettes) limits its handling and transport, and the application in metallurgy. The combination of acid leaching, briquetting and secondary heat treatment can produce renewable cokes with chemical, mechanical and physical properties approaching those of metallurgical coke. The mechanical properties are highly affected by the chosen binder, binder to charcoal ratio and post-treatment temperature of the carbonaceous material [104,111].

The large energy demand by secondary heat treatment results in the largest increase of additional greenhouse gas emissions by fossil fuel-based heat supply (up to 1350 kg CO<sub>2</sub> t<sup>-1</sup> FC),

whereas the additional greenhouse gas emissions by acid leaching are negligible under atmospheric conditions. Off-gases from SAF can be utilized to provide the heat for on-site processes such as charcoal upgrading, reducing the global warming potential possibly caused by power supply. Briquetting is useful to utilize charcoal fines produced by handling and transport, and can increase the charcoal potential by 10–20%. The largest uncertainties of briquetting are the used binder and the ratio of a charcoal to a binder, in which bio-oil has been proven as a superior binder compared to other organic binder, e.g., lignin or starch [111]. Blends of different binders may further increase the mechanical and abrasion strengths but will concomitantly increase the indirect global warming potential [61].

An increase in global warming potential by charcoal conditioning routes is minor when renewable energies are used for binder and power production, in which combining the different conditioning routes can minimize additional energy and solvent demand. The additional global warming potential for ash removal and secondary heat treatment was calculated to  $\approx 5$ –10% compared to classical charcoal production. Such charcoal substitute would require a  $\approx 20\%$  larger charcoal input into open hearth SAF based on the higher volatile matter content and reactivity of charcoal. Removal of volatile matter by the secondary heat treatment for closed hearth SAF would increase the global warming potential by  $\approx 18$  kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC. By-product utilization from the upgrading processes in combination with renewable power supply can further decrease the global warming potential by 10–20%. Economical limitations of low value reductants outweigh the technical hurdles by inferior properties of classical and industrial charcoal. Similar results were obtained by iron and steel industry, where a carbon tax may play an important role to increase the application of tailor-made charcoal or renewable coke in SAF [18].

The secondary heat treatment can be combined with methane densification to further improve the physicochemical properties of charcoal [59], concomitantly reducing the energy demand for process heating. Biomethane can be produced sustainably by biogas production of manure, plant material or biowaste, in which the largest specific saving potential is stated for wet manure [134], where the biogas is produced in closed digestates to minimize methane slip. More than 50% of the methane are decomposed to secondary char and synthesis gas (H<sub>2</sub>, CO, C<sub>n</sub>H<sub>m</sub>) at temperatures larger than 1000 °C [59]. However, the quality of the off-gas has to be further investigated to be suitable as a synthesis gas. At current stage, unconverted methane in the off-gas must be separated and recycled or combusted with the remaining off-gas stream to provide the heat for the process. Natural gas as a methane source would increase the global warming potential by  $\approx 17$  g CO<sub>2</sub> MJ<sup>-1</sup> [134], resulting in a global warming potential of 28–36 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC. Fossil methane decomposition would increase the global warming potential of charcoal briquettes and renewable coke by 55–75 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC, more than the ash removal and secondary heat treatment when renewable energy sources are integrated.

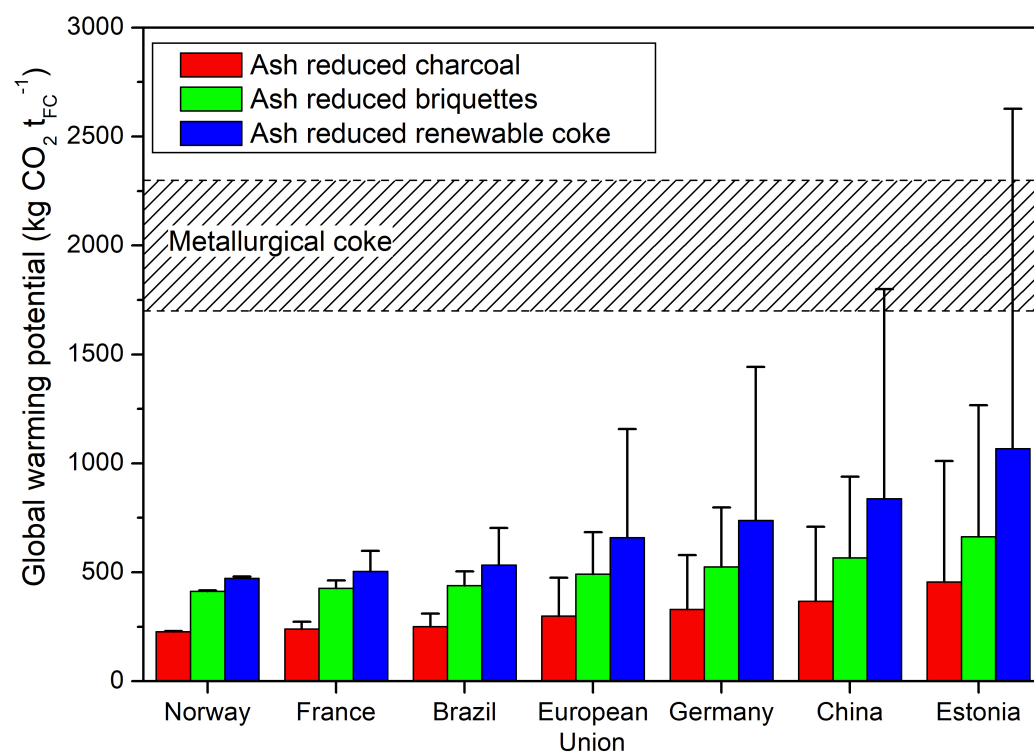
A complete leaching, briquetting with bio-oil binder and secondary heat-treatment increases the global warming potential by  $\approx 250$  kg CO<sub>2</sub>-eq. t<sup>-1</sup>, resulting in a total maximum global warming potential of  $\approx 470$  kg CO<sub>2</sub>-eq. t<sup>-1</sup> of renewable coke produced from industrial charcoal [135], whereas non-sustainable charcoal production can increase the global warming potential up to 2000–3000 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC [136,137]. Renewable coke production from unsustainable produced classical charcoal would result in a global warming potential similar to that of metallurgical coke [121,138,139]. A fully replacement of metallurgical coke by renewable coke would decrease the direct global warming potential by 70–80%, whereas further measures are required for a net zero industry. About 50% of the remaining emissions are related to the production of bio-oil and can partially be reduced by by-product utilization. However, additional processes are required for net zero emission metallurgy.

Thus, it is required to optimize the production chain of ash reduced charcoal briquettes and renewable coke, mainly by the production of charcoal in industrial retorts and the usage of bio-oil from pyrolysis, and from sustainable binder production. Due to the accumulation of alkali metals in closed SAF, it is assumed that the whole carbon feedstock should be washed or leached. However, it is not required for open hearth furnaces that the volatile

matter content of the carbon feedstock is reduced to less than 3%, decreasing the necessity of the secondary heat treatment. For closed hearth furnaces, it is assumed that  $\approx 30\%$  of the charcoal should be compacted to briquettes, whereas the volatile matter content of the ash reduced charcoal and renewable coke should be reduced to less than 3%. A heat treatment temperature of  $1300\text{ }^{\circ}\text{C}$  is sufficient to reduce the volatile matter to this level, concurrently decreasing the  $\text{CO}_2$  reactivity. A selective post-treatment of the remaining high value charcoal at a ratio of 40% leached charcoal, 30% leached and heat treated charcoal and 30% of leached, briquetted and heat-treated charcoal for open hearth SAF would increase the global warming potential by  $80\text{ kg CO}_2\text{-eq. t}^{-1}\text{ FC}$  to  $\approx 300\text{ kg CO}_2\text{-eq. t}^{-1}\text{ FC}$ . Closed hearth furnaces with 50% ash removed and heat treated charcoal, and 50% renewable coke would increase the global warming potential to  $\approx 350\text{ kg CO}_2\text{-eq. t}^{-1}\text{ FC}$ . This renewable reductant blend can reduce the global warming potential by 80–87% compared to metallurgical coke if renewable power supply is available. Similar emission savings are reported for ultra-low carbon technologies in iron and steel production [43] and current technologies combined with CCS [11].

#### 4.7. Country Depending Upgrading

National regulations and access to renewable power supply will affect the global warming potential of the ash reduced charcoal, briquettes and renewable coke, especially for coal fired power supply. A comparison of different regions based on their power supply is shown in Figure 7.



**Figure 7.** Global warming potential of ash reduced charcoal, briquettes and renewable coke based on countries with different power supply including references values for the global warming potential of metallurgical coke production and usage in iron and steel industries [121,135].

The difference between countries can be reduced by a sustainable heat supply, for example, by the utilization of side streams, the combustion of biomass or other renewable sources. However, a reduced biomass potential may balance the savings in power supply. In long term, biomass potential may be the limiting variable for the fully replacement of fossil fuel-based reductants by ash reduced charcoal, briquettes or renewable coke. Hydrocarbon discharge by wastewater and volatile matter can increase the overall global warming

potential, which were neglected in the current study. In summary, the increase in global warming potential is small for renewable power supply, whereas coal fired power supply can result in a global warming potential similar to that of fossil fuel-based reductants.

The combination of ash reduced charcoal, briquettes, and renewable coke can minimize the global warming potential. While ash removal is required for all renewable reductants with high alkali and alkali–earth contents, it is assumed that only 30–50% can be compacted and heat treated to provide properties similar to that in coke bed. However, inferior mechanical properties of charcoal necessitate the compaction and briquetting to decrease dust emissions and charcoal losses. The consecutive heat treatment of charcoal briquettes made with bio-oil binder increases the mechanical and abrasion strengths of the renewable coke. Furthermore, volatile matter release by bio-oil binder can be recovered or used as a sustainable heat source, decreasing the risk of local pollution. However, the more complex recovery and production of bio-oil may hamper an on-site upgrading at the pyrolysis plant, and increasing local emissions.

## 5. Conclusions

The novelty of the paper relies on the fact that the global warming potential from ferro-alloy production can be further reduced using sustainable reductants by leached charcoal, briquettes, or renewable coke. Charcoal's properties can be improved by leaching, briquetting, and secondary heat treatment to be on a par with fossil fuel-based reductants. This LCA study showed that integration of renewable charcoal in ferro-alloy industries will lead to a global warming potential of less than 500 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC, whereas metallurgical coke global potential is ≈2300 kg CO<sub>2</sub>-eq. t<sup>-1</sup> FC.

The combination of ash reduced charcoal, charcoal briquettes and renewable coke can decrease the global warming potential by carbon reductants used in SAF by up to 80%. By-product utilization from the pyrolysis and upgrading processes in combination with renewable power supply can further decrease the global warming potential by 5–10% points, reducing the global warming potential of carbon reductants by 80–90% compared to metallurgical coke. The integration of charcoal-based reductants in metallurgical industries will require the development of the labeling and legislation framework to enhance the transition of EU countries and Norway to a sustainable metallurgy. Moreover, carbon tax may play an important role to increase the application of charcoal.

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## Abbreviations

The following abbreviations are used in this manuscript:

AR	Ash removal
BR	Briquetting
CAPEX	Capital Expenditure
CCS	Carbon capture and storage
eq.	equivalent
FC	Fixed carbon content
FeMn	Ferromanganese
GHG	Greenhouse gas
GWP	Global warming potential
LCA	Life cycle assessment
OPEX	Operating expense
SAF	Submerged arc furnace
Si	Silicon
SiMn	Silicomanganese
SHT	Secondary heat treatment

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