Review

Life Cycle Assessment of Renewable Reductants in the Ferromanganese Alloy Production: A Review

Gerrit Ralf Surup [1],*, Anna Trubetskaya [2] and Merete Tangstad [1]

[1] Department of Materials Science and Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway; merete.tangstad@ntnu.no

[2] Department of Chemical Sciences, University of Limerick, V94 T9PX Limerick, Ireland; anna.trubetskaya@ul.ie

* Correspondence: gerrit.r.surup@ntnu.no; Tel.: +47-934-73-184

Abstract: This study examined the literature on life cycle assessment on the ferromanganese alloy production route. The environmental impacts of raw material acquisition through the production of carbon reductants to the production of ferromanganese alloys were examined and compared. The transition from the current fossil fuel-based production to a more sustainable production route was reviewed. Besides the environmental impact, policy and socioeconomic impacts were considered due to evaluation course of differences in the production routes. Charcoal has the potential to substantially replace fossil fuel reductants in the upcoming decades. The environmental impact from current ferromanganese alloy production can be reduced by $\geq 20\%$ by the charcoal produced in slow pyrolysis kilns, which can be further reduced by $\geq 50\%$ for a sustainable production in high-efficient retorts. Certificated biomass can ensure a sustainable growth to avoid deforestation and acidification of the environment. Although greenhouse gas emissions from transport are low for the ferromanganese alloy production, they may increase due to the low bulk density of charcoal and the decentralized production of biomass. However, centralized charcoal retorts can provide additional by-products or biofuel and ensure better product quality for the industrial application. Further upgrading of charcoal can finally result in a CO_2 neutral ferromanganese alloy production for the renewable power supply.

Keywords: charcoal; life cycle assessment; sustainable biomass growth; mining; metallurgical coke

1. Introduction

Climate change caused by anthropogenic CO_2 emissions is considered one of the most prominent issues of the present time. About 5–10% of anthropogenic CO_2 emissions are emitted by metallurgical industries [1,2]. Most of these emissions are direct emissions generated in the smelting furnace, such as blast, electric arc, and submerged arc furnaces. The indirect emissions originate from coal dust, ore mining, metallurgical coke, and power production. Ferroalloys, such as ferromanganese (FeMn), silicomanganese (SiMn), or ferrochromium, are mainly produced in submerged arc furnaces [3], where between 40 and 70% of the required thermal energy is provided by electrical dissipation, emphasizing the importance of renewable power production [4,5]. The annual CO_2 emissions for the production of ferroalloys accumulate to ≈ 87 Mt (million tonnes) [6].

The differences in greenhouse gas (GHG) emissions generated by ferroalloy manufacturers vary in dependency on the source of energy and reductant material (biomass, coal, or metallurgical coke) [7,8]. The renewable hydropower makes Norway one of the most environmental friendly ferroalloy producer worldwide. However, the ferromanganese alloy production still relies on the use of fossil-based fuel reductants, e.g., metallurgical coke. The transition from fossil fuel-based to renewable reductants is hampered by the differences in properties, such as the low mechanical strength of renewable reductants and its high gas reactivity. In addition, the physicochemical properties of classical charcoal

can vary from batch to batch because of the undefined process conditions in charcoal kilns. However, the renewable charcoal-based reductant together with the carbon capture and storage (CCS) or carbon capture and utilization (CCU) are intended to eliminate the anthropogenic emissions in Norway by 2050 [9,10].

Life cycle assessment (LCA) is an analytical tool that supports users with the reduction of CO_2 emissions and sustainability challenges using ISO standards 14,001 and 14,040. Traditional cost and process optimization can be combined by linking environmental calculations for each process step within life cycle analysis. The important aspect of LCA is the system boundary, including processes and production routes which are considered and where the system begins and ends [11]. While a complete LCA evaluates the overall life time of a product (cradle-to-grave), cradle-to-gate approaches are commonly used to describe production of raw materials [8,11–13]. The cradle-to-gate approach includes the transition phases such as feedstock growth, pretreatment, transport, storage, and postprocessing by metallurgical smelters. However, not all aspects of sustainability can be considered within LCA [11]. Technical issues caused by the different properties and the economics of renewable reductants can play a significant role in replacing fossil fuel-based reductants [14,15]. In addition, renewable reductants may require more energy for handling and transport. For example, the milling of biomass requires more energy than that of coal samples [16], which will affect the overall energy demand in the pretreatment process. A systematic effort is needed to overcome technical and economical hurdles to realize a shift from fossil fuel-based to renewable reductants [17]. The low mechanical strength and high gas reactivity of charcoal hamper the direct replacement of fossil-based reductants in metallurgical industry [18,19]. However, charcoal is used as a major carbon source in mini blast furnaces in Brazil [17]. The low burden height of small size blast furnaces can result in a compaction pressure that makes the mechanical properties of reductants of less importance [14].
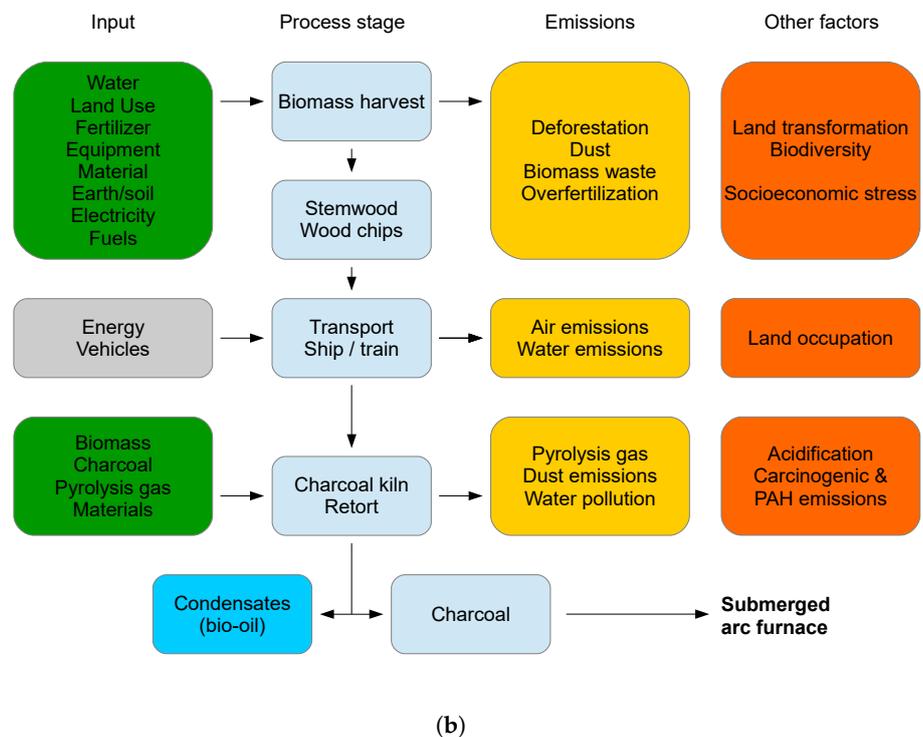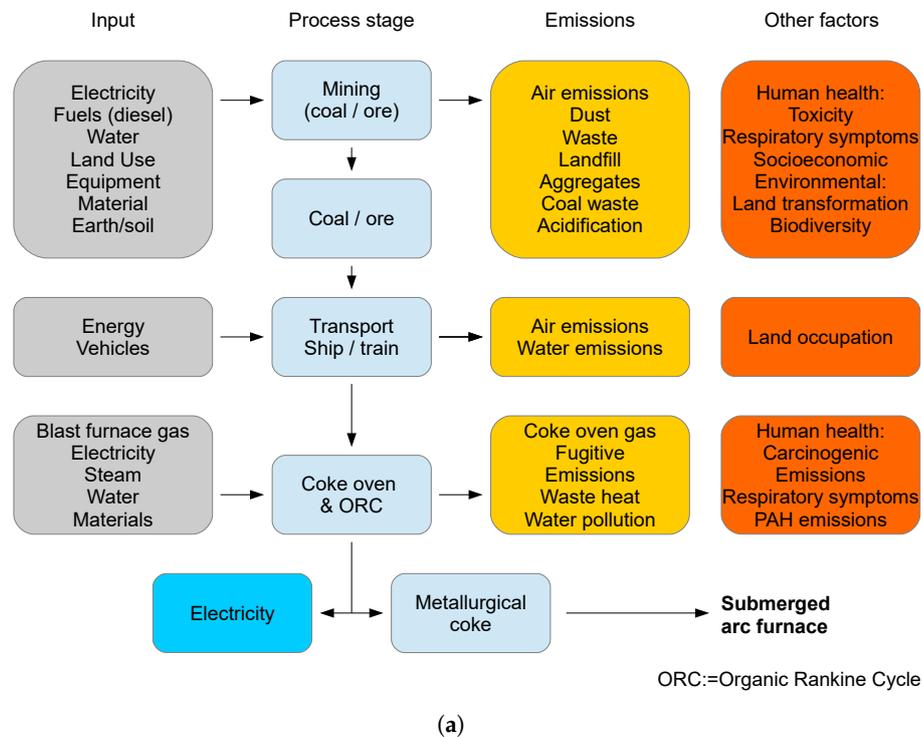
To the knowledge of authors, this review is the first attempt to examine the literature on life cycle assessment of ferromanganese alloy production route. This work aims to evaluate possible GHG emission sources and savings for the production routes of fossil fuel-based and renewable reductants used in ferromanganese alloy production. Post-treatment processes to adjust properties of charcoal to the fossil fuel-based counterparts were neglected, as the industrial process route for the replacement of metallurgical coke with renewable charcoal reductants is unknown. Three cases were reviewed in the present study: (1) the base case with the metallurgical coke as the reductant, (2) charcoal produced using classical charcoal kilns, and (3) charcoal formed by a sustainable production.

2. Ferromanganese Alloy Production

The total ferroalloy production has increased from 18 Mt in the 1990s to 36 Mt in 2008 and to 40 Mt in 2020 [7,20,21]. About one-third of the total ferroalloy production are ferromanganese alloys in a form of high-carbon ferromanganese (HC FeMn), silicomanganese, and refined ferromanganese alloys [7,8]. Ferroalloys are often used in high-quality steel production for the improvement of product strength and hardness [8,22]. The high-quality steel contains on average 3% of silicon, manganese, aluminum, or chrome as alloying elements [6]. Ferromanganese is mainly produced from manganese-ore by carbothermal reduction in submerged arc furnaces (SAF), in which metallurgical coke is used as reductant. About 59 Mt of manganese ore is estimated to be produced in 2020, with more than 50% reduced and refined in China [23].

The fossil fuel-based production route of ferromanganese alloy is shown in Figure 1. When this study was initiated, metallurgical coke has been mainly used as a reductant in closed hearth SAF to produce HC FeMn and SiMn. Metallurgical coke is produced from blends of coking coals in coke oven batteries at the temperature range 1100–1400 °C [24]. Charcoal is mainly produced from wood in kilns and medium sized retorts for the ferroalloy purposes [25,26]. The low bulk density of charcoal increases the transport and storage demand compared to fossil fuels, resulting in more complex logistics, higher emissions,

and overall process cost. The efficiency for reducing manganese-ore to pure manganese is assumed to depend on the used furnace and is similar for fossil fuel-based and renewable reductants. Thus, similar emissions from mining during manganese-ore production occur using the different process routes.

Input	Process stage	Emissions	Other factors
Electricity Fuels (diesel) Water Land Use Equipment Material Earth/soil	Mining (coal / ore) ↓ Coal / ore	Air emissions Dust Waste Landfill Aggregates Coal waste Acidification	Human health: Toxicity Respiratory symptoms Socioeconomic Environmental: Land transformation Biodiversity
Energy Vehicles	Transport Ship / train	Air emissions Water emissions	Land occupation
Blast furnace gas Electricity Steam Water Materials	Coke oven & ORC	Coke oven gas Fugitive Emissions Waste heat Water pollution	Human health: Carcinogenic Emissions Respiratory symptoms PAH emissions

Electricity ← → Metallurgical coke → **Submerged arc furnace**

ORC:=Organic Rankine Cycle

(**a**)

Input	Process stage	Emissions	Other factors
Water Land Use Fertilizer Equipment Material Earth/soil Electricity Fuels	Biomass harvest ↓ Stemwood Wood chips	Deforestation Dust Biomass waste Overfertilization	Land transformation Biodiversity Socioeconomic stress
Energy Vehicles	Transport Ship / train	Air emissions Water emissions	Land occupation
Biomass Charcoal Pyrolysis gas Materials	Charcoal kiln Retort	Pyrolysis gas Dust emissions Water pollution	Acidification Carcinogenic & PAH emissions

Condensates (bio-oil) ← → Charcoal → **Submerged arc furnace**

(**b**)

Figure 1. Production route of ferromanganese alloys using (**a**) metallurgical coke or (**b**) charcoal as reductant. Each process step can be accounted as a possible source for greenhouse gas (GHG) emissions. (**a**) Fossil fuel-based reductant. (**b**) Renewable reductant.

The system boundary is mostly set as a cradle-to-gate approach on the basis of 1 t final ferromanganese alloy. The reviewed articles concerning LCA for the ferromanganese alloy production route are summarized in Table 1. A bottom-up, layered approach should be chosen to evaluate sustainability for a charcoal use in a ferroalloy reduction process [17]. The fixed carbon yield of charcoal can be used to calculate the useable carbon content for metallurgical applications [27]. The physicochemical properties of renewable reductants are inferior to those of metallurgical coke and must be adjusted to the application in SAF. Previous studies have shown that charcoal can be post-treated to achieve properties which approach those of metallurgical coke [28,29]. However, classical charcoal and sustainably produced charcoal are considered as possible reductants for ferromanganese production, in which post-treatment processes, such as acid leaching or a secondary heat treatment, can close the gap between renewable to fossil fuel-based reductants [30,31]. In addition, renewable reductants can improve metal quality and productivity by their low ash content and ash composition [32,33].

Power generation and manufacturing of reductants are the main parameters which affect the overall GHG emissions in ferromanganese alloy production [8]. As power supply is considered CO_2 neutral in Norway, fossil fuel-based reductants are the main sources of GHG emissions. The overall emissions can be reduced by the recovery of CO off-gas and the on-site utilization [8], which is already performed by smelters in Norway. Between 50 and 85% of the total GHG emissions in ferroalloy production are generated by coal and coke [7]; 25–35% of the GHG emissions can be ascribed to the on-site air emissions [8]. GHG emissions for the production of metallurgical coke, mining, and transportation and possible reduction by renewable reductants are estimated from the steel industry [7,34]. About two-thirds of particulate matter emissions are associated with mining, handling, and preparation of the raw feedstocks, whereas only one-third are direct emissions from the SAF [35]. Direct emissions from tapping can be reduced by simple measures, such as the addition of curtains and ventilation of the tapping area [36].

Previous studies have shown that the emission factor of ferromanganese alloy production was between 1.04 and 6.0 kg CO_2 per kg FeMn, respectively, 2.8 kg CO_2 per kg SiMn and 3.4 kg CO_2 per kg FeSi [7,8,37]. The acidification potential for ferromanganese alloy production was stated to be 45 g SO_2-eq. per kg FeMn, while the photochemical ozone creation potential was determined to be 3 g C_2H_4-eq. per kg FeMn [8]. However, no complete LCA study has been found for ferromanganese alloy production.

Table 1. LCA studies reviewed to evaluate GHGe for ferromanganese production.

Process Stage	Region	Economics	Human Health	Environment	Other Factors	Source
BM, coal mining	US				land occupation and regeneration time	[38]
BM	North America, Europe		toxicity	GHG	land occupation, acidification	[39]
BM		considered	considered	considered	policy and societal impacts	[17]
BM,CC	South America			gas, water		[40]
BM,CC	IN, East Africa	considered		gas		[41]
BM (harvest,pyro)	US		TRACI	TRACI	activation of charcoal	[42]
Mining	CN			air, water	land occupation	[43]
Coal mining	PL			IPCC	human health, ecosystems and resources	[44]
Coke (Ferro)			considered	considered		[45]
BM,coke	FR	feedstock, CO_2 tax		GHG	transport (regional < 100 km)	
Coke production	CN		considered	considered	air and water emissions	[46]
Coke production	UK(steel),AU(coal)	considered	considered	GHG,gas,water		[47]
Coke production						[48]
Coke production	TR		considered	considered	by-product utilization	[49]
Mn-alloy production	AU, CN, FR, IN, ZA, US			GHG, SO_2e, C_2H_4e	LCIA, energy demand	[8]
Mn-alloy production	AU			GHG		[7]

LCIA:= Life cycle impact assessment

2.1. Mining

Mining of both manganese ore and coal contributes to the GHG emissions by ferromanganese alloy production. The emissions depend mostly on the country of origin and if surface mining or underground mining is applied. Coal mining can lead to air pollution (especially dust formation), surface and ground water pollution, solid waste land occupation, and destruction of local ecological environment [38,43,50]. This includes biodiversity, which has attracted more focus in the recent years [51]. Underground mining requires significantly more electrical energy, and thus GHG emissions from power production can become predominating. Methane emissions from the shaft system and auxiliary vents are additional air pollutants and GHG emissions for underground mining of coal [44,47]. Acidification is the main problem for water pollution at long-established mining operations. An advanced water management can improve the discharged water quality by prevention and innovative water treatment technologies. Other direct impacts of land use include landscape transformation, vegetation removal, and soil destruction [38].

Most of the energy required for surface mines is provided by diesel-powered mobile equipment [8,47], resulting in GHG emissions from combustion of the required fuel. Underground mines can also require more electricity, but produce less waste rocks than surface mines [8]. Overall, the environmental impact of power supply for surface mining is small compared to the particulate matter (PM) or dust formation, that has the largest impact on the environment ($\approx$37%), followed by global warming ($\approx$29%) or acidification ($\approx$23%) [8,43]. Other studies have shown that the largest impact on the GHG emissions from underground mining is related to the energy demand, methane emissions, and processing of wastes [44]. The effect of methane emissions for a time frame of 20 and 100 a (85 and 121 kg CO_2-eq. per kg) represents about two-third of all factors, while electricity production is the main GHG factor (representing 50%) for the timeframe of 500 years [44].

For a cleaner production, the main aim is to improve the environmental performance of mining, whereas sustainable development requires minimization of environmental costs [51,52]. In addition, the negative health effects due to mining, handling, and processing should be taken into consideration [44]. The treatment of mining water, especially acidic water or water with high contamination (heavy metals, total suspended solids, total dissolved solids and oils), will effectively decrease the environmental impact from coal and manganese ore mining [53]. The CO_2 emission factors for underground coal mining per tonne of coal were $\approx$15 kg CO_2 for electricity production, $\approx$11 kg CO_2 for coal processing, $\approx$9 kg CO_2 for haulage and hoisting coal, $\approx$7 kg CO_2 for ventilation work, and $\approx$5 kg CO_2 for exploitation [44]. However, secondary effects on the biodiversity and land recultivation after post-mining have not been considered in previous LCA studies [38,54].

2.2. Reductants

Direct GHG emissions in SAF are mainly produced from fossil fuel-based reductants, e.g., metallurgical coke. This currently used fossil fuel-based reductants can be replaced by renewable reductants, such as bio-coke and charcoal. However, the inferior mechanical and chemical properties of bio-coke and charcoal hamper the direct replacement of metallurgical coke [55]. Most likely, metallurgical coke will be partly replaced by bio-coke in the short-term [17] and by tailor-made charcoal in the long-term [15]. Other technologies, such as electrolytic manganese metal production, COREX® or FINEX® in combination with renewable reductants may also provide a CO_2 neutral production route as an alternative to the SAF [56,57].

Charcoal as an alternative reductant was mainly investigated for steel making, including pyrolysis by-product utilization [17,58]. However, renewable reductants have been also studied in ferroalloy, silicomanganese, and manganese alloy context [59–61]. The main obstacles for using charcoal in metallurgical industry are its high costs, inferior properties of charcoal, and less investigated efficiency of the tailor-made conversion process. Cost of the feedstock followed by the consecutive economics of renewable reductants and by-products are the key parameters to evaluate the performance of renewable reductants in

ferromanganese alloy production [17]. On LCA basis, production and conversion routes of fossil fuel-based reductants must be compared to renewable ones. Socioeconomic factors are especially important for the biomass and charcoal production in developing countries, in which biomass and charcoal are the main fuels for heating and cooking [62–65]. While a larger charcoal demand positively affects the economy of the producers [65], low- and middle-income countries rely on affordable and sustainable cooking fuel supply [64].

Less than 30% of the GHG emissions are related to coal mining, handling, and preparation, whereas ≈60% of GHG emissions are emitted by the metallurgical coke production [66]. The remaining emissions are generated by the combustion of diesel fuel (transport) and electricity production. A similar ratio is given for charcoal production, where ≈61% of GHG emissions are emitted during charcoal production, and the remaining 39% occurred during its usage [40]. Unsustainable biomass growth can decrease savings related to CO_2 emissions.

2.3. Fossil Fuel Reductants

The main GHG emissions from fossil fuel-based reductants beside its usage occur from mining, transport, and processing of the coal. The energy demand for surface mining, washing, and transport of coal is stated to be small [66], whereas emissions such as dust formation or acidification can have a significant impact from LCA perspective. Coal conditioning, such as coking or metallurgical coke formation, can increase the GHG emissions by the required energy demand and volatile matter release. The coke production by dry quenching can result in up to 15% less air emissions compared to the traditional wet quenching [46].

2.3.1. Coal

Similar to ore mining, coal can be obtained by surface and underground mining. For underground mining, the average power consumption per washed tonne of coal is stated to ≈25 kW h [66], resulting in ≈64 kg CO_2 emissions [67]. Power consumption for coal transportation is 1–2 kW h/(t km) [68] and is often neglected due to the low impact [66]. However, the on-site preparation of coal at the coke production can highly influence the environmental performance of the coke production process [46]. As a result, coal mining and coke production have the highest impact on the depletion of fossil fuels, whereas the energy demand for surface mining and coke formation is low [49]. Domestic long-range transport is carried out by railway, where GHG emissions are based on the power supply of the train grid system. For example, the average CO_2 emission factor for EU railway transport in 2009 was 370 g CO_2 per kW h [69], whereas average CO_2 emissions factor in China was 627 g CO_2 per kW h [67].

2.3.2. Metallurgical Coke

Metallurgical coke is produced from blends of several coal types in coke oven batteries. About two-thirds of the total production are formed in China by classical technologies from the 1990s [46,70]. Previous studies have shown that the production of metallurgical coke is one of the main GHG emission factors for pig iron production [45]. The upstream coal mining in combination with the coke production are the main sources of GHG emissions, in which CO_2 and CH_4 significantly contribute with fractions up to ≈61% and ≈32%, respectively [46].

About 2% of the energy demand of coke production is covered by electricity (16–43 kW h/t) [66,71]. Most of the energy demand for coke production (>90%) is covered by natural gas, blast furnace gas, or coke oven gas [47]. The overall emission factor for coke production was estimated to ≈0.8 kg CO_2 per kg coke [47]. Energy demand for gasification coke is about 25% larger than for metallurgical coke production due to the lower yield of reductant [66].

The emission factor is reduced to 0.5 kg CO_2 per kg coke when the metallurgical coke yield is increased by 10% or by the usage of natural gas if no coke oven gas is used [47]. One

possibility to increase the solid yield per tonne of coal is the production of bio-coke, where charcoal is added to the coal blend. Previous studies have shown that 2–15% of charcoal can be added to the coal mixture without any negatively impact on the coke properties [72–74]. A 20% replacement of fossil fuel-based coke with the renewable charcoal can result in a reduction of 15% GHG emissions [75]. As an alternative feedstock, low rank coals may be utilized in the coking process to improve economics and energy efficiency of the overall reduction process [66].

Using the coke oven gas for heating and power generation can improve the environmental impact of coke production. For example, the organic Rankine Cycle (ORC) technology for coke oven and blast furnace gas can reduce GHG emissions by $\approx$6% [47]. Coal charging and pushing can release additional emissions to the air and freshwater [46]. The increased coke production results in an increase of PAH and benzo[a]pyrene emissions [76], which have an adverse impact on local ecosystems and human health [77,78]. The post-treatment of airborne emissions and wastewater in combination with strict control policies can significantly reduce these emissions [46].

Current coke oven batteries have an emission factor of $\approx$0.4–1.27 kg CO_2-eq. per kg of coke, resulting in $\approx$2.3 kg CO_2-eq. per kg liquid steel [7,45,66]. Other fossil fuel-based reductants, such as gasification coke showed about 17% greater emission factor [66]. Overall, the release of organics and fine dust affecting human health, as well as the consumption of resources and the environmental impact by emissions have the largest impact from metallurgical coke production [49]. To minimize fossil fuel depletion and anthropogenic CO_2 emissions, alternative reducing agents can replace coal and metallurgical coke partially nowadays and fully in the future [1]. The replacement of metallurgical coke by anthracite or charcoal can decrease GHG emissions by $\approx$3.1 and 3.2 kg CO_2 per t of metal, as reported for the steel manufacturing [75].

2.4. Biomass Growth

Sustainable biomass growth is essential to reduce GHG emissions from metallurgy. Deforestation, soil degradation, as well as air and water pollution are the main challenges to avoid unsustainable charcoal production [79]. To avoid deforestation in developing countries, only wood from secondary forestry or biomass waste should be used as feedstock material in charcoal production. The charcoal production in Brazil showed the transition from primary to secondary forestry in the last decades [80,81], whereas African countries rely on the production of charcoal from primary forestry due to the high demand and low price [82,83]. Additional measures are carried out in Brazil to improve biomass growth in a frame of circular economy [84]. Biomass certification, such as the Programme for the Endorsement of Forest Certification (PEFC), Forest Stewardship Council (FSC), or European Biochar Certificate (EBC), can support the production of charcoal as a renewable reductant from sustainable source.

Between 2 and 7% of the anthropogenic CO_2 emissions are attributed to the production and usage of fuelwood and charcoal [85]. Most of the GHG emissions are caused by deforestation and combustion-related pollutants [85]. Poor plantation management, fuels for harvesting and transport can result in an emission factor of 105–120 kg CO_2 per t of charcoal [14]. Thus, the combination of GHG emissions from charcoal production by kilns in combination with deforestation can result in a net increase of global warming potential [86]. When a sustainable biomass production is ensured, the main sources of GHG emissions occur from thermochemical conversion and raw feedstock processing [11].

Non-sustainable land use and soil degradation are expected to occur mainly in regions with high poverty and uncontrolled state management, resulting in deforestation and degradation of the environment [87]. Such unsustainable biomass growth can result in an emission factor of $\approx$40 kg CO_2 per t of dry biomass, which can increase to $\approx$80 kg CO_2 per t if additional biomass treatment (e.g., chipping) is required [14]. A land usage with maximizing the biomass growth may negatively affect biodiversity and soil properties [39]. Thus, a sustainable biomass production has a larger land requirement to maintain the

biodiversity in the region [38]. The land requirements can be divided into the size of transformed land to produce the biomass and the land occupation for the time the land is used to produce the biomass. Growth rates of biomass mainly depend on biomass species, climate, irradiation, and soil and are between 10 and 20 t/(ha a) [14,38,88].

Charcoal produced from both sustainable biomass and waste by-products is beneficial to reduce GHG emissions from metallurgy and fossil fuel depletion [1]. Biodiversity is the basis of ecosystem health [89] and has attracted more attention in recent years. The LCA for wood from secondary forestry should therefore comprise the environmental, social, and economic impacts of the whole value chain [90]. Forest residues and waste streams from wood industry can support a sustainable biomass production without transforming natural forests to secondary forestry [79]. The GHG emissions from indirect land use can increase GHG emissions by factor of $\approx$13 [17].

2.5. Biomass Pretreatment

Wood is mainly used as feedstock in the classical charcoal production and will be the most reliable feedstock for metallurgy. Stemwood is the best feedstock material based on the low ash content. Previous studies have investigated the forest management, harvest, transport, and processing of biomass, as well as the biomass pyrolysis [42]. The emissions from harvest and transport of biomass are low for short distance transportation and can be neglected if these emissions are biogenic [75].

Most of the carbon losses occur by the thermochemical conversion process, where about 50% of the carbon is lost as CO_2 and volatile gases [75]. Biomass sizing is necessary to provide a particle size which is required for the pyrolysis process. The processing of biomass and charcoal can require less energy than coal, resulting in lower GHG emissions for power production. For example, milling of dry biomass requires up to 50% less energy than wet biomass [91]. On the other hand, bio-oil production can result in GHG emission factor of up to 84 kg CO_2-eq. [75].

2.6. Classical Charcoal Production

Charcoal in Africa and Asia is often produced in earthmound kilns and pits at a low efficiency (batch processes), whereas charcoal in industrialized countries is produced in continuous retorts with by-product utilization [13–15,79]. Classical charcoal production results in the emission of incomplete combusted volatile matter, such as particulate matter, volatile organic carbon, organic acids, or polycyclic aromatic hydrocarbons (PAHs) [86,92], which are considered hazardous to health and environment [93,94]. One kg of smoldering wood can pollute $\approx$700 m^3 of air [41]. Thus, the LCA of charcoal production should include different environmental impact categories, such as GHG emissions, acidification, eutrophication, as well as by-products and waste management [13,43].

At least 80% of the unburnt volatiles can be fully combusted by using an after-burner [92], resulting in a 33–40% reduction in the environmental impact of charcoal production [13]. Although CO_2 emissions from biomass and its derivatives are accounted as CO_2 neutral, toxicity, and land acidification of volatile matter can result in net GHG emissions. Based on the emissions, the selection and used technique of the carbonization process is as important as the sustainable biomass production [11]. Previous studies have shown that GHG savings from charcoal fines in metal production can be similar to lump charcoal ($\approx$1780 kg CO_2-eq. per t hot metal) [75].

Classical charcoal production can result in an emission factor of up to 9 kg CO_2 per kg of charcoal [83]. The high emission factor is based on the low charcoal yield ($w < 20\%$) and the incomplete combustion of volatiles. The release of volatile matter (e.g., tars and organic acids) can increase overall GHG emissions, making the replacement of fossil fuel-based reductants with the renewable materials redundant. For example, the emission factor for charcoal as an energy carrier can be 10 times larger than that of the direct combustion of wood due to the excess of methane and CO_2 release in the pyrolysis [41]. In worst case, production of charcoal by earthmound kilns can result in net GHG emissions [11].

The gross GHG emission factor of charcoal production was 1.6–4.7 kg CO_2-eq. per kg charcoal [13,14,86] with a 100-year global warming potential of up to 5.685 kg CO_2-eq. [95]. The lowest reported emission factor for biochar production was 0.22 kg CO_2 per kg of biochar [7]. These emissions can be accounted as CO_2 neutral if the volatiles are completely combusted in the process. However, the biomass feedstock, transport distance and plant size must be considered for the LCA and pyrolysis location [17,96]. The main factors that have to be considered in LCA for classical charcoal production are climate change, photochemical oxidant formation, and human toxicity due to the release of unburnt hydrocarbons [13]. The impact on climate change can be between 2700–4700 kg CO_2 per t of charcoal for classical charcoal production and can be reduced by 33–40% for the advanced charcoal production [13].

2.7. Sustainable Charcoal Production

Sustainable charcoal production is assumed as the currently best available case scenario. The charcoal production in industrial retorts results in a twice to three times larger solid yield compared to classical charcoal production [25,97,98], while the volatile hydrocarbons are recirculated and utilized in the process [13]. Both benefits improve the economics of the process, decrease the GHG emissions, and reduce the risk of local pollution [13]. However, these processes have high capital expenditures (capex), and thus are not used in Africa or Asia. In France, $\approx$50 kt of charcoal are produced in industrial retorts for households, barbeque or catering, and thus cannot cover the demand from metallurgical industry for high quality charcoal [75]. However, modern technologies charged with licensed biomass from secondary forestry shall avoid deforestation and ensure a defined income for the biomass producers in developing countries [85].

Industrialized charcoal production requires higher capex than classical charcoal production, and thus is economically feasible only for large scale applications [13]. Decentralized biomass growth can be combined with a centralized charcoal production to exploit by-products and use other synergistic effects [99]. The amount of by-products depends on the feedstock quality and process conditions, such as heating rate, gas residence time, and final temperature [14]. The liquid by-products from pyrolysis can be condensed and post-treated to biofuels or chemical feedstocks [100]. New technologies, such as multi-stage pyrolysis units, can decrease the energy demand for the process and enable the utilization of the by-products [101]. These by-products can replace other fossil fuel-based feedstocks and further reduce anthropogenic CO_2 emissions.

In the long-term, sustainable biomass growth and high efficient charcoal production will have a much lower area demand, stable economics for producer and consumer, and greater environmental savings than classical charcoal production. The conditioning of liquid by-products can open new markets for biofuels, chemicals, or pharmaceutics and should reduce the environmental impact to minimum [100,102]. Although GHG emissions from biomass growth and charcoal production are considered CO_2 neutral, handling and transportation of reductants will rely on fossil fuels for the next decades.

2.8. Transport

The transport of ore, coal, coke, and charcoal is another source of GHG emissions and land occupation. Previous studies have shown that the GHG emissions are negligible (<5%) for coal and coke transportation in steel industries [11,46,103]. However, charcoal has a twice lower density than coal and coke that can affect the cost and environmental impact of charcoal transportation, especially since volume limitations occur for these low bulk density [14]. The transport of whole stem wood is most favorable for the charcoal production chain, as bulk density is highest and handling and sizing can be carried out at the charcoal retort [104].

The metallurgical smelters in Norway are located on the coast and international transport is mostly operated using seaways. Thus, only biomass transport from harvest to the pyrolysis plant and charcoal transport to the harbor are expected to use road ground

transportation. Previous studies have shown that an increased transport distance from 50 to 100 km has mainly an effect on the economics, whereas the effect on total energy consumption and GHG emissions was small [66]. Loose biomass, such as forest residues or straw can be mechanically densified to improve transport efficiency [104,105]. Wood or forestry residues can also be used as a transportation biofuel to reduce GHG emissions by up to ≈45–75% [106,107].

3. Environmental Impact

Most LCA studies are carried out for the environmental impact, e.g., GHG emissions, acidification, and land occupation, whereas some also include human health issues and economics. Solid waste, eutrophitcation, and dust formation are also environmental impacts which should be considered due to the feedstock growth [43]. While the standard approach for LCA is "cradle-to-grave", the "cradle-to-gate" approach is most suitable for the metallurgical industry. This approach can be used according to ISO 14040 for silicomanganese or ferromanganese alloys [8]. The emission factors of ferroalloy production vary between 1.04 and 1.15 kg CO_2 per kg ferromanganese [37], 1.4 and 6.9 kg CO_2 per kg silicomanganese, 2.5 and 4.8 kg CO_2 per kg ferrosilicon [8,108,109], and 6.0 kg CO_2 per kg manganese [8]. The large differences in the emission factors were mostly observed due to the electric power supply by hydropower or coal.

Mining and biomass growth have the largest impact on the land consumption and local biodiversity. The direct and indirect GHG emissions from mining expands over time and are often driven by global factors which are uncontrollable by the local management or policies [110]. The renaturation of mining areas to the full recovery can take several decades to hundreds of years [38] and is concomitant with changes in the landscape, in which the change in landscape may result in environmental and social impacts [110]. Secondary forestry and other biomass growth scenarios have a large area consumption to provide sufficient biomass for renewable reductant production. The increased global biomass demand will open new markets and rise the risks of rapid changes in local landscapes and ecosystems [87] and the local impacts in the biomass production countries [52].

Industrialized countries will ensure by policies a sustainable biomass growth and charcoal production, whereas developing countries may have challenges to execute the policies at district or regional level [79]. However, markets and policies are driven by global factors and create the opportunities and constraints for the new land users [87]. To ensure the sustainable ferromanganese alloy production, global factors, as well as natural and social sciences in foreign countries have to play an increasing role in the process chain from cradle-to-gate. Fuel and power supply in developing countries will be a source of GHG emissions for mining and railway transportation. However, the energy demand for both process stages is small compared to the metallurgical coke and ferromanganese production. Replacement ratios of fossil fuels by bioenergy can significantly reduce the emission factors in each process stage [17].

4. Socioeconomic Effects

Charcoal is mainly produced in Africa and Asia by households with low income. In some countries the charcoal market accounts for more than 2% of the GDP [111], and the biomass demand is greater than the sustainable biomass growth [82]. To supply biomass for the industrial scale production, ecological and ethical criteria must be followed to avoid social tension. Local policy, structured governance, and well-funded instructions can improve the long-term success of sustainable charcoal production in these countries [79]. The charcoal production costs in Brazil are ≈200 EUR/t of charcoal, whereas production costs in Finland or Austrilia are between 270–480 EUR/t without considering the by-products as value-added compounds [17]. Bio-oil from flash pyrolysis ranges at 200–300 EUR/t [17], indicating an economical value of the liquid by-products.

Simple retorts can be constructed for ≈300 EUR [41], whereas industrial retorts such as Lambiotte retorts have an capex of 0.5–2 million EUR [112]. The high capex of industrial

retorts is not economically reasonable for local farmers in developing countries. From socioeconomic perspective, centralized charcoal production units can be provided as a development assistance to minimize emissions from charcoal production, create local jobs, ensure high conversion rates and stable charcoal properties for a long period. The production in industrial retorts would increase the available charcoal by a factor of ≈ 2 without increasing the demand in the raw feedstock.

Biomass certification such as the Programme for the Endorsement of Forest Certification (PEFC), Forest Stewardship Council (FSC), or European Biochar Certificate (EBC) can support local farmers with the licensing of sustainable wood sourcing. The sustainable biomass growth in combination with the industrial charcoal production will maximize CO_2 emission saving potential and concomitant reduce local toxic emissions formed by classical charcoal production. An adequate income will be provided to farmers for a sustainable biomass growth, and the additional charcoal yield will at least partially cover the carbon demand of ferromanganese alloy production without increasing social tension in the charcoal producing countries.

5. Discussion

Previous studies have shown that charcoal has the potential to reduce the GHG emissions for the integrated steel making route by 31–74%, respectively, up to a CO_2 neutral production by EAF [14]. The power supply in Norway makes it most likely that ferromanganese alloys can be produced CO_2 neutral by compensating direct emissions from SAFs by renewable reductants. Other ferromanganese alloy-producing countries can increase the renewable energy production in their energy mix to reduce indirect emissions from power supply [9,10]. When the properties of carbon reductants inhibit a complete replacement of fossil fuel-based reductants, CCS and CCU can be used to compensate remaining emissions. Previous studies have shown that CO_2 neutral reductants can be used for silicon and silicomanganese production [113], whereas closed hearth SAF still rely on metallurgical coke due to the low volatile matter content. Post-treatment of charcoal may improve physicochemical properties to replace fossil fuel reductants in the future [28,29,55]. The possible impacts of a classical and sustainable charcoal production on the LCA of ferromanganese alloy production are summarized in Table 2.

Mining and metallurgical coke production are the main GHG emitters in the process chain upstream of the metallurgical industry. Environmental effects such as dust formation and acidification are often not considered in the life cycle analysis, and will further improve the application of renewable reductants in ferromanganese alloy production. Land consumption for mining, biomass growth, or road construction for transportation have received more attention in recent studies, but the environmental impact is considered negligible compared to the coke production for the metallurgical processes. While renaturation of coal mining can take centuries, sustainable biomass growth can provide biodiversity in the regions. Short rotation coppice or classical forestry can provide biomass with low ash content. Transport of biomass and coal has only a minor impact on the GHG emissions which are often neglected in LCA studies.

Biomass growth and charcoal production are the key process variables to decrease GHG emissions during ferromanganese alloy reduction. Sustainable biomass growth requires large areas, and large areas of monocultures should be avoided for plant diversity. A stem wood production in Southern Norway was estimated to $18\,m^3/(ha\ a)$ of solid wood [114], approximately $8\,t/(ha\ a)$. An average growth rates of $10–15\,t/(ha\ a)$ (dry basis) can be realized in temperate climate for short rotation coppice [88,115]. However, the lower material density of short rotation coppice such as willow may limit the transport distance and storage time of this biomass [116]. Thus, GHG emissions by transport may be covered by the additional biomass growth in southern European region for selected biomass species.

Table 2. Impact of classical and sustainable charcoal production on the LCA in the ferromanganese alloy production.

Process Stage	Current Situation and Main Impacts	Changes by Classical Charcoal Production	Changes by Sustainable Charcoal Production
Ore mining	Dust emissions, water pollution (acidification), land transformation, and destruction of local ecological environment.	No changes expected by renewable reductants.	
Coal mining	Dust, CH_4 and CO_2 emissions, water pollution (acidification), fossil fuel depletion, land transformation, and destruction of local ecological environment	Reduced coal demand to a fully replacement of coal by charcoal as a renewable reductant results in a decreased fossil fuel depletion, reduced air and water pollution and avoids land transformation.	
Biomass production	Partly deforestation and soil degradation	Additional land occupation, deforestation and reduced biodiversity.	Reduced demand of additional biomass by an efficient and sustainable charcoal production, as well as consideration of socioeconomic factors.
Transport (local)	Mainly conveyor belt and railroad transport for coal, respectively truck transport for biomass and charcoal.	Increased diesel consumption by truck transport for biomass and charcoal transport expected.	
Coke production	Local emissions, resulting in air and water pollution.	Charcoal can replace up to 20% in bio-coke production, resulting in a reduced volatile matter.	Bio-cokes and tailor made charcoal may fully replace metallurgical coke in long-term.
Charcoal production	Incomplete combustion and release of volatile matter, resulting in air and water pollution, photochemical oxidant formation and human toxicity.	Increased biomass demand can result in an increased non-sustainable production and additional local emissions.	Improved conversion technologies result in an increased conversion efficiency, by-product utilization and improved charcoal quality. The greater conversion efficiency can compensate the increased land demand for sustainable biomass production.
Transport (international)	Emissions by ship and railroad transport (<5% of total emissions)	Emissions may increase due to the lower bulk density of charcoal and the volume limited transport (emissions may increase by a factor up to 2)	By-products may be utilized as fuel for transport, making long-distance transport more sustainable
Smelting (SAF)	CO_2, CO and dust emissions	CO_2 emissions from charcoal are considered CO_2 neutral, additional gas cleaning required for high volatile matter content	

About 50% of the carbon content in the raw biomass can be converted to charcoal in industrial retorts [117], resulting in a carbon yield of $\approx$2.5–5 t/(ha a). The low conversion efficiency of earthmound kilns and pits in combination with the incomplete combustion of the volatile matter makes these technologies counterproductive for the large replacements of fossil fuel-based reductants in ferromanganese alloy production. Replacing 20% of the metallurgical coke by bio-coke can reduce the GHG emissions by 10–15% for classical charcoal production, whereas the sustainable charcoal production would further reduce local emissions and environmental impact by acidification and water contamination. In addition, the sustainable charcoal production would further reduce the resource consumption by the twice to three times greater charcoal yield compared to classical charcoal production.

An ensured price range by certified biomass can convince local farmers to produce biomass sustainable. Centralized industrial retorts can create high-quality local jobs and improve the quality of charcoal concomitant to the increased charcoal yield. The current charcoal production of $\approx$55 Mt [85] would be increased to >75 Mt without the consumption of additional biomass. The high capex of industrial retorts can be covered by government subsidies or financial aid.

6. Conclusions

Renewable reductants can decrease the direct and indirect GHG emissions from ferromanganese alloy production. The sustainable charcoal production can reduce the indirect GHG emissions due to the improved feedstock growth and additional area occupation, whereas the direct emissions can be decreased by the integration of energy efficient pyrolysis retorts. GHG emissions generated due to the transportation of feedstocks and charcoal are expected to be greater than emissions from transportation of metallurgical coke and fossil fuels due to their low bulk density. The utilization of pyrolysis by-products with the concurrent production of biofuels can further decrease the emissions related to transportation. In the next few decades, the integration of renewable charcoal reductants is expected due to the increased governmental requirements and policies towards development of environmental and sustainable processes in metallurgical sector within a circular economy. Overall, the authors believe that ferromanganese alloys can be manufactured in a CO_2 neutral way using carbothermal process with the addition of charcoal that has properties striving metallurgical coke and electricity provided by renewable sources.

Abbreviations

The following abbreviations are used in this manuscript:

BM	Biomass
capex	capital expenditures
CC	Charcoal

CCS	carbon capture and storage
CCU	carbon capture and utilization
EBC	European Biochar Certificate
FeMn	ferromanganese
FSC	Forest Stewardship Council
GHG	greenhouse gas
LCA	life cycle assessment
ORC	organic Rankine Cycle
PAHs	polycyclic aromatic hydrocarbons
PEFC	Programme for the Endorsement of Forest Certification
SAF	submerged arc furnace
SiMn	silicomanganese
tonne	metric ton

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