

Use of biomass in integrated steelmaking – Status quo, future needs and comparison to other low-CO₂ steel production technologies

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Highlights:

- Biomass upgrading processes to produce fuels for iron and steelmaking are reviewed
- Insights and recommendations for biomass-based reducing agent research are suggested
- Process integration opportunities to increase economics and efficiency are proposed
- Biomass use in steelmaking is compared to other low-CO₂ steel production technologies

Nomenclature

Abbreviations

BF	Blast Furnace
Bio-SNG	Synthetic Natural Gas produced from biomass
BOF	Basic Oxygen Furnace
CCS	Carbon Capture and Storage
CRI	Coke Reactivity Index
CSR	Coke Strength after Reaction
DTF	Drop Tube Furnace
DRI	Direct Reduced Iron
EAF	Electric Arc Furnace
EU	European Union
EU ETS	European Emission Trading Scheme
GHG	Greenhouse Gas
HM	Hot Metal
IPCC	Intergovernmental Panel on Climate Change
LCA	Life Cycle Assessment
LPG	Liquefied Petroleum Gas
NG	Natural Gas
PC	Pulverized Coal
PCI	Pulverized Coal Injection
PSA	Pressure Swing Adsorption
RAFT	Raceway Adiabatic Flame Temperature
RHF	Rotary Hearth Furnace
SR	Smelting Reduction
SRP	Self-Reducing Pellet
TGA	Thermogravimetric Analysis
VM	Volatile Matter

Abstract

This paper provides a fundamental and critical review of biomass application as a reducing agent and fuel in integrated steelmaking. The basis for the review is derived from the current process and product quality requirements that also biomass-derived fuels should fulfill. The availability and characteristics of different sources of biomass are discussed and suitable pretreatment technologies for their upgrading are evaluated. The existing literature concerning the biomass application in bio-coke making, blast furnace injection, iron ore sintering and production of carbon composite agglomerates is reviewed and research gaps filled by providing insights and recommendations to the unresolved challenges. Several possibilities to integrate the production of biomass-based reducing agents with existing industrial infrastructures to lower the cost and increase the total efficiency are given. Comparison of technical challenges and CO₂ emission reduction potential between biomass-based steelmaking and other emerging technologies to produce low-CO₂ steel is conducted.

1 Introduction

Global climate change has initiated huge attempts to reduce carbon dioxide emissions. European Union (EU) has been a forerunner in combating the climate change through the policy development towards low-carbon economy [1-3]. The ambitious goal is to gradually reduce greenhouse gas emissions to 80% below 1990 levels by 2050. Milestones are 40% emission cuts by 2030 and 60% by 2040 [3].

Iron and steel industry is one of the biggest industrial carbon dioxide emitters accounting 4–7% of the global emissions [4] and a similar range in Europe [5]. A study by Pardo and Moya [5] showed that the attainable CO₂ reduction, while still maintaining the competitiveness of European steel sector, is in the range of 14–21% by the year 2030 compared to 2010. This requires both incremental development of current technologies and incorporating new, innovative technologies. The adoption of these innovative technologies is heavily dependent on the future prices of the fuels, energy and other resources as well as the carbon pricing. According to another recent study of steel industry decarbonization by Boston Consulting Group and VDEh [6], there is no feasible option to economically

decrease the CO₂ emissions by 2050 to the extent of European Commission targets. In the economic scenario, the steel sector's specific CO₂ emissions would decrease by about 15% in 2050 compared to 2010. The maximum specific CO₂ emission reduction potential achievable by European steel industry according to BCG/VDEh study is around 57% in 2050 compared to 2010 level. This would require the retrofiting of all the blast furnaces (BFs) with top-gas recycling and carbon capture and storage (CCS) [7].

The use of biomass in iron and steelmaking has been acknowledged to be one possible solution to decrease the fossil-based CO₂ emissions. However, it is not considered alongside with other drastic measures to mitigate CO₂ emissions in iron and steelmaking. The main reason might be that there is a lack of knowledge concerning the full potential of biomass-based fuels in metallurgical applications including reachable CO₂ emission reduction. There are review papers available in the scientific literature, in which the biomass-based fuel use in metallurgical industry has been investigated [8-11]. The previous review papers have dealt wide ranges of steel production routes from economic and environmental perspectives with highlights in technical issues. This review will, in contrast, concentrate on biomass application in most commonly used integrated steel production route. The process requirements will be evaluated for specified units with more structured manner. The process requirements define the limitations in physical, chemical and metallurgical properties of reducing agents, which biomass-based reducing agents should meet. This review will highlight the developments in biomass upgrading to meet the aforementioned requirements and investigates the current state-of-the-art literature of biomass-based reducing agent research. Critical issues that have been solved and those challenges that remain to be unsolved are discussed. Special emphasis is placed also to the economic and environmental feasibility of biomass use and comparison to other drastic CO₂ emission reduction technologies. Insights for the future research are given for technology and supply chain development.

2 Iron and steelmaking

2.1 Steel production routes

Iron and steelmaking technologies can be generally classified into four main routes including blast furnace/basic oxygen furnace (BF-BOF route), melting of scrap in electric arc furnace (mini mill route), direct reduction iron/electric arc furnace (DRI-EAF route), and smelting reduction/basic oxygen furnace (SR-BOF route). The integrated steel production (BF-BOF route) is considered the most important route for steel production and it represents about 70% of the world steel production. The mini-mill route consists of EAF in which recycled steel scrap is melted and then cast into semi-finished forms of slab, bloom, or billet, accounting for 25% of global steel production. DRI-EAF route mainly uses natural gas (NG) as a source of energy and reducing agent and produces approximately 5% of the world steel. The SR-BOF route is based on the combustion of coal fines for the reduction of iron ores fines without any type of agglomeration and it produces merely 0.4% of the world steel production [8].

The integrated steel plant consists of cokemaking, sintering, BF, BOF, continuous casting, hot and cold rolling. This route is mainly based on coal and coke as a source of heat and reducing agents meanwhile sinter and pellets are used as a source of iron. The majority of modern BFs are working at 70–80% sinter, 20–30% pellets and 10–20% lump iron ore [12]. In Sweden and Finland, the BFs are working with almost 100% pellets. These integrated steel plants are supported by briquetting plants to recycle fines and secondary materials [13].

The production of one ton of hot rolled coil with BF-BOF route is accompanied by about 1.8 tons of CO₂ emission as shown in Fig. 1 [14]. The ironmaking processes; sintering, cokemaking and BF contribute together ~90% of this amount. The energy usage in the BF and the accompanied CO₂ emissions are the highest in BF-BOF steelmaking route and account for 12.31 GJ/tHM and 1.22 tCO₂/tHM; respectively [15].

Fig. 1. to be inserted here.

2.2 Blast furnace process

The ironmaking BF is the central unit process in the integrated steel plants. A BF is operated according to a counter-current flow principle. The main inputs of BF consist of iron-bearing burden, coke and flux which are charged from the top while auxiliary reducing agents and hot blast are injected through tuyeres in the lower part (Fig. 2). The outputs of BF are liquid hot metal (HM), liquid slag and off-gases [16]. The oxygen from the injected hot-blast air at about 1200 °C reacts with coke and auxiliary reducing agents in the raceway to form CO and H₂ as reducing gases. A mixture of reducing gas and nitrogen moves upward through the shaft to the top, while the charge materials descend to the bottom. The reduction and melting of iron burden take place through mass and heat exchange between hot gases and descending materials. At the lower part of BF, the reduced iron simultaneously melts, drips and collects as HM at the hearth. The liquid HM and molten slag are then tapped with the temperature around 1500°C.

Fig. 2. to be inserted here.

The majority of modern BFs are working nowadays at coke rate in the range of 286–320 kg/tHM and pulverized coal injection (PCI) at 170–220 kg/tHM [18]. Other injected materials include NG and in some cases coke oven gas, converter gas and waste plastics [19]. The injection of oil to the BF has been practiced widely in the past, but nowadays it has decreased substantially due to the high price. Typical composition of solid and liquid reducing agents used in the BF are presented in Table 1. The carbon content and heating value of reducing agents should be high to ensure efficient BF operation. The bulk density of the coal and coke is usually in the range of 800–850 and 400–500 kg/m³, respectively and energy density in the range of 18–24 and 15 GJ/m³, respectively [20–21]. Typically, the reactivity of the BF coke towards CO₂ should be low, but high reactivity coke use in BF has also been suggested [22]. The volatile matter (VM) content in the coke is low. A broad range of coals with respect to VM content has

been successfully injected to the BF. High volatile coals are gasified easily in the BF raceway but have lower coke replacement ratio. High oxygen content of the coal decreases its heating value and coke replacement ratio [16]. The NG composition varies depending on the source: 90–99% CH₄, 0.3–4.5% C₂H₆, 0.1–1.2% C₃H₈, 0.1–0.8% C₄H₁₀, 0–0.3% C₅H₁₂, 0.1–1.0% CO₂, 0.5–3.0 N₂ [19]. The lower heating value of the NG is around 36 MJ/Nm³. The composition of coke oven gas after cleaning is 55–63% H₂, 22–28% CH₄, 6–8% CO, 2–4% CO₂, 2–3% C_mH_n, 0–1% O₂, 2–4% N₂, 2–3% H₂O. The calorific value of coke oven gas is usually in the range of 18.0–19.0 MJ/Nm³ [19]. The ash composition of the reducing agents is important for the BF process. Typical ash compositions of coke and pulverized coal (PC) are presented in Table 2. Coke and coal ash are acid in nature (high share of SiO₂ and Al₂O₃), which is balanced with limestone charging to the BF to reach feasible basicity for the generated BF slag.

Table 1. to be inserted here.

Table 2. to be inserted here.

The BF input materials also introduce harmful elements to the BF, which have a different kind of impacts on the process, reactions in the furnace and equipment. The most significant elements affecting BF process are zinc (Zn), lead (Pb), Potassium (K), sodium (Na), phosphorus (P) and sulfur (S) (Table 3). The selection of iron burden raw materials, sources of reducing agents and material recycling options have huge impact on the input of harmful elements to the BF. Introduction of biomass to the BF should not increase the burden of these harmful elements to a large extent.

Table 3. to be inserted here

3 Biomass properties and upgrading

3.1 Carbon neutrality of biomass

The use of fossil-based fuels in energy production, industrial processes and society are one of the main reasons for accelerated global warming and climate change. When fossil-based fuels are burned, the carbon which has been sequestered and stored in the earth's crust over thousands and millions of years is released to the atmosphere in a form of carbon dioxide. The earth's ecosystem is not able to sequester this additional carbon, which leads to a net increase of CO₂ concentration in the atmosphere. By converting the use of fossil-based fuels to the use of biomass-based fuels, the net increase of direct CO₂ emissions is avoided since the plants will capture the emitted CO₂ from the atmosphere during their growth. [35] However, the reality is not that simple, since there are various other impacts that affect the CO₂ emission accumulation and nature's possibility to sequester the emissions. The question of direct and indirect land use change and its impact to carbon neutrality of biofuels has been raised in recent years [36]. The biomass and soil carbon stocks are reduced when biomass is used for biofuel production [37].

3.2 Biomass supply potential

There are several sources of biomass for energy production purposes. World Bioenergy Association [38] has classified sources of biomass for energy in three different main sectors, namely agriculture, forestry and organic waste. According to their statistics, the global biomass supply for energy in 2012 was 5.6, 48.9, and 1.7 EJ for agriculture, forestry and organic waste, respectively. Global biomass potential is expected to increase in the following decades (Table 4). The global techno-economic biomass potential in 2035 is projected to be in a range of 134–166 EJ, which is 2.4–3.0 times higher than the use of biomass as an energy resource in energy production in 2012. Biomass from agriculture represents the biggest opportunity to increase the biomass use.

Table 4. to be inserted here

The range of biomass potential differs significantly between studies. Slade et al. [39] have provided an interesting review of the global bioenergy resources by evaluating more than 90 recent biomass availability studies. Most of the studies were conducted for the year 2050. According to their review, the biomass potential ranges from under 100 EJ/year to over 1100 EJ/year. Instead of strictly categorizing potentials into theoretical, technical and economic potentials, they indicated preconditions for achieving certain biomass potential. Estimation of market bioenergy potential found from the literature suggests that 100–200 EJ/year should be achievable [40,41]. In European scale, Bentsen and Felby [42] have reviewed the recent assessments of European biomass potential in 2020, 2030, and 2050. There is a large variation in technical biomass potential in reviewed studies. Energy crop potential varies between 4.3–6.0 EJ/year in 2030 and 3.0–56.0 EJ/year in 2050. Residue potential from agriculture range from 0.9 to 3.1 EJ/year in 2030 and from 0.6 to 5.0 in 2050. Forest biomass potential in 2050 range from 0.8 to 10.6 EJ/year.

3.3 Biomass properties

The properties of the fossil-based fuels and biomass are inherently different for different biomass sources described in the previous section. It has been highlighted that from the metallurgical process point of view, the most suitable raw materials are wood-based biomasses [10]. The main reason is that in stem wood-based materials, the ash and sulfur contents are usually low and the amount of harmful elements (such as K, Na) in stem wood ash is usually at a feasible level. The chemical composition of wood-based raw materials is presented in Table 5 and chemical composition of woody fuel ashes in Table 6. The wood-based raw materials listed in Table 5 represent different hard and soft-wood species, residues from logging operations and sawmills and by-products from pulp production (lignins). In case of herbaceous biomass such as straw and husks, the ash content may exceed 20% [43] and the number of harmful elements is above the critical limit. Kraft-lignin shows high S content, which could limit its use in metallurgical applications. Therefore, more studies are needed to minimize the sulfur content in the Kraft-lignin.

The carbon content of the wood-based raw materials is low and oxygen content high compared to coals and coke used in the metallurgical processes. VM content of the wood-based material is high. These fundamental differences in chemical composition mean that it is not efficient to utilize wood-based biomass as such in the metallurgical processes, but they need to be upgraded before their use. One of the critical factors is also the moisture content of the biomass, which may be up to 60 wt% of the freshly cut wood [44]. There is a need for efficient technologies to reduce the moisture content of the biomass and to produce products with high carbon content and low oxygen content to be used in reducing agent purposes.

Table 5. to be inserted here.

The share of ash-forming elements differs to some extent in different parts of the wood (Table 6). From the perspective of metallurgical processes, a number of alkalis and phosphorus should be as low as possible. On the other hand, the high share of Ca in the ash is favorable for the metallurgical processes. It seems that there is no abnormally high share of harmful elements (Na, K, P) in different wood species and in different parts of the wood. The exception seems to be Kraft-lignin ash, which has a high share of sodium. Further comparison of potential increase of unwanted elements (Na, K, P) input to the metallurgical processes by using woody biomasses and their chars is presented in Fig. 3. The raw material properties were taken from Tables 3-4 and 5-6. Fig. 3 shows that the amount of Na₂O, K₂O and P₂O₅ (presented as mg/kg fuel, dry basis) in woody biomasses is lower or comparable to metallurgical coke and pulverized coal. However, if it is assumed that woody biomasses are pyrolyzed for more efficient utilization in metallurgical processes (30% yield assumed), the input of Na₂O, K₂O and P₂O₅ in wood-based chars could exceed the input of these harmful compounds compared to metallurgical coke and pulverized coal.

Table 6. to be inserted here.

Fig. 3. to be inserted here.

In addition to the differences in chemical properties between fossil fuels and woody biomass fuels, biomass fuels, such as wood chips, have low bulk and energy density, they are hydrophilic and suffer from biological degradation [20]. Grinding of the raw biomass is energy intensive and requires dedicated milling set-ups. These properties have a negative influence on the energy and transportation costs, and storage arrangements.

3.4 Biomass upgrading

As summarized in the previous section, raw biomass does not necessarily satisfy the properties required for the application as reducing agent, including moisture content, heating value, fixed carbon, grindability, and, in some cases, undesired inorganic elements (e.g. Na, K, S, Cl and P). Therefore, biomass resources often require pretreatment prior to the utilization in the metallurgical processes to upgrade their properties.

3.4.1 Biomass drying

Biomass drying is an essential step in many of the thermochemical conversion processes. Usually, the moisture content should be decreased from 50–60% to 10% before pyrolysis to avoid thermal ballast and effects to the yield of charcoal. There are several drying technologies available for biomass drying. Table 7 shows the typical performance figures of the dryers, which can utilize a variety of different heat sources [44]. The most common dryers applied for biomass in bio-energy plants are direct rotary dryers or belt dryers. The maximum capacity of the rotary dryer today is 75 t/h of the dried product [52]. The selection of dryer technology is dependent on the drying medium and thermal energy source, as well

as capacity, among other things. A belt dryer is suitable when there is a low-temperature heat source available.

Table 7. to be inserted here.

3.4.2 Thermochemical conversion technologies

Thermochemical conversion technologies, as summarized in Table 8, can be categorized primarily by the reaction atmosphere, and secondarily based on the reaction temperature and a heating rate of biomass. Combustion, gasification, and fast pyrolysis are set outside of scope since their final products are heat, syngas (H_2+CO), or bio-oil. The other technologies are described in detail for their relevance to produce final products suitable as reducing agent.

Table 8. to be inserted here.

Pyrolysis is a thermal decomposition process of biomass in the absence of oxygen, producing solid residue, liquid (bio-oil and water), and gas. The solid residue, usually called biochar or charcoal, is a carbonaceous compound with a porous structure. Here, the term charcoal is used, because “biochar” often implies the application for soil amendment. Chemical, physical, and mechanical properties of charcoal depend on pyrolysis conditions and type of biomass. Lower oxygen content in char compared to original biomass leads to increase in heating value. However, inorganic elements such as Ca, Si, Mg, Al, Fe or Ti are also present in char due to non-volatile nature [53]. Yields of biomass pyrolysis products depend on the reaction conditions and raw biomass. Pyrolysis technologies can be categorized into slow pyrolysis and fast pyrolysis, which belong to two extreme conditions with respect to heating rate and particle residence time.

Slow pyrolysis is operated at a low heating rate, long residence time, large particle size and moderate temperature to maximize char yield. In practice, slow pyrolysis has been traditionally carried out in

batch operations using pit, mound, or brick kilns, which are still common in Brazil and African countries [54]. They consist of a pile of large wood logs (10-50 cm in diameter and up to a meter in length), covered by sand or bricks to avoid contact with surrounding open-air [55]. Heat for pyrolysis is supplied by that from partial combustion, and gas and bio-oil are usually emitted to the environment. The efficiency of these processes could be as low as 10% [54]. More modern technologies are operated as continuous operation including fixed bed reactors, rotary kilns and screw reactors [56,57].

Torrefaction is similar to slow pyrolysis, but operated at a lower temperature (typically at 200–300 °C). Torrefaction yields a more solid product with higher VM content than charcoal since the operating temperature is lower than the temperature at which major fraction of cellulose decomposes. Energy yields of torrefied biomass varies 70–90% in comparison with 40–50% of charcoal from pyrolysis process [58]. Fixed carbon content could vary 14–48% [59] compared with 50–95% of charcoal from pyrolysis [60]. Meanwhile, torrefied biomass has improved grindability, hydrophobicity, and energy density [58]. With respect to the property as a reducing agent, the relatively low heating value of torrefied biomass may hinder the replacement ratio of injection coals [61]. In addition, inorganic elements might become an issue if forest residue such as bark, branches, needles and stamps are utilized due to high retention rate under such conditions.

Hydrothermal carbonization, sometimes called wet torrefaction, is a thermal decomposition process with the help of saturated water-steam mixture at the temperature range of 150–250 °C. Solid product, often called HTC biomass, has similar property as torrefied biomass while the process is suitable for wet biomass such as sludge and has the function to remove water-soluble inorganic elements such as K and Cl [62,63].

To illustrate the differences in the properties of solid products from three major processes, Fig. 4 shows Van Krevelen diagram of torrefied biomass, HTC biomass, and charcoal from woody biomass. The severe reaction conditions, i.e. high temperature, of slow pyrolysis resulted in low H/C and O/C ratios. Its similar fuel property with coal means that charcoal from slow pyrolysis has a potential to replace a

higher portion of fossil coal as reducing agents without major modification of existing processes. Both torrefied and HTC biomass showed lower H/C and O/C ratios than those of original biomass, but they remained comparable to original biomass. Fuel composition indicate that thermochemical pretreatment should be carried out at relatively high temperature, leaving slow pyrolysis as most promising technology to upgrade biomass as a metallurgical reducing agent.

Fig. 4. to be inserted here.

3.4.3 Effect of operation conditions on slow pyrolysis

In slow pyrolysis, the major reaction parameter that affects to product yield and char qualities is pyrolysis temperature and original biomass, especially lignin content. Reaction parameters with minor effects include heating rate, pressure, and contact between char and volatiles (gas and vapor) via sample size and reactor configurations among others.

Mass and energy yields of charcoal are important factors for the economic feasibility of upgraded biomass. Fig. 5 shows the effects of temperature, pressure, and heating rate on charcoal yield from woody biomass. The effects of temperature and heating rate only include the data obtained at atmospheric pressure. In summary, low temperature, high pressure, and low heating rate result in high charcoal yield. Expected charcoal yield is 15–30% on the mass basis under the reaction conditions that produce charcoal with the similar property as injection coal (see next sections).

Notable variances are seen among literature data even when all three reaction conditions seem to be comparable. The remaining differences in reaction conditions include the type of biomass (for example, softwood yielded ca. 5% more charcoal due to higher lignin content [76]), particle forms and sizes (wood chip, pellets, or briquette), and reactor configurations. In fact, several literature sources have reported that difference in sample mass or particle size would affect the char yield [77,78]. It indicates that it is possible to improve charcoal yield with these remaining reaction parameters at the

constant reaction temperature. Higher charcoal yield at the constant reaction temperature, i.e. same heat input, means higher energy efficiency, and better economic performances.

Fig. 5. to be inserted here.

The reaction conditions also affect fuel properties. Some important properties are fuel composition (C, H, and O), fixed carbon content, and heating values. In general, high temperature, heating rate and pressure seem to result in high C content, fixed carbon, and heating values, with low H and O contents. However, the effects of heating rate and pressure are less pronounced than that of temperature, especially at high temperature.

Fig. 6 shows the effect of temperature on carbon content in charcoal. Carbon content increases significantly at the temperature interval of 300–500 °C to reach around 80%, and keep increasing at a higher temperature, but with less sensitivity. It has less variance among literature data than yields or other fuel properties. Although omitted from the graph, H content monotonically decreases at the reaction temperature between 300 and 1000 °C while the decrease in O content seems to reach an asymptotic value at the temperature around 600 °C. Compared to the composition of injection and coking coal currently used in BF's, the most suitable reaction temperature is above 500 °C.

Fig. 6. to be inserted here.

Reaction temperature has similar effects on fixed carbon content and higher heating values of charcoal [64,67-69,76,80,84]. Fixed carbon content increases significantly between 300 and 500 °C, at which it reaches the values comparable to those of coal. Higher heating value of charcoal is generally similar values with that of fossil coal and increases slightly with the temperature.

Reactivity of charcoal from biomass is a few orders of magnitude higher than that of coal without the effect of mass diffusion and much more sensitive to pyrolysis conditions than charcoal yield. High heating rate and low pyrolysis pressure (total pressure) produce reactive charcoal [85-87]. In addition, char reactivity reduces significantly at the high reaction temperature (at the same heating rate) and long pyrolysis time due to thermal annealing [88-89]. Char reactivity is also affected by the amount and composition of inorganic content in charcoal [90-91].

In the practical conditions in BFs (both as coke and injection materials), the effect of mass diffusion also plays significant roles in determining the apparent reaction rate. Under the influence of mass diffusion, char reactivity is affected by intrinsic reaction rate, particle size, pore size and tortuosity, and density [92-93].

3.4.4 The release and retention of critical ash-forming elements

During pyrolysis of biomass, a fraction of the inorganic matter remains in the produced charcoal while the rest releases as volatile matters. Depending on the type of biomass, major ash-forming elements can be K, Na, Ca, Mg, Mn, Fe, Al, Si, P, Cl, S. As previously discussed, the retention of some of the ash-forming elements in the produced biomass-based reducing agents may limit their use.

It has been found that during thermal conversion of biomass, several parameters may affect the release and retention of critical ash-forming elements such as temperature, atmosphere (e.g. reducing/oxidizing conditions), fuel composition, fuel particle size and structure, residence time, and heating rate [94-98]. Among these parameters, the temperature has a significant effect on the release rates of several critical elements. Reducing conditions may facilitate the release of metal elements such as K, Na, Zn and Pb [94]. Fuel composition has also a major effect on the release and retention of critical elements since presence and abundance of some element can increase or prohibit the release of the certain elements. For example, Cl content of biomass may increase the release of K by facilitating its mobility and stabilizing high-temperature gas phase alkali-containing species [99] while Si and Al can cause the retention of K by forming K-silicates and K-aluminosilicates [100]. Another important

parameter is the association of ash-forming elements in the biomass, for example, organically associated elements may increase the release of these elements in lower temperature than inorganically bound elements due to the thermal decomposition of the organic structure at lower temperatures [97,100-101]. In the following section, effects of the abovementioned parameters on the release and retention of K, P, S, and Cl during thermal conversion of biomass, especially pyrolysis, are discussed. Since it is known that the concentration of Na in various biomass is significantly lower than K and they behave similarly in the ash transformation reactions [102], only K is discussed. There is a lack of Zn and Pb release data during the pyrolysis of biomass in the literature while some data are available during the combustion of biomass [103-104].

The release behavior of P during the thermal process is strongly dependent on the fuel composition and temperature [96,105-107]. It seems that the most effective elements on P release and retention are K to produce volatile melted K-phosphate, Ca to form nonvolatile phosphoric mineral, and Si in the form of SiO₂ together with reducing gas or carbon for decreasing the required temperature for the reaction that produces volatile P [96,106-107]. The P release takes place at high temperature (> 900 °C) for bran and algae or even at higher temperatures (> 1100 °C) for sludge. Therefore, it seems that almost all P in the biomass will remain in the slow pyrolyzed charcoal at temperatures below 600 °C.

The K-release during the thermal process strongly depends on temperature, atmosphere, residence time, and fuel composition. Compared to combustion, lower and slower release of K has been observed during pyrolysis [95-96,100]. These results show that release of K from char is much slower than from the ash due to a higher diffusional resistance caused by the intact organic matrix, higher stability of K carbonate in the H₂O-free pyrolysis, and presence of K associated with functional groups [95,108]. The K release during pyrolysis of biomass is strongly depended on the chemical composition of biomass especially presence and abundance of Cl, Si, and S in the biomass. According to the literature, it is expected that more than 80 wt% of K in the original biomass will remain in the slow pyrolyzed charcoal [96,100,107-109].

The release of Cl during the pyrolysis depends on the initial Cl content of biomass so that biomass containing lower Cl shows higher Cl release [95,97] due to the availability of methyl groups from the organic constituents of biomass [97]. In general, woody biomass has a lower Cl content (<0.04 wt%) than herbaceous biomass (0.15–0.19 wt%), Therefore; it is expected that higher Cl release from woody biomass compared to herbaceous biomass during the thermal conversion [97]. There are lots of quantification data on the Cl release during slow pyrolysis of different type of biomass. Depending on the type of biomass, 30–80 wt% of Cl will remain in the slow pyrolyzed charcoal.

Since sulfur can be present in both organic and inorganic compounds, a two-step release mechanism for S was suggested in the literature [97,100-101]. In the first step, organically associated S is released at low temperatures (< 500 °C) by decomposing the organic fuel matrix during pyrolysis. At the second step, inorganically associated S is released at higher temperatures (> 800 °C) by the evaporation or dissociation of sulfates. Depending on the fuel type, 40-95% of S may be released at low temperatures (< 700 °C) during pyrolysis [96-97,100-101,107-108]. S release is strongly depended on its association with the organic or inorganic part of biomass. Therefore, biomass with a higher amount of organically associated S shows higher release rate at low temperature. Depending on the fuel type, 5–60% of S will remain in the slow pyrolyzed charcoal [96-97,100-101,107-108].

4 Biomass use in metallurgical unit processes

4.1 Biomass use in metallurgical coke production

Coke is unavoidable raw material in the BF due to its many roles in the process [16,110-111]. Metallurgical coke is produced from coking coals by carbonization at high temperature (1000–1100 °C) in the absence of air [110]. There are strict quality requirements set for coke that also bio-coke with part of the coking coal replaced with some sort of biomass should fulfill. Coke property measurements in the industry include strength (stability, hardness), CRI and CSR tests. Advanced coke hot strength [112-113] and coke reactivity test in simulated BF shaft conditions [114] have been developed. According to Alvarez et al. [115], good quality coke has a CRI under 30 and CSR above 55. According to

Babich et al. [19], CRI and CSR requirements in European BF's are 23 and 65, respectively. However, there is also another line of literature suggesting that high reactivity coke could enhance the BF efficiency [22].

The current literature concerning the addition of biomass into the coal blend is quite broad even though the research field as such is young. The serious research efforts to apply biomass to coking coal blends have been started in the 21st century [e.g. 116]. In bio-coke research, several biomass-based materials have been evaluated as suitable additives to the coal blend. These materials include different raw biomasses and wastes [117-118], woody components; xylan, cellulose and lignin [119], torrefied biomass [118,120], pyrolysis products; charcoal, tar and bio-oil [118-119,121] and solid residues from pulping process [122-123].

During the coking process, coking coal goes through several chemical and physical changes including softening, contraction and resolidification, which are a prerequisite for the formation of strong coke matrix [21]. Thermoplastic properties of the coals are important for the quality of the final coke [124]. The addition of any type of biomass-based raw material seems to have a degrading impact on the fluidity of the coal blend [e.g. 119,121,125]. The development of the blend fluidity is affected by the physical and chemical properties of the coal and biomass, and the evolving volatiles during the carbonization [125]. Thermal decomposition of raw biomasses occurs at low temperatures and the majority of the volatiles are released before the plastic stage of the coking coal occurs (around 400–500 °C) [119]. This means that there is very little amount of volatiles and residue biomass that will act as active substances interacting with the coal and affecting the fluidity development. Charcoal produced at 415 °C behaves differently during the plastic stage. Only 9.7 wt% of the charcoal has decomposed before the plastic stage of the coal starts. According to Diez et al. [119] charcoal has two roles during the coal plastic stage: it acts as an inert material that does not soften and melt and as an active material that binds the components from the plasticized coal. Devolatilization stages of coal and charcoal overlap partially. Charcoal emits oxygen-rich volatiles during carbonization that can block the fluidity by establishing cross-linked O–C bonds [125].

Castro Diaz et al. [117] have found that biomass type affects the development of the fluidity. In their study, 5 wt% sugar beet could be added without impairment of viscoelastic properties of the coal, whereas the addition of 2 wt% of pine wood and *Mischanthus* had a negative effect on fluidity development. They suggest that there must be gas-solid and/or liquid-solid interactions during the plastic stage. Zhu et al. [126] used an innovative approach to firstly produce carbon-rich products from biomass wastes by a degradative solvent extraction method and applying these products (soluble and deposit) in cokemaking. Addition of soluble and deposit had minor effect to softening temperature, but resolidification temperature increased significantly. Plastic range enhanced up to 9 °C and logarithmic maximum fluidity fell within the optimum window.

The particle size of the charcoal seems to have an effect to coal fluidity. Finer particle size reduces the fluidity more than coarser particles [116]. This may be caused by the fact that with smaller particle size charcoal, the surface in contact with metaplast is greater resulting in increased interaction between the matrix and the inert components [125]. Briquetting of the biomass before the coking process with or without plasticity increasing materials such as coal tar improve the Gieseler fluidity to some extent, but still, the feasible share of biomass in the coal blend is low, around 2 wt% [127-128].

The addition of biomass-based materials to coal blend typically increase the reactivity of the produced coke and decrease the strength. These effects depend mainly on the biomass type, size of the biomass particles, addition amount and applied pre-treatment procedures [121,129,130]. Reactivity of the bio-cokes have been evaluated with CRI [e.g. 121,131], with isothermal and nonisothermal thermogravimetric methods in CO₂ atmosphere [130,132] and in BF shaft gas simulating atmosphere including also other gas components beside CO₂ [123,133]. All of these studies confirm that reactivity of the coke increases when biomass is introduced to the coal blend. By comparing the reactivity results of different studies, it seems that bio-coke with charcoal addition is more reactive compared to bio-cokes with raw biomass or bio-briquette addition. This is probably due to the fact that with charcoal, there is more reactive biomass structure available in coke. In case of raw biomass, the yield of parental

biomass is low in coke structure. As mentioned earlier, the slight increase in CRI might not be detrimental for the bio-coke quality. However, too high reactivity leads also too low strength after reaction, which impairs the BF process performance. The reactivity of the bio-coke can be controlled e.g. by the larger particle size of the biomass [134].

The cold strength of the bio-cokes does not weaken dramatically compared to metallurgical coke [123,135] when the biomass or charcoal addition is in the range of 5–10 wt%. The smaller particle size is more beneficial for cold strength [134]. More deleterious effect is seen in bio-coke strength development after reaction with gasifying gas. Only a small share of biomass or thermally treated biomass (0–5 wt%) can be added to coal blend while maintaining the coke quality. More basic ash composition of the bio-coke increases the reactivity of the cokes towards CO_2 , thus resulting in lower CSR. The larger particle size of charcoal is beneficial for maintaining the CSR of the cokes [130,134] since the reactivity increasing effect of high calcium content in charcoal is less harmful when contained in larger pockets instead of being finely dispersed [121].

Addition of biomass to the coal blend results in a lower bulk density of the blend and lower coke yield. Majority of the raw biomass devolatilizes during the carbonization. In fact, it seems that the coke yield decreases more than calculated values would assume, which confirms the synergetic effects of biomass and coal during the co-pyrolysis [135]. The bulk density decrease is in the range of 1.3–1.4% when the sawdust addition in the blend is 3–5% [127].

It has also been reported that metallurgical coke could be replaced by lumpy charcoal up to 20% [136]. Charging of 20 kg/tHM of lumpy charcoal could reduce the coke consumption by 30 kg/tHM due to decreasing of the temperature of the thermal reserve zone [137]. Although the nut coke in the iron ore burden layers could be completely replaced by small size charcoal, the low density and low strength of charcoal could lead to a segregation and dust generation at the BF top shaft.

To summarize, the use of biomass in cokemaking could provide feasible option to decrease the use of fossil coking coal and CO_2 emissions in moderate fashion. In addition, the use of highly reactive bio-

coke in BF might increase the efficiency of the furnace. The future research topics in bio-coke research should aim to enhance the biomass addition to coal blend without deteriorating the coke quality. This can be achieved through the careful selection of coals for blending with biomass, appropriate preparation and treatment of raw biomass, optimization of particle size, proper design and addition scenario, testing different types of biomasses from agriculture and pulp residues, addition of fluidity increasing substances and stamping bio-coke production.

4.2 Biomass injection to the blast furnace

Auxiliary injected reducing agents are used in the BF to decrease the coke rate. Recently, stable BF operation with PCI rates of around 200 kg/tHM and coke rate below 300 kg/tHM has been successfully maintained [18]. In contrast with other fuels which could be injected through the tuyeres (NG, oil, plastics), PC has the minimum negative impact on the raceway adiabatic flame temperature (RAFT) and therefore, it has higher injection rate compared to other fuels [16].

Tuyeres injection provides a flexible option for biomass utilization in the large modern BF. In this case, the mechanical strength is not required as in case of top charging materials; however, the chemical and physical properties of biomass are very important factors affecting the RAFT, coal burnout in the raceway, and distribution and composition of reducing gases. Possibility to inject biomass-based reducing agents to the BF via tuyeres has been investigated with several methods. Combustion behavior has been investigated with drop tube furnaces (DTFs), injection rigs and thermogravimetric analysis (TGA) [138-141]. Reactivity of residual carbon exiting the raceway has been evaluated with thermogravimetric methods [26]. Detailed numerical tuyere-raceway modeling has been applied in combustion behavior evaluation [142]. Six phase 3-D BF model based on the multi-fluid theory has been developed to compare charcoal and PC injections [143]. Investigations of biomass injection to BF process have been further evaluated with BF models, based on the mass and heat balances [61,144-145].

The experimental research conducted with TGA, DTF and injection rigs gives quite uniform results concerning the burning behavior of biomass-based reducing agents in BF simulating conditions. The combustion rate of charcoal in TGA experiments in air is considerably higher compared to PC [140]. The peak temperature, at which maximum reactivity occurs, was 29–79 degrees (°C) lower compared to reference coals. The burnout of raw biomass, torrefied biomass, and pyrolyzed biomass in DTF experiment was compared to mid-volatile and high-volatile coals [138]. The oxygen input to the reactor via an oxidizing agent (air) was maintained at the same rate, which explains why raw biomass and torrefied biomass had higher burnout ratios compared to charcoal. In real BF process, the O/C ratio is controlled according to fuel analysis, and it should also be taken into account in laboratory-scale studies. A recent study comparing the burning behavior of charcoal and PC with similar VM contents revealed that charcoals are more reactive compared to fossil coals [139]. The reactivity towards CO₂ was also higher with biomass chars, mainly because of the higher surface area and isotropic disordered physical properties of the materials. This is also beneficial to BF process to prevent soot formation. Lab-scale injection rig results suggest that with rising injection rate, charcoal conversion behavior is better [144]. It is explained that the deficit of oxygen at high injection rate may be compensated by oxygen in charcoal pores promoting its further gasification. Mathieson et al. [141] compared the burnouts of hardwoods with VM content of 4.2, 9.6, and 18.8% to high volatile (36.2%) PCI coal in pilot-scale injection rig. The comparison was made on an O/C ratio of 2 on a total fuel basis, which represents around 140–150 kg/tHM injection in BF. This gives more reliable results than many of the burnout experiments found from the literature. From Fig. 7 it can be seen that all the hardwood charcoals had comparable or higher burnouts compared to high-volatile PCI coal.

Fig. 7. to be inserted here.

A static heat and mass balance BF models have been applied to investigate the substitution rate of biomass products (charcoal, torrefied material, bio-oil and wood pellets) for PCI [e.g. 61,146-147]. Wang et al. [61] found that 166.7 kg/tHM charcoal is able to fully replace 155 kg/tHM PCI. The torrefied material and wood pellets could partially replace PCI by 22.80% and 20% respectively. Charcoal demonstrated the highest potential for PCI substitution with an almost insignificant change in top gas temperature. The oxygen enrichment of hot blast had to be increased from 23.9 to 24.6%. On the other hand, the top gas temperature was found to be decreased by the injection of torrefied material and wood pellets. Based on these results, the maximum injection rate of torrefied material and wood pellets was found to be 134.2 kg/tHM and 98.9 kg/tHM; respectively at the minimum allowed top gas temperature. Moreover, if the O₂ content in the blast is limited to 25.4%, the maximum amount of torrefied biomass and wood pellets has to be decreased to 60.7 kg/tHM and 59.1 kg/tHM; respectively. The high level of VM in the torrefied biomass and wood pellets reduce the RAFT and hence more O₂ enrichment in the hot blast is required. It has to be highlighted that the chemical composition and heating value of the biomass injectants have an impact on the coke replacement ratio and required oxygen enrichment.

The reactive structure of charcoal improves the combustion process in raceway to become better or comparable to that of coal [141,144]. It was reported that the maximum injection rate of charcoal will be in the range of 200–220 kg/tHM which is able to reduce the net CO₂ emissions by 40% [148]. Besides the environmental benefits, the injection of charcoal will result in the lower amount of slag and higher production rate due to the lower sulfur and ash content and higher content of CaO compared to PCI [149]. The results of mathematical modelling indicated an increase in the BF productivity by about 25% when 100 kg/tHM of charcoal is injected with 150 kg/tHM PC with an optimization of the oxygen enrichment [150]. The slag rate in BF simulations was almost unchanged between coal and charcoal cases even though the charcoal ash content was considerably lower compared to coal [143,150]. Babich et al. [144] reported a slag rate reduction from around 18 to 31% depending on the charcoal and iron

burden properties. Also, the required oxygen enrichment in the study of Babich et al. [144] was lower with charcoals compared to PC. Fig. 8 shows the comparison of reducing agent consumption in different biomass injection cases conducted with mathematical BF models. Despite the fact that underlying assumptions in the different studies are different (BF model, properties of the raw materials, etc.), it can be seen that the coke replacement ratio is heavily dependent on the type of biomass. Charcoal is superior compared to other biomass-based injectants. Depending on the carbon content, it outperforms also the PC. Wood pellets, torrefied biomass, and bio-oil may be used in BF injection, but the coke replacement ratio is low.

Fig. 8. to be inserted here.

The effect of biomass injection on the gaseous reduction behavior of iron ore pellets in the BF shaft was evaluated in laboratory conditions by Kemppainen et al. [153] with simulated biomass injection scenarios obtained with BF model described in [61]. Partial replacement of PCI by torrefied biomass showed slightly higher iron oxide reduction rate and minor effects on iron ore pellet reduction behavior compared to the PCI scenario indicating minor impact on the BF process.

The practical limitations of using biomass injection could be summarized in four main points [148]:

(i) lower calorific value of biomass products compared to coal require efficient pre-treatment and pyrolysis, (ii) difficulties in biomass injection at high rate due to the porous nature and the low density which require an optimization for the injection process, (iii) wider particle size distribution of biomass after grinding which requires an efficient sieving to get the proper particle size for injection and (iv) higher alkalis in some biomass products which should be controlled and minimized before utilization to avoid its negative impact on the refractory materials.

To summarize, the future studies should include the BF raceway area and whole BF effects investigations, but also the pre-treatment steps. There is a lack of knowledge of the grinding behavior

of coal, biofuels and their blends in vertical roller mills, which are used in many steel plants for pulverization of fossil coal. There might be a need for additional sieving of larger biomass particles exiting vertical roller mill [148]. Flow properties of fine powder mixtures in pneumatic conveying pipes of PC operation should be evaluated. Preliminary investigations have shown that coal-charcoal blends up to 50 wt% share of charcoal with similar particle size distributions could be viable [154]. There are also further needs to evaluate the impact of varying particle size distributions on flow properties and burning behavior. It might be possible to have larger biomass particle size due to its higher burning efficiency. Combining the burning models of injected materials with total BF mass and energy balance models should be further developed. The existing inner state BF models have used high combustion efficiencies for both PC and charcoal [143,150], which could be further refined.

4.3 Biomass use in iron ore sintering

The sintering process is an important pre-treatment step in the production of iron, where fine particles of iron ores and in some plants, also secondary iron oxide wastes like filter dust and mill scales are agglomerated by combustion of coke breeze and other carbonaceous materials. The iron ore fines and other additives are agglomerated into large, hard, and porous pieces to become suitable for the high pressure and facilitate the gas flow in the BF. Iron ore sinters are considered as multi-phase materials, with a heterogeneous microstructure. The main mineral phases in the sinter structure are iron oxides (~ 40–70 vol.%), ferrites (mostly silico-ferrite of calcium and aluminium ~20–50 vol.%), glassy phases (up to ~10 vol.%) and dicalcium silicates (up to ~10 vol.%) [155].

Coke breeze, which constitutes around 3–5 % of the total mass of the sinter mix [156], has been replaced with different sources of biomass fuels up to 100%. Untreated biomasses, mildly carbonized charcoals and charcoals produced at high temperature have been studied as candidates for coke breeze replacement. The main fundamental difference between coke breeze and biofuels affecting the sintering process and sinter quality is the higher reactivity of biomass-based fuels [157]. Biomass-based

fuels have a higher surface area [156] and higher porosity [158], which increases its reactivity compared to coke breeze.

Use of high reactivity biofuels, such as charcoal, in sintering, increase the vertical sintering speed [159], decrease the peak temperature of sintering and shortens the time of holding high temperature [160]. Changes in the sintering process caused by the use of biofuels affect the product quality. It is reported that the sinter yield, measured with the percentage of sinter above 5 mm after the screening, decreases substantially when straw char is used instead of coke breeze resulting in lower productivity [160]. However, Lovel et al. [158] reported an increase in balanced productivity when charcoal is used instead of coke. Use of biofuels decreases the bulk density of the sinter. Sinter produced with charcoals was 12–19% lighter compared to sinter made with black coal char [158]. The porous structure of bio-sinter demonstrated higher reduction rate compared to that of conventional sinter [161].

Since physical properties of the biofuel affect the reactivity to a large extent, research has been conducted to control the reactivity by increasing the particle size of the biofuel or by compacting the biomass before sinter mix preparation. Kawaguchi and Hara [162] have shown that sinter yield and tumble index can be improved when the coarse particle size of highly carbonized biomass is used. Gan et al. [157] report an increase in peak temperature and the holding time at high temperature when a coarser biofuel particle size was used. A coarser particle size reduces the reaction area and makes the O₂ diffusion into internal pores of charcoal particles more difficult. This results in better sinter quality, close to that of coke breeze used as a fuel [163]. Lowering of the biofuel reactivity can also be done by producing agglomerates from coal and charred straw. The produced structure suppresses the separate combustion and results in good quality sinter [160]. Porosity and specific surface area can be decreased with preformation, which leads to combustion characteristics of the coke-biomass agglomerates becoming closer to that of coke breeze. The maximum weight loss rate and the maximum heat release values of agglomerates are closer to that of coke breeze, which means that heat release could be maintained similar even though part of the coke breeze is replaced with coke-biomass agglomerates in

sintering. Preformation with temperature and/or agglomeration of raw biomass before carbonization is a viable methodology to increase the share of renewable fuel in sinter production [164-165].

Biofuels have both positive and negative effects on the sintering process and sinter quality. It seems that pyrolyzed biomass can be added in higher shares to the sinter mix compared to raw biomasses [162]. Up to 25% replacement of coke breeze with pyrolyzed biomass without significant impact on product quality has been reported in [161]. Gan et al [157] reported that the replacement ratio of biomass for coke breeze should not exceed 40% in order to get sufficient mineralization of sinter product. The increased proportion of biofuel addition decreases the yield and productivity. The reviewed literature is consistent that the combustion rate of the biofuel is a factor that should be controlled to reach better sintering performance and sinter quality.

4.4 Biomass use in carbon composite agglomerates

Several iron and carbon-bearing by-products are generated in integrated steel plants. Some of the steel plants recycle these materials back to BF via sintering process while another possibility is to have a briquetting plant which can efficiently convert such secondary materials into cold bonded briquettes. Cement is usually used as a binder to give the proper mechanical strength of top charged briquettes into the BF [166]. Recently, a great attention has been paid to investigate the influence of iron ore-carbon composite on the BF operation [167-171].

The studies carried out on iron ore-carbon composite have demonstrated higher reduction rate and lower coke consumption compared to the ordinary burden materials [172-173]. It was demonstrated that the starting temperature of carbon solution-loss reaction decreased as the degree of contact between iron ore and carbonaceous material increased [174]. The iron ore carbon composites are considered as a type of micro-reactors [167]. These composites are highly reactive due to the close contact between Fe_2O_3 and carbon particles which enhances the reduction process [168]. The CO_2 generated from the reduction of iron oxide (e.g. $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$) and CO generated from the Boudouard reaction can be exchanged quickly in vacancies inside such type of micro-reactors. The trials

in the large BF using cement-bonded self-reducing pellets (SRP) have been demonstrated with a maximum rate of 54 kg SRP/tHM [175].

The top charged bio-agglomerates should be able to achieve the minimum requirements of mechanical strength for BF; otherwise, they will deteriorate the process efficiency [176]. In addition, any change in the BF input materials will directly affect the mechanism of mass and heat transfer, temperature profile and gas distribution inside the BF from raceway zone to the upper shaft. The main drawback of iron ore-biomass composites is the low crushing strength [171]. The weak strength of iron ore-biomass composite compared to iron ore-coal composite is attributed to the absence of coal thermal plasticity. The thermal plasticity of coal provides the proper mechanical strength of iron ore-coal composites. In addition, the volatiles of biomass are often escaped at relatively low temperature before starting the reduction of iron oxides. Besides the efficient utilization of by-products and waste fines, potentials have been conducted on the partial substitution of cement with biomass lignin from pulp and paper industry [177]. The replacement of cement with biomass lignin up to 25% demonstrated good mechanical strength and enhanced the reducibility of the briquettes. The replacement of cement with lignin increased the total carbon content while the sulfur content did not significantly change in the briquettes.

Special design for iron ore-biomass composite is still required to enhance the utilization of biomass in the reduction of iron oxides in CCAs. Ahmed et al. [169] have discussed the future development needs in self-reducing CCA research, concerning the agglomerates for BF use as well as for other reduction processes. In relation to BF, there is a need for further studies conducted in a BF gas composition and temperature. Majority of the research has been related to the investigation of self-reducing properties of CCAs rather than reduction with ascending BF gas. There is still a lack of knowledge in regards to the requirement of physical strength of the CCA's in BF conditions and preceding handling stages, even though some research has been conducted [171]. Further studies are needed to realize the effect of contact between the carbonaceous material and iron ore in CCA. The effect of CCA to the reduction and

swelling of the iron ore charge (pellet) has been recently studied [178]. Preliminary investigations show that iron ore pellets showed a change in reduction behavior leading to higher reduction degree and a lower tendency for shrinking when having contact with CCA compared to ones without contact. This should be further investigated. Ahmed et al. [169] highlight also the importance of the thermal conductivity of the CCAs and further studies of softening and melting behavior of CCAs.

5 Environmental aspects and economics of biomass use in iron and steelmaking

5.1 CO₂ emission reduction with biofuels

Several biomass-based fuels have shown potential to replace fossil-based reducing agents in integrated steelmaking. Solid biofuels (torrefied biomass, charcoal) could be used to replace coke breeze in sintering, coking coal in cokemaking, coke breeze/coal in agglomerates and PC in BF injection. Gaseous fuels (Bio-H₂, Bio-SNG) could be injected to the BF or used in reheating furnaces (Bio-SNG) to replace liquefied petroleum gas (LPG) [179]. The biofuel production technologies differ e.g. in relation to product mass and energy yields, and energy consumption. Life cycle CO₂ emissions of four biomass-based fuels are shown in Fig. 9. It seems that there is no remarkable difference in the carbon footprint of biomass-based fuels. There is variance depending on the reference, which is mainly related to the used assumptions of the studies. The carbon footprint of torrefied biomass range from 4.0 to 17.5 gCO₂/MJ [180-184], charcoal from 3.4 to 59.8 gCO₂/MJ [181,185-187], Bio-SNG from 10.2 to 14.0 gCO₂/MJ [181,188-189] and Bio-hydrogen from 3.4 to 17.1 gCO₂/MJ [190-193]. The only study that took also land use change into account is Roberts et al. [186]. It can be seen that it has a strong impact on life cycle CO₂ emissions (Fig. 9). Life cycle CO₂ emissions of biomass-based fuels are still below the life cycle CO₂ emissions of NG and coal, which are 75.0 and 115.0 gCO₂/MJ, respectively [194].

Fig. 9. to be inserted here.

Life cycle CO₂ emissions from BF-BOF-based steelmaking are 2.2–2.5 tCO₂/t steel [185,195]. Fick et al. [196] found that by using charcoal in sintering, lump charcoal top charging, torrefied biomass or charcoal fines injection, greenhouse gas (GHG) emissions could be reduced by 6.7, 14.4, 14.7, and 14.5% respectively. The CO₂ reduction was calculated for one ton of HM and the by-product credits from additional electricity were included. Biogenic emissions and possible land use change impacts were not taken into account. Norgate and Langberg [136] estimated the life cycle impacts with two cases where charcoal replaces 20 and 100% of coke and coal in BF. The base case life cycle emissions with fossil-based reducing agents were 2.17 tCO₂/t steel. With 20% charcoal substitution rate, the reduction in CO₂ emissions was 0.33 tCO₂/t without by-product credits and 1.17 tCO₂/t steel with by-product credits. In case of 100% charcoal substitution rate, the reduction was 1.32 tCO₂/t without by-product credits and 4.46 tCO₂/t with by-product credits. By-product credits were received from bio-oil that would replace diesel fuel and use of pyrolysis by-products in electricity production to replace electricity produced from black coal. Land use change impacts were not accounted. Norgate et al. [185] refined their LCA study with more moderate credits for charcoal production by-products and realistic charcoal substitution rates. The attainable CO₂ emission reduction in integrated steelmaking route was 31–57% without by-product credits and 42–74% with by-product credits. Land use change was not incorporated.

Even though the life cycle assessment studies conducted in iron and steelmaking give valuable information about the magnitude of CO₂ emission reduction in iron and steel industry, there is a need for more in-depth analysis of life cycle impacts. One of the most important issues is to take into account the land use change, which may have a significant impact on the emissions [36]. Sustainability of the raw materials used in the production of biomass-based reducing agents such as charcoal should be guaranteed. The sustainability of the charcoal production depends also on the used technologies. There is a need for life cycle assessment case studies utilizing industrial data from charcoal production with efficient technologies and realistic indication of available by-products.

5.2 Economics of biomass-based fuels

The main issue related to use of biomass in iron and steel industry seems to be related to the economics [8-10]. Production of reducing agents from biomass-based sources differs considerably from that of fossil-based raw materials. The biomass raw materials are low in energy density, they are usually collected from a broad area and require a significant amount of energy in their upgrading stages. Labor work, transportation costs, and energy costs become substantial. The production cost of torrefied biomass range from 113 to 183 €/t [181,197-199]. Charcoal production costs are 233–513 €/t, mainly depending on the applied raw materials [181,200-201]. Bio-SNG production cost range from 722 to 974 €/t [181,189,202] and bio-hydrogen from 890 to 2002 €/t [203-204]. In mass basis, the production cost of solid fuels is lower. However, in energy basis, the difference is not that remarkable [10].

In recent analysis, the abatement cost curve was calculated for four different fuel substitution scenarios where the achieved CO₂ emission reduction and mitigation cost are compared to the base case with fossil fuels used as reducing agents (Fig. 10) [179]. The most economical measure would be the use of Bio-SNG in rolling mills instead of LPG. Actually, this shows a negative mitigation cost with applied fuel prices. The CO₂ emission mitigation potential is quite low, 1.8% compared to the base case. The second most beneficial measure would be the injection of charcoal in to the BF. With 150 kg/tHM injection rate, the achieved CO₂ emission reduction at plant scale would be 24.6%. The mitigation cost would be 92.3 €/tCO₂ with average and 50.9 €/tCO₂ with minimum charcoal prices found from the literature. Use of charcoal (5 wt%) in coke making reduces the emissions by further 3.3% at plant scale, the mitigation cost being 99.6 and 52.0 €/tCO₂ with average and minimum charcoal prices, respectively. The fourth option considered is the injection of charcoal (150 kg/tHM) and also Bio-H₂ (13 kg/tHM) to the BF. These measures would sum up to around 43% reduction at plant scale. It should be stated that any additional investment costs related to fuel switch were not considered. The abatement cost depends greatly on the used prices for fuels. In this analysis, coking coal price was 89.5 €/t, PC price 62.6 €/t and LPG price 980 €/t. 20 €/t additional cost was added to cover transportation.

Fig. 10. to be inserted here.

6 Process integration opportunities

6.1 Integration of biomass upgrading to existing infrastructures

Today, there are no existing biomass-based reducing agent supply chains for iron and steel industry, except in Brazilian steel industry. Also, markets for large-scale densified biomasses suitable for reducing agent purposes are almost non-existent, at least in Europe [205]. As mentioned in section 3.4, biomass properties have to be enhanced by drying and thermal processing. This requires efficient supply chains and extensive amount of energy for drying and thermal treatment. With a proper integration of the biomass upgrading process to the existing infrastructures (e.g. steel plants, sawmills), material and energy efficiency and the further CO₂ reduction could be facilitated. In the following paragraphs, suggestions are made to develop biomass-based reducing agent supply chains and increase the sustainability of biomass upgrading for the steel industry.

In integrated steel plants there is a huge amount of excess heat available in different forms and temperatures [206]. Several technologies have been proposed for the heat recovery and utilization of excess heat from steel plants [207]. A lot of attention has been paid to high-temperature slag waste heat recovery and utilization, however, industrial applications are still missing [208]. In recent publications, the coupling of biomass upgrading and waste heat from steel plants have been proposed. Hot steel industry slags have been studied as heat carriers for biomass gasification and fast pyrolysis to produce bio-oil [209-210]. Integration of biomass upgrading processes in the integrated steel plant infrastructure to produce reducing agents for the BF has been evaluated in some publications. The most recent and thorough investigations have been conducted at Åbo Akademi in Finland [145,211]. In these studies, the heat from BF hot stoves flue gases and combustion of BF top gas is utilized in biomass drying. The dried biomass is then subjected to torrefaction, slow pyrolysis or fast pyrolysis and the produced char is utilized as a BF injectant [145]. Slow pyrolysis outperformed the two other options regarding the

economic performance. Availability of waste heat sources for biomass drying and upgrading could enhance the economics of biomass conversion, however, logistic costs might increase due to the requirement of a large amount of low bulk density raw biomass in one location.

Another alternative could be the integration of biomass upgrading technologies with the sawmills. By-products from sawmills are generally used as raw materials in pulp production, particleboard and fiberboard production, pellet production and in energy production [212]. However, at the moment, there are market disturbances at least in Finland due to the incentives given to forest chip production for energy. This has led to the accumulation of bark and sawdust in sawmill sites. Long transportation distances and an oversupply of sawmill by-products has launched the development of new by-product utilization opportunities [213-214]. Arpiainen and Wilén [213] compared the economic performance of different sawmill–torrefaction plant integration scenarios to the economic performance of three stand-alone plants with different production capacities and origin of raw material supply. The economic comparison shows that scale of the production and the location of the plant have the largest influence on the production costs in case of stand-alone plants. Increase in the plant capacity brings down the production cost. The production of torrefied pellets in North America and shipment to Europe is economically more favorable because of the lower cost of forest fuel. Integration of torrefaction with sawmills lowers the production costs compared to stand-alone plants in the Nordic region. Sawmill industry is strong in countries with abundant forest resources (e.g. Nordic countries) and could provide an efficient option to produce reducing agents from sawmill by-products for iron and steel industry. The supply chain is already existing and logistic costs could be lowered with more energy dense biomass products.

Integration of biomass upgrading technology with biomass-based combined heat and power (CHP) plant has already been demonstrated in Joensuu, in Eastern Finland where fast pyrolysis process has been integrated with existing biomass CHP plant. The plant capacity is 50 000 tons of bio-oil annually from forest residues and sawdust [215]. Biomasses are dried with steam and district heat water from

CHP plant and heat from the bio-oil condensation. The bed sand from the fluidized bed boiler is used as a heat carrier in fast pyrolysis process. The fast pyrolysis process generates pyrolysis vapors, non-condensable gases, water, and char. Char and sand are separated from the pyrolysis vapors in cyclones. The pyrolysis vapors are rapidly cooled and condensed. Char and non-condensable gases are combusted in the fluidized bed boiler. One option could be the separation of char from the bed sand to be utilized in iron and steel production. The amount of char produced in Joensuu fast pyrolysis plant is around 12 000 tons annually. Kohl et al. [216] have presented the similar type of integration scheme where CHP plant and fast pyrolysis are combined. They performed energetic and environmental analysis for different pyrolysis product uses. According to their assessment, integration would bring benefits, also with a scenario where char is separated from the bed sand. Sermyagina et al. [217] received similar results with torrefaction integration to CHP plant. There are several heat sources available for biomass drying and torrefaction that would promote heat integration. The biomass supply chains have also been established.

Integration of biomass upgrading technologies to pulp mills has been proposed in several publications. There are several waste heat sources available for biomass drying and the biomass supply chain logistics with required infrastructure have already been established. Available heat sources include hot water in a temperature range from 65 to 90 °C, low-pressure steam and flue gases from lime kiln [218]. The proposed biomass upgrading technologies include gasification, pyrolysis and torrefaction options. Gasification of black liquor and further treatment into methanol, DME or CH₄ has been described by Naqvi et al. [219-220]. Utilization of wood residues from wood handling as a raw material for torrefaction, pyrolysis, and gasification has been proposed by Hamaguchi et al. [221]. Pyrolysis of extracted Kraft-lignin could also be viable option to produce reducing agents for BF ironmaking [222].

Finnish company St1 has commercialized a wood-based ethanol production technology (Cellunolix®), based on thermal pre-treatment, hydrolysis, fermentation, and distillation. The first plant has been built in Kajaani, Finland, producing 10 million liters of ethanol annually when in full production [223]. The by-

products from wood-based ethanol production include lignin, which can be further upgraded to charcoal. Compared to Kraft-lignin, the quality of the lignin from hydrolysis is better with a lower share of unwanted elements such as sulfur and sodium. At the moment, wood-based ethanol production is a small-scale operation, but in the future, the availability of by-product lignin could be substantially increased.

In order to get a holistic view, there is a need to develop system models for analyzing the environmental and economic feasibility of different biomass upgrading scenarios. The system studies should take into account the availability of biomass in different regions and current uses of biomass. Supply chain models including transportation and biomass upgrading stages would provide further knowledge for the development of feasible concepts for biomass-based reducing agents. Up to date, there are no such studies conducted.

6.2 Upgrading of process gases to increase economics and environmental friendliness

Typically, the process gases from the steel industry and from slow pyrolysis are burned to produce heat for the needs of processes in the steel plant or to maintain the pyrolysis process. The upgrading of steel plant process gases and pyrolysis vapors from slow pyrolysis of biomass into more valuable fuels and chemicals have gained increasing attention in recent years [224-225]. This could increase the economics of biomass use in the future, but also helps to bind the formed CO₂ in a form of fuels and chemicals.

The process gases formed in the steel production contain mainly hydrogen and carbon monoxide but also high concentrations of nitrogen, and can be compared to producer gas obtained by gasification of biomass or coal [226-227]. The gases have rather high energy content and can be utilized as such for energy production, heat or combined heat and electricity. The gases contain also building blocks that can be used in synthesis processes, namely in fermentation with micro-organisms or in catalytic conversion. The pyrolytic conversion of biomass produces a gas mixture with a composition close to the one of producer gas. The amount of gas produced in a pyrolytic process and especially in a slow pyrolysis

process is rather low compared with the gasification process. Furthermore, the gas obtained by a pyrolytic process contains more impurities, especially tars due to the low temperatures used [225].

Fermentation is an alternative to the utilization of metal catalysis in the conversion of synthesis gas. Organisms using fermentative pathways are divided into autotrophic plants and organisms that use C1 compounds, such as CO, CO₂, and methanol as carbon source and hydrogen as their energy source and unicarbonotrophs that use C1 compounds alone for both these purposes. These microorganisms also utilize metals such as cobalt and nickel (which are contained in their enzymes) for the conversion of C1 compounds into value-added products such as ethanol and higher alcohols. According to Mohammadi et al. [228] different *Clostridium* species, especially *C. Ljungdahlii* can convert synthesis gas into ethanol and acetate in a fermentative process. The syngas fermentation is still under development, mainly due to the low solubility of the gas in the fermentation broth. The most flexible way to convert synthesis gas into new products is to use catalytic conversion methods. A number of products can be produced by catalytically mediated reactions, including alcohols, linear hydrocarbons, olefins, diesel and gasoline fractions. There are principally two main routes for the conversion of syngas, one route starts by direct conversion of the syngas while the other main route includes an initial production of methanol from syngas.

The different gas-upgrading methods set demands on the gas compositions according to the products produced in the process (Table 9). The requirements are mostly regarding the H₂ to CO ratio and the purity of the gas. A Fischer-Tropsch reaction producing linear hydrocarbons and waxes as main products needs a H₂ to CO ratio close to 2 while the same reaction producing olefins demands a H₂ to CO ratio < 1. If the synthesis gas is upgraded in fermentation processes, there is no demand for the H₂ to CO ratio even if some impurities in the gas can inhibit the fermentation process. In order to be used in catalytic upgrading processes the synthesis gas has to be pressurized, the pressure used is highly dependent on the catalytic route used and ranges from 1–2 Bar (fermentation) over 10–40 Bar (Fischer-Tropsch synthesis) up to 50–300 Bar (mixed alcohol synthesis). Normally the reactions are run at

elevated temperatures from 20 to 425 °C. All the catalytic conversions are highly exothermic; the removal of the heat is critical in order to run the processes at isothermal conditions. The catalytic processes have the highest demands concerning the purity of the gas, most compounds are allowed at low ppb levels in order to avoid de-activation of the catalysts by adsorption of compounds onto the surface of the catalyst (catalyst poisoning) (Table 9). The most critical compounds regarding deactivation are tars (coke formation on the catalyst), sulfur-containing compounds (binds covalently to the active metals) and alkali metals. Particles present in the gas can also form deposits.

Table 9. to be inserted here.

In integrated steel production plant (BF-BOF), three gas streams can be used as input for synfuel production, i.e. blast furnace gas (BFG), coke oven gas (COG) and basic oxygen furnace gas (BOFG). The future technology; top gas recycling blast furnace (TGR-BF), in which top gas is recycled back to the BF, generates a significantly different gas composition compared to a conventional BF. The composition of the produced process gases in integrated steel plant would be suitable for syngas and further e.g. transportation fuel production (Table 10).

Table 10. to be inserted here.

In previous literature, it has been proposed that coke oven gas or syngas with a composition similar to coke oven gas could be converted to alcohols and organic acids in fermentation processes [231], to olefins over Co catalysts [232] and to chemicals like methanol, traffic fuels in different catalytic processes as described by Dry [233] and Leckel [234]. Most likely, the different steel plant gases have to be mixed in order to obtain $H_2:CO$ ratios suitable for the catalytic processes. The high concentration of nitrogen in BFG is a major challenge for efficient gas utilization synthesis routes, increasing the

equipment size and energy costs. Uribe-Soto et al. [224] have proposed that pressure swing adsorption (PSA) or chemical absorption could be used to separate CO from BFG for further use as synfuel building block.

Slow pyrolysis vapor upgrading into more valuable fuels has been studied with experimental and modeling studies. Recently, a slow pyrolysis scheme with two reactors has been developed, where the formation of tars is reduced and pyrolysis gas properties enhanced with second high-temperature reactor with catalysts [225,235-236]. High-quality charcoal for metallurgical purposes and slow pyrolysis gases with a high concentration of CO and H₂ were successfully produced. After CO₂ removal, slow pyrolysis gas could be used e.g. as reducing agent. Shabangu et al. [200] have evaluated the techno-economics of biomass slow pyrolysis concept producing charcoal and methanol. Larsson et al. [237] have proposed a concept that utilizes slow pyrolysis gases in Bio-SNG production. These examples show that there might opportunities to improve the economics of charcoal production.

7 Comparison of biomass use in integrated steelmaking to other low-CO₂ steel production technologies

EU policies and governmental interventions will play a vital role in the development of deeper decarbonization in the future [238]. This has been also highlighted by the European Steel Association, Eurofer in a report “A steel roadmap for a low carbon Europe in 2050” [239]. They raise several points that should be fulfilled to ensure competitive steel production in Europe. These include, among other things, coherent and predictable policy framework and adequate support for the development and implementation of new drastic CO₂ emission mitigation technologies. There is a critique towards the European Emission Trading Scheme (EU ETS) to achieve cost-efficient emission reductions in the EU steel industry after 2020. It is evident that breakthrough technologies and associated programmes run all over the world play a vital role in the future iron and steelmaking. The development of new iron and steelmaking technologies within these programmes are in different development stages. The common

feature of the technologies is that their wider adoption to industrial use is unlikely to occur before 2030 (Table 11).

Besides these breakthrough programmes, there are several other innovative technologies under development, which could lead to decarbonization of steel industry. In Sweden SSAB, LKAB and Vattenfall have formed a joint venture to facilitate fossil-free steel production by utilizing hydrogen as reducing agent [240]. In HYBRIT project, hydrogen is produced by electrolysis and the electricity is produced from renewable sources. In Germany, ArcelorMittal is involved in Steelanol project in which the steel plant process gases are transformed into ethanol or other chemicals by using microbial fermentation [241]. ThyssenKrupp has similar on-going development project, Carbon2Chem, in which steel plant gases are upgraded into chemicals and fuels [242].

Table 11. to be inserted here.

Even though the biomass use in blast furnace ironmaking could considerably decrease the amount of fossil-based CO₂ emissions, it has not been thoroughly compared to other drastic CO₂ emission reduction technologies. Potential of biomass use has been investigated in the context of ULCOS, in Australian breakthrough programme and in international and national development projects [61,179,185,247-249].

Comparison between different iron and steel production technologies to reduce CO₂ emissions is presented in Table 12. Technologies examined in ULCOS project; TGR-BF with CCS and HIsarna with CCS, could reduce the CO₂ emissions by 60–80% compared to current technologies. If CCS is not applied, the reduction potential is around 20% [250]. The CO₂ emission reduction achieved with NG-based shaft furnace DRI-EAF steel production route could be 40–60% compared to BF-BOF route, depending on the plant location [251]. Use of hydrogen as a reducing agent in fluidized bed or shaft furnace DRI-EAF production could facilitate 50–90% CO₂ emission reduction compared to BF-BOF route [252]. Production

of iron with iron ore electrolysis accompanied with steel production in EAF could result in CO₂ emissions of 180 kg/tCS, which is over 90% reduction compared to BF-BOF route [253].

CO₂ emission reduction achieved by using biomass in iron and steel industry could be substantial as already highlighted in section 5.1. In BF-BOF plant site, the reduction may be up to 57% compared to the use of fossil-based reducing agents [185]. Compared to other drastic technologies, biomass provides an alternative with comparable CO₂ emission reduction potential without the use of expensive and uncertain CCS, regarding the geological storage of captured CO₂. In contrast to many other technologies, biomass use could be facilitated with modest investment costs. The shift from current steel production technologies to alternative technologies (lock-in solutions), such as TGR-BF or Hlsarna technologies with CCS, require major investments resulting in high CAPEX costs. With the use of biomass, only limited modifications to current production facilities are anticipated, which means that the pressure of increased costs is in OPEX costs. The shift towards the biomass use could be gradual, i.e. the share of biomass in reducing agent portfolio could be increased according to desired fossil CO₂ emission reduction, economics, and CO₂ emission allowance limits.

Local biomass resources are not available in every region of the world where there is steel production. This will certainly have an impact on the adoption of biomass-based reducing agent technologies. Competition from raw materials may also hinder the possibilities. Use of by-products from bioeconomy industries may be one feasible option as already mentioned in section 6.1. Currently, there is no quantitative evaluation that would compare the availability of different biomass sources for iron and steelmaking globally taking into account the competition. Suopajärvi and Fabritius [254] and Wang et al. [61] have evaluated the availability of wood-based biomass in Finland and Sweden, but both of these countries are minor players in global steel production. Piketty et al. [255] have evaluated the land availability in Brazil to produce biomass for charcoal production for steelmaking. All of these studies highlight that there could be biomass sources available for iron and steel industry use. The common concern in increasing the use of biomass in energy applications is the sustainability of the biomass. The

international trade of biomass and biomass-based energy carriers is small compared to international coal markets. However, it is possible that densified biomass products, such as torrefied pellets, are more readily available in global markets in the future [20,256].

Table 12. to be inserted here.

8 Concluding remarks

Biomass use in integrated steelmaking could be one of the future solutions to decrease the environmental impact of steelmaking. This review has gone through the recent relevant literature concerning the biomass properties, availability and biomass upgrading processes to produce reducing agents with feasible properties for metallurgical use. The current status of the biomass-based reducing agent research including unit process development, CO₂ emission reduction and techno-economic assessment, and process integration opportunities have been reviewed. Comparison to other low-CO₂ steel production technologies has been conducted. The findings and future development needs are summarized in the following points:

- 1) Acquisition of biomass-based raw materials should be made carefully from sustainable sources, preferably from by-products and wastes. At the same time, the selection of biomass-based raw materials should be done to avoid the increase of unwanted element (e.g. S, Na, K, P) input to the metallurgical processes.
- 2) Raw biomass has high moisture content, low carbon content and a high share of oxygen and volatiles. Biomass upgrading is needed to decrease the O/C ratio, thus resulting in biofuels with chemical properties comparable to fossil-based coal. According to reviewed pyrolysis literature, temperatures above 500 °C should be used to reach the carbon content and heating value of the coal and coke used in the BF. Some of the unwanted elements in parental biomass can be partly

removed in thermal processing. The selection of the biomass materials should be carefully conducted to avoid increase of alkali and P inputs.

3) Current literature suggests that the feasible share of biomass-based material in coal blend to produce bio-coke is in the range of 2–10 wt%, providing a moderate option to decrease the fossil CO₂ emissions. The main weakness of the biomass in the coke is the absence of active solid-solid interaction during the coking coal plastic stage due to the physical properties of biomass. Devolatilization of biomass during the plastic stage changes also the gas-solid and/or liquid-solid interactions. The reactivity of the bio-coke could be decreased and subsequent strength after reaction better maintained by carefully choosing the particle size and source of the biomass. It seems that pyrolyzed biomass can be added in larger portions compared to raw biomass. Further increase in the share of biomass in coal blend could be facilitated with coal blend stamping procedure.

4) Injection of biomass, especially charcoal, to the BF represents the most drastic technology to reduce the fossil-based CO₂ emissions. According to modeling results, torrefied biomass could also be injected to the BF, but that would cause significant changes to the current BF operation principles. It has been proposed that PCI could be entirely replaced by high carbon content charcoal, thus contributing up to 44% of the reducing agent rate in the BF. Charcoal produced from wood has higher burnout ratio in the raceway compared to coal, and it has lower ash and S contents, which are beneficial for its use. Further investigations are needed especially in the grinding, drying, and sieving of the charcoal together with PC, its transportation properties in PCI pneumatic conveying lines and behavior in storage silos. Coupling of total mass and energy balance BF models with more detailed injection burning models should be further developed. Ultimately there is a need for pilot and industrial trials in large-scale BF.

5) Biomass use in sintering is a viable option to replace around 40% of the coke breeze. It has been discovered that pyrolyzed biomass is a better option than using raw biomass. The main drawbacks

of using biofuels (raw biomass or pyrolyzed biomass) in sintering are their higher reactivity, which affects the sintering process and product sinter itself. The further development areas should focus on the methods to reduce the reactivity of the biofuel by controlling the particle size of the biofuel, and by preforming the biofuels before sintering. Porosity and specific surface area are reduced, which is beneficial for reactivity reduction.

- 6) Carbon composite agglomerates are gaining more attention as an alternative to recycle in-plant residues back to the BF, but also to bring renewable carbon to the BF process. Cold-bonded briquetting of in-plant residues is used in some steel plants in the world replacing the sintering process. The use of CCAs in BF can increase the efficiency of the whole furnace due to the decrease in starting temperature of carbon solution-loss reaction by close contact between iron ore and carbonaceous material. The main limitation is the strength of the CCAs, especially with biomass addition, which might not be adequate to the large-scale BF. Further development areas should cover at least agglomeration technology development, and reduction studies in BF shaft simulating conditions.
- 7) Process integration, which extends from one industrial sector to cover several industries in a manner of industrial symbiosis could bring new opportunities for biomass upgrading and also to the utilization of by-product gases both from biomass upgrading and from steel production. Utilization of waste heat and biomass by-products from different industrial sectors and exploitation of already available biomass supply chains could increase the competitiveness of biomass-based reducing agents in comparison to fossil-based reducing agents. Upgrading of slow pyrolysis and steel plant gases into high-value chemicals or fuels should be also investigated further. There is a need for large-scale system analysis studies in which different biomass-based reducing agent integration options are compared, but also to investigate the possibility for by-product upgrading.
- 8) Biomass use in integrated steelmaking has the potential to decrease the fossil CO₂ emissions above 50% compared to the current BF-BOF route. In comparison to other drastic CO₂ emission reduction

technologies proposed for future steelmaking, biomass use provides potential option without the use of carbon capture and storage. Majority of the drastic technologies developed today will penetrate the markets after several decades. Biomass use in iron and steelmaking may not be a feasible option in every region of the world due to the biomass availability and competition issues, but should be considered as an alternative to start the decarbonization of steel industry already today.

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Figure captions

Fig. 1. CO₂ emissions in an integrated steel mill (BF-BOF route), redrawn from [14].

Fig. 2. Inputs and outputs of iron blast furnace [17-18].

Fig. 3. Total content of K₂O, Na₂O and P₂O₅ in pulverized coal, metallurgical coke, raw woody biomasses and woody biomass chars (mg/kg fuel, dry basis).

Fig. 4. Van Krevelen diagram of thermochemical conversion products from woody biomass. Adopted from [58] with additional data of raw biomass (non-filled symbols), torrefied biomass (red symbols), HTC biomass (blue symbols), and charcoal (black symbols) [58,59,63-75].

Fig. 5. Charcoal yields from literature data. (a) Effect of temperature; (b) Effect of pressure; (c) Effect of heating rate; (d) Effect of temperature on energy yield. [64-70,76,79-83].

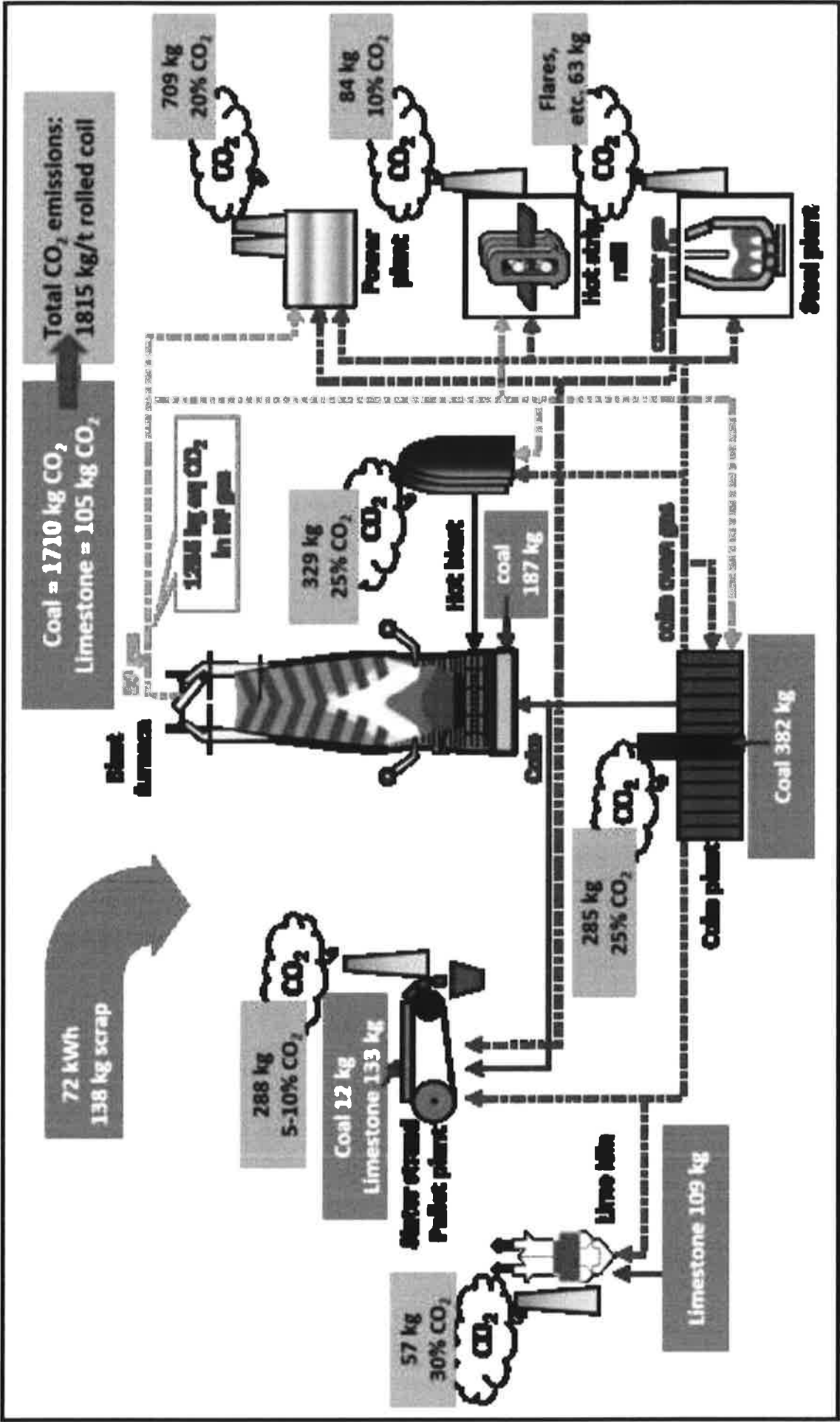
Fig. 6. Carbon content of woody biomass-derived charcoal from literature data [64,67-70,76,79,80,84].

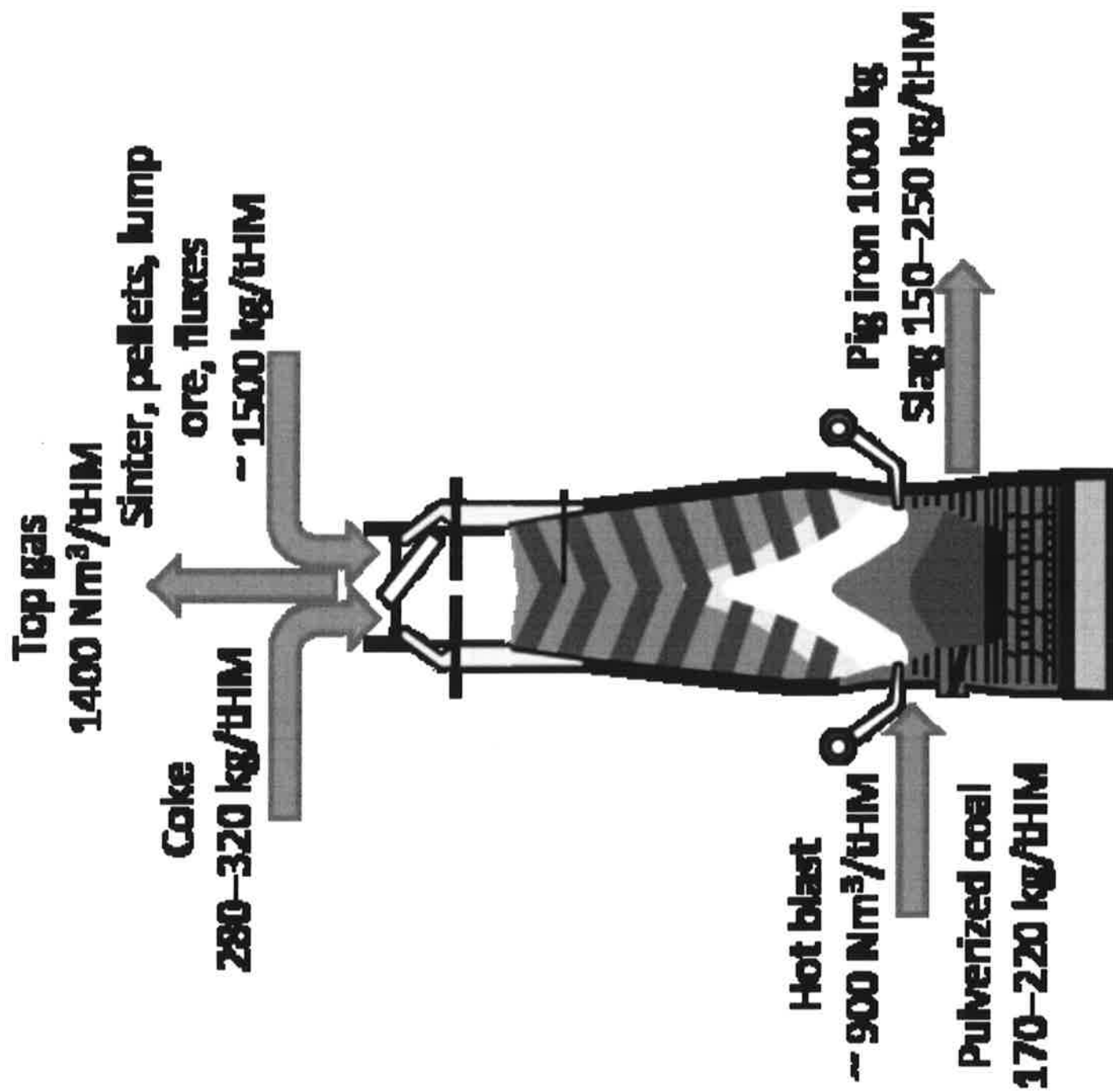
Fig. 7. Comparison of PCI and charcoal burnouts in O/C ratio = 2 (redrawn from [141]).

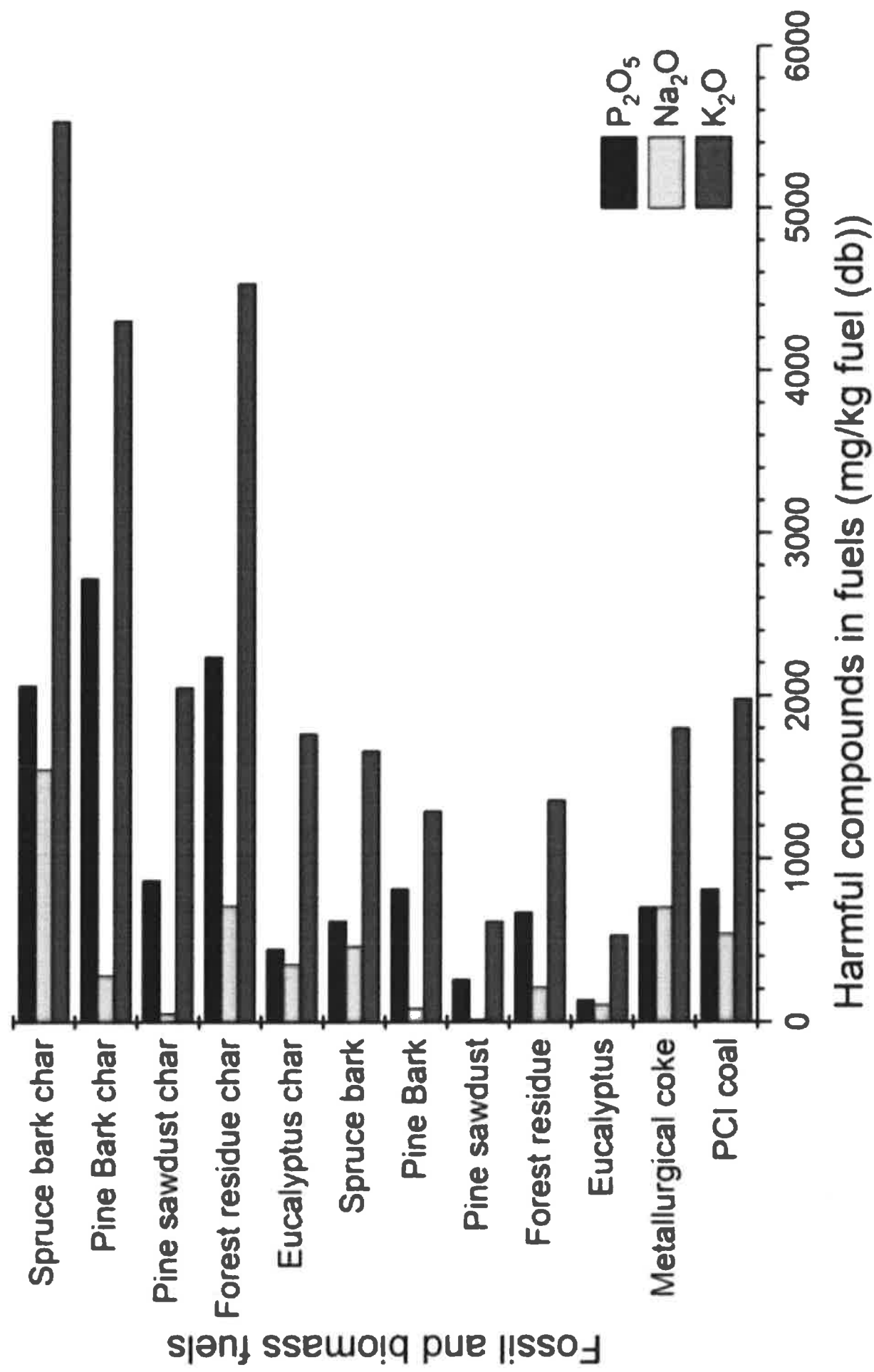
Fig. 8. Reducing agent rates in different injection cases [17,61,144,147,149,151-152].

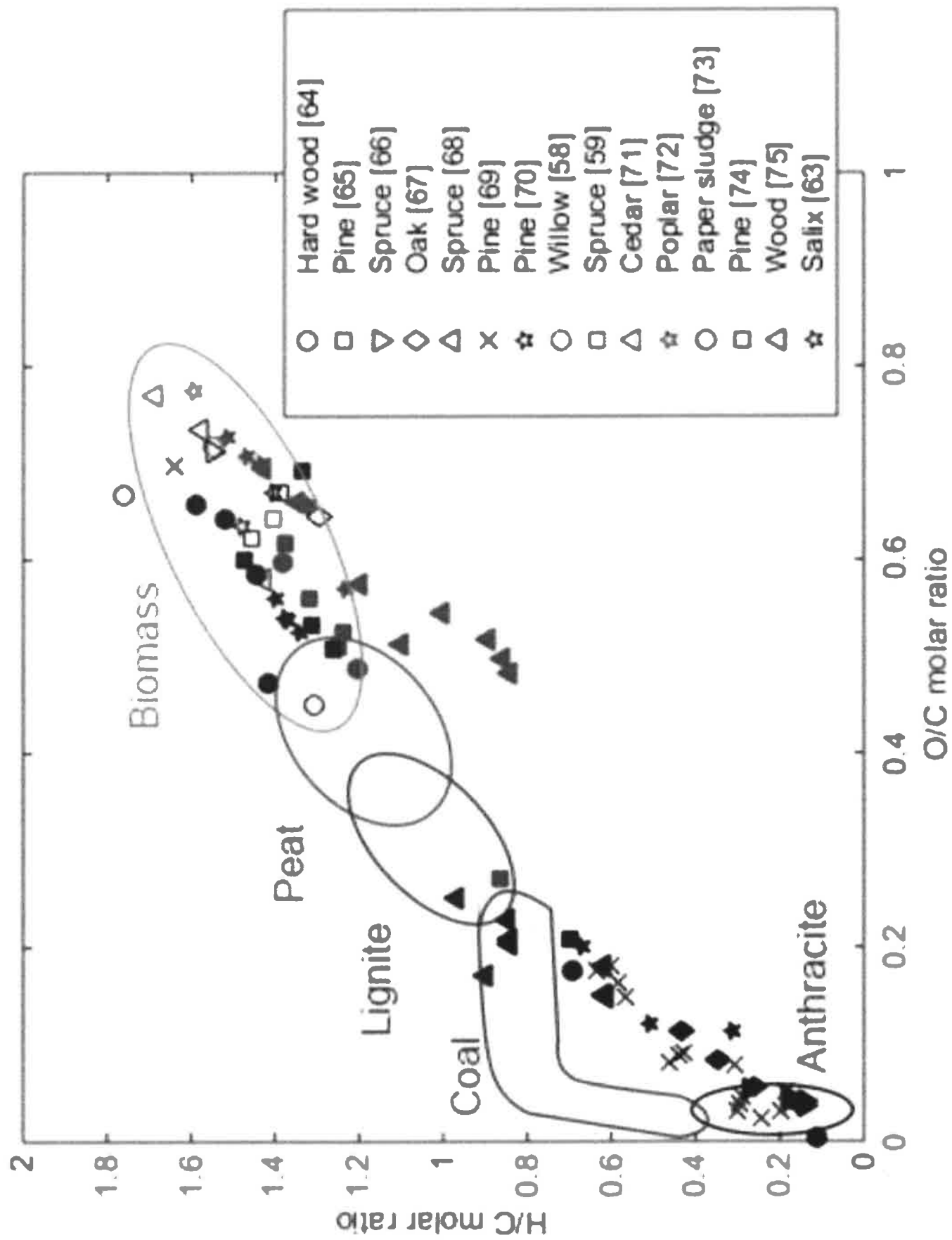
Fig. 9. Life cycle CO₂ emissions of biomass-based fuels, NG, and coal [180-194].

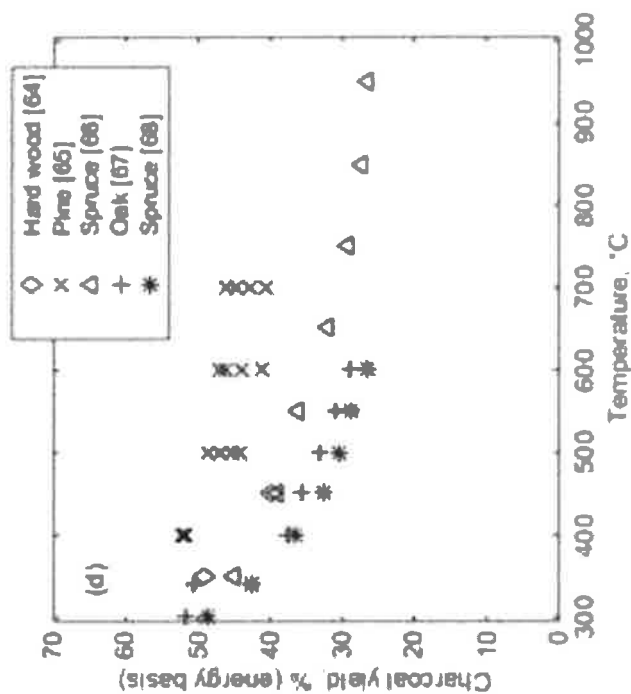
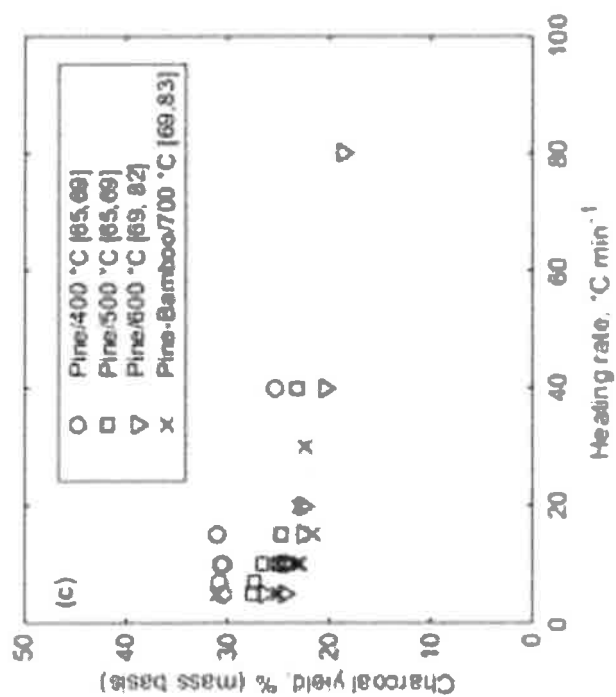
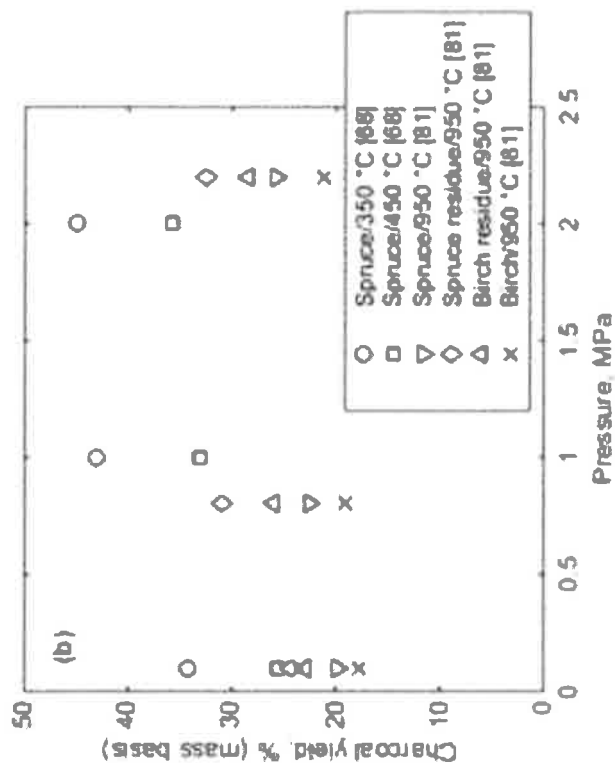
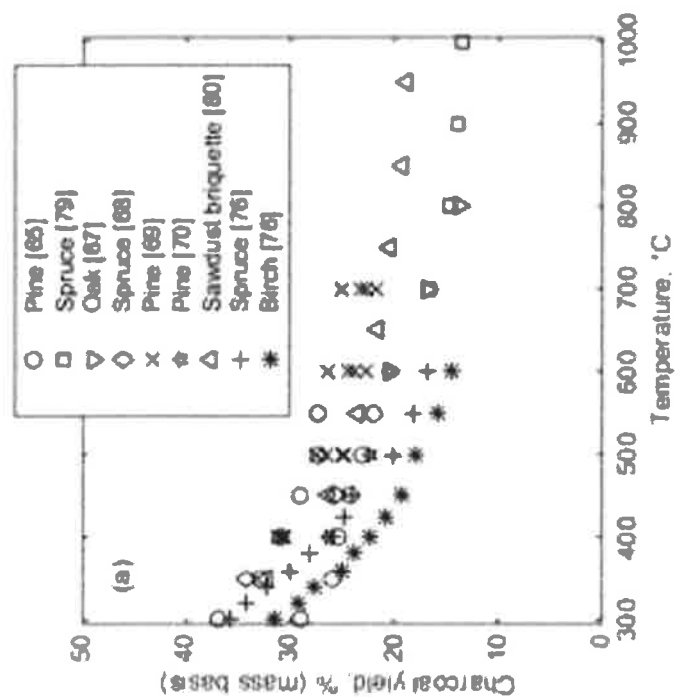
Fig. 10. Abatement cost curve for biofuel utilization in integrated steel plant [179].

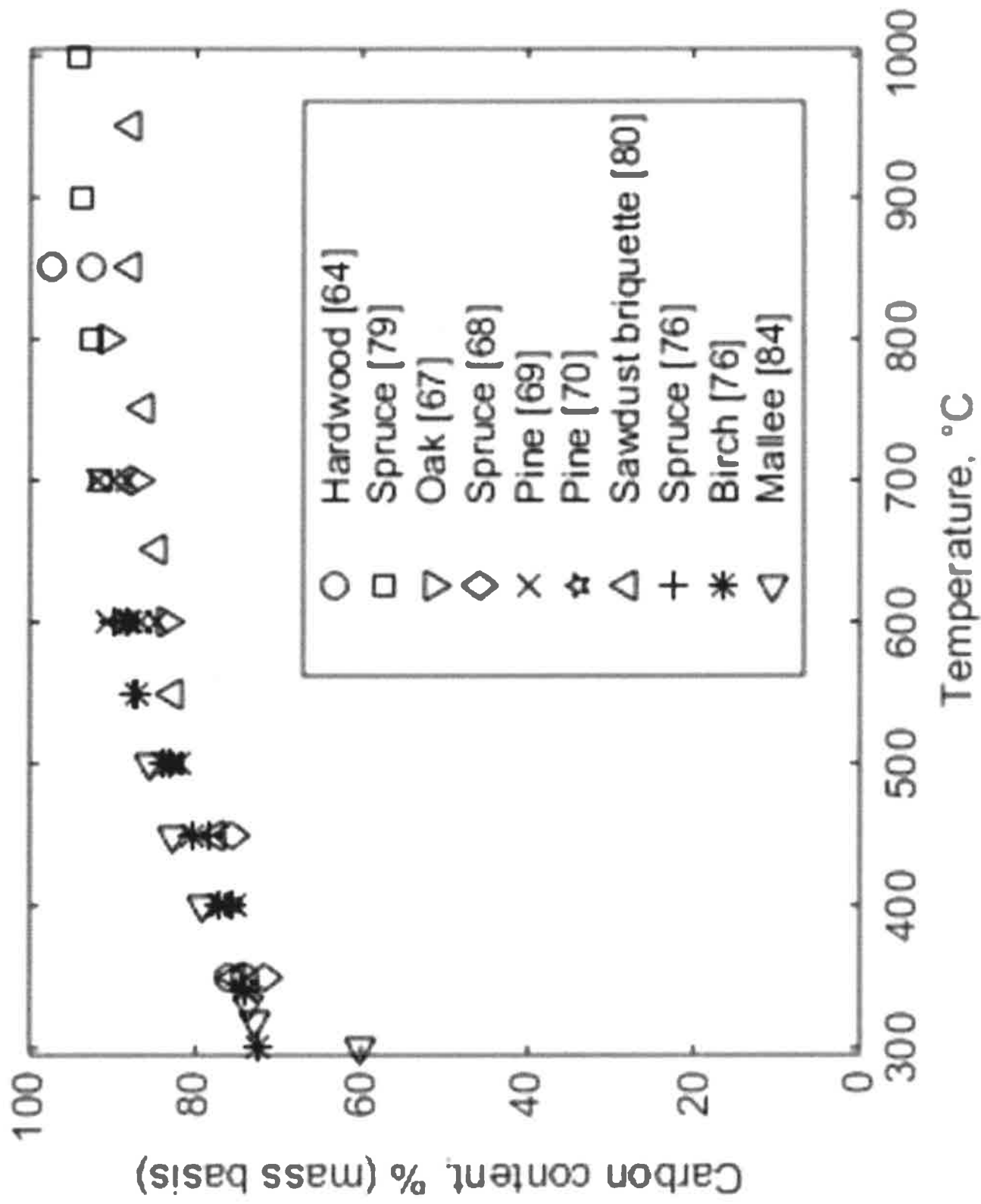




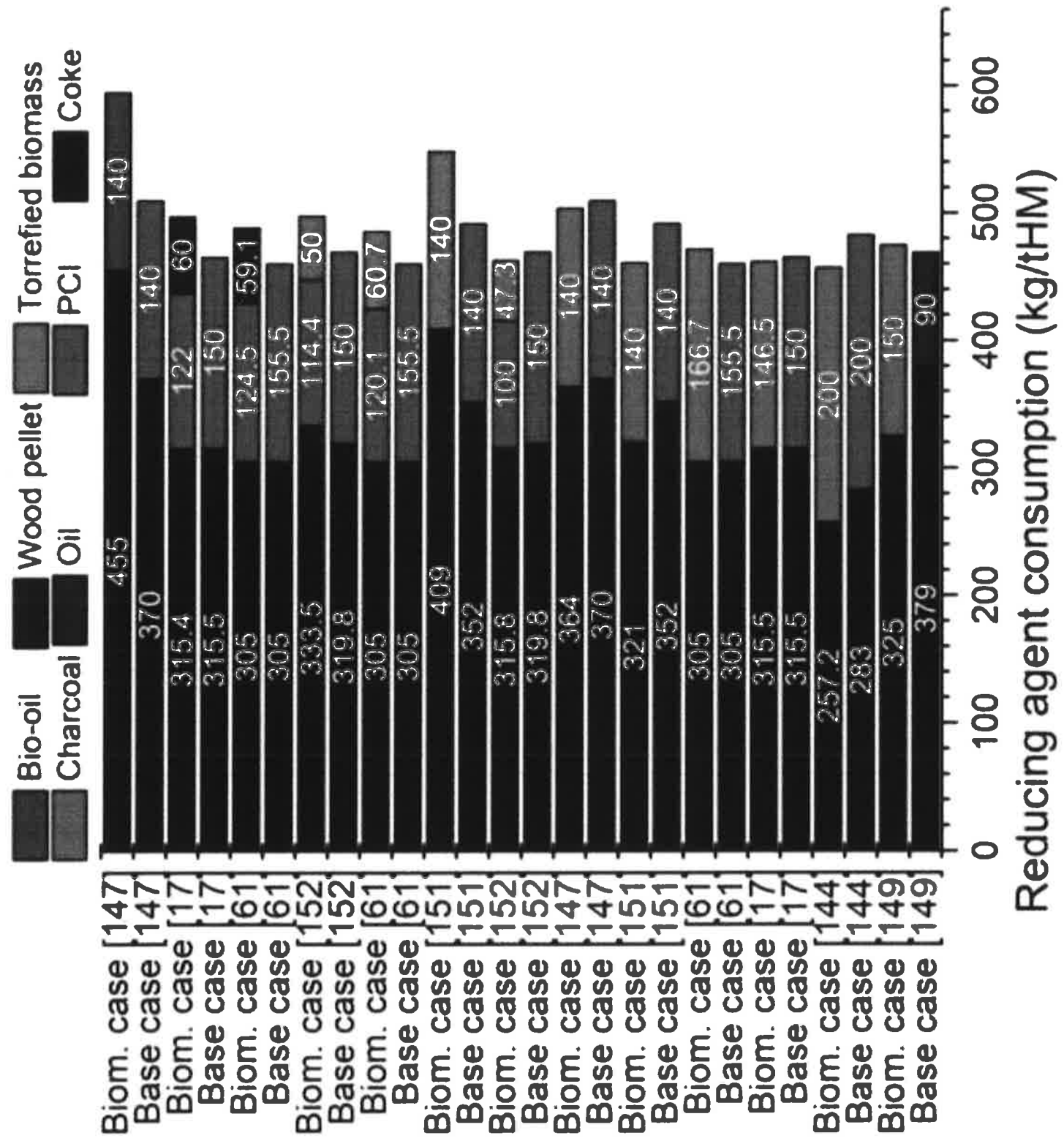


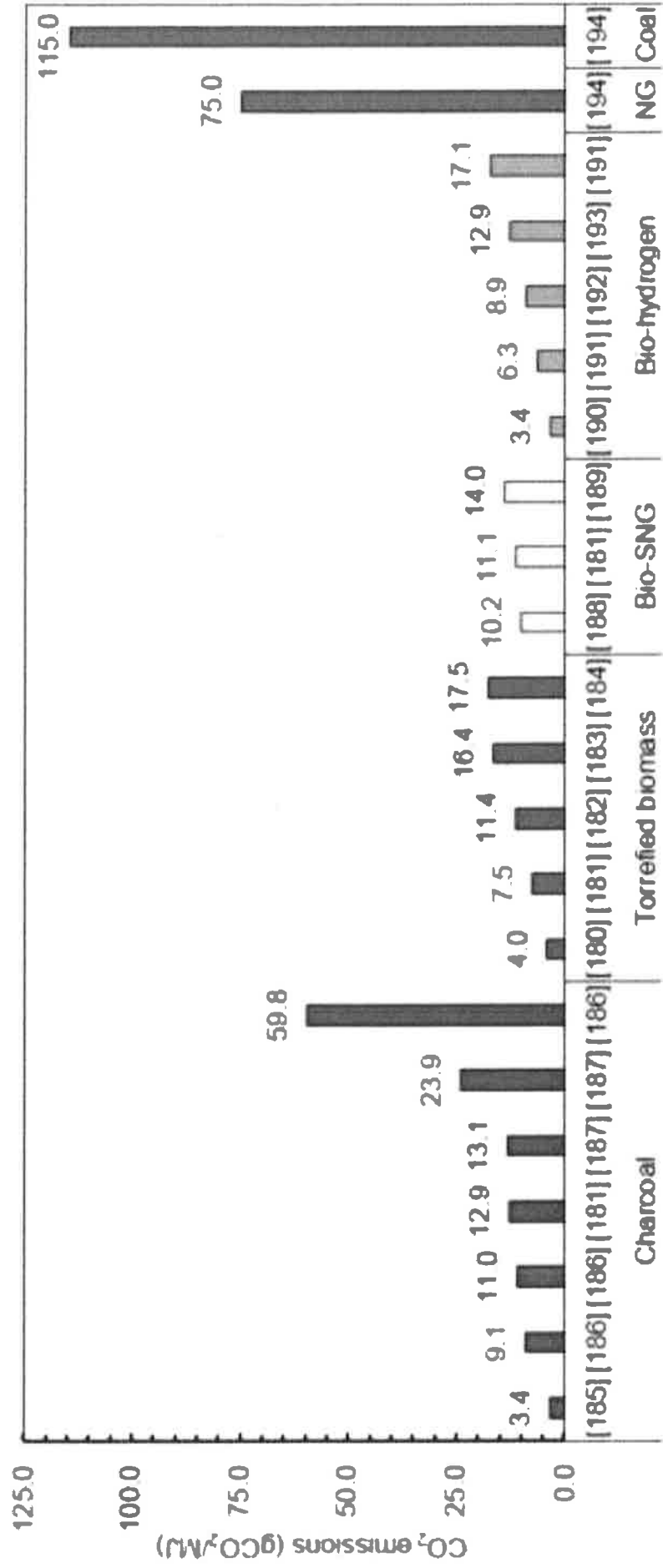






Fossil coal and biomass injection cases





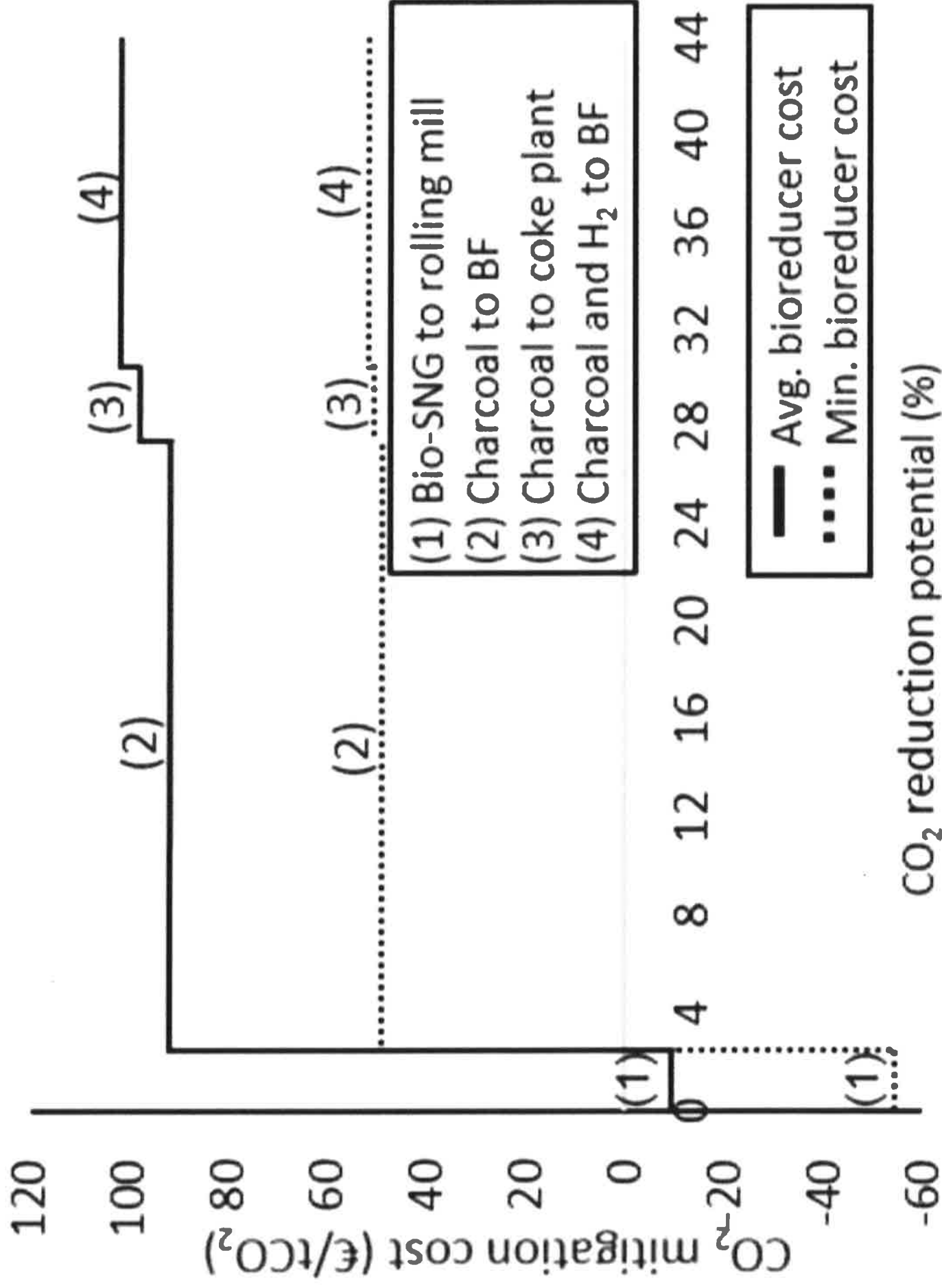


Table captions

Table 1. Typical properties of blast furnace reducing agents [16,19,23-25].

Table 2. Typical ash compositions of metallurgical coke and pulverized coal [16,24,26]

Table 3. The effect of harmful elements in the blast furnace process [16,19,27-34].

Table 4. The global techno-economic potential of biomass in 2012 and 2035 (EJ) [38].

Table 5. The chemical composition of wood-based raw materials (wt.%, dry basis) [45-51].

Table 6. Fuel ash compositions of some wood-based raw materials (wt.%) [46,48-49,51].

Table 7. Biomass drying technologies [44].

Table 8. Comparison of thermochemical conversion technologies.

Table 9. Gas quality requirements for F-T, methanol, mixed alcohol syntheses and syngas fermentation modified from [229-230].

Table 10. The composition of steel plant process gases [226-227].

Table 11. CO₂ mitigation breakthrough programmes [5,243-247].

Table 12. Comparison of drastic CO₂ mitigation technologies [10,15,61,179,185,241,250-253,257-264].

Component	Coke [16,23]	Pulverized coal [16,19,23,24]	Waste plastic [23]	Heavy oil [16,25]
Ultimate analysis (wt.%)				
C	87–92	80–85	61–67.6	84–88
H	~0.4	3.5–5	14.0–18.2	10–10.5
O	~0.5	3–8	9.1–17.8	ND
N	~0.4	~1.5	0.5–1.5	ND
S	0.6–0.8	0.4	<0.01	0.3–2.0
Proximate analysis (wt.%)				
C _{fix}	87–92	57–76	6–7	ND
VM	0.2–0.5	8–38	80–89	ND
Ash	8–11	5–11	6–12	0.02
Lower heating value [MJ/kg]	~30	30–34	27–35	40.04

Ash analysis (wt.% db)	Coke [16]	Pulverized coal [24,26]
SiO ₂	52	46–64
Al ₂ O ₃	31	17.4–29.9
Fe ₂ O ₃	7 (as Fe)	7.6–14.6
CaO	2.5	0.9–4.7
MgO	1.2	1.1–3.2
TiO ₂	ND	1.1–2.0
P ₂ O ₅	0.3 (as P)	0.2–1.6
SOx	ND	0.04–1.2
Na ₂ O	0.7	0.2–1.0
K ₂ O	1.8	1.0–3.4

Element	Effect to BF	Input	Output
Zinc (Zn)	Increases the wear of the BF refractory linings [27]. Blocks the pores in iron-bearing materials and coke, impairing the gas permeability [19,28]. Increases coke reactivity index (CRI) and decreases coke strength after reaction (CSR) [29]. Increases coke consumption [30].	Iron burden and reducing agents, the major source being sinter [30,31]. Majority of the Zn comes from BOF sludge that is recycled via sintering back to the BF [31].	Majority of the Zn is removed from the furnace with the dust. Roughly 10% leaves the furnace with HM and slag [31]. Zn in the BF can be enriched to 80 times of its concentration in raw materials [30].
Lead (Pb)	In BF, Pb locates under a layer of metal, accumulates there and penetrates actively to the lining of the bottom and leads to structural damage of the hearth. Pb can also penetrate into pores of the furnace lining and form skulls. [32,33].	Iron ore burden or limestone in a form of PbS and PbSO ₄ , and with dusts or sludge mainly in a form of PbO [19,32].	Molten Pb has higher density compared to slag and HM and its dissolution in HM is weak [33].
Potassium (K) and Sodium (Na)	Alkalis reduce the strength of the coke and pellets, impair the gas distribution drainage of liquid products, promote the scaffold formation and increase the reducing agent consumption [19,30].	Alkalis enter the BF with iron ore burden, coke and coal. Their share depends greatly on the applied raw materials. In European BFs the alkali input (K ₂ O and Na ₂ O) is about 1.5–5.0 kg/tHM and in China from 2.0 to 12.0 kg/tHM [19,30].	K and Na create circulating loops inside the BF through a reduction and oxidation reactions [30].
Phosphorus (P)	P content of HM should be kept as low as possible to avoid extensive refining in the further processing steps in steel plant converters with adding lime to increase basicity of the slag [34]	Majority of the phosphorus in the BF comes from the coke and coal, some from the flux and iron ore in a form of P ₂ O ₅ , 3(CaO)·P ₂ O ₅ and 3(FeO)·P ₂ O ₅ [19,32].	Large majority of the P enters to the HM, depending on the literature source, 90–98% [16,32,33]
Sulfur (S)	S is detrimental for steel properties and the majority of the S should be removed already in BF [19].	About 80–90% of the sulfur enters the BF with coke and PC or oil [34]. The rest comes from the burden materials [19]	Majority of S leaves the BF in slag [19].

Main sector	Sub sector	Current (2012)	Range (2035)	Average (2035)
Agriculture	Dedicated crops -- main products	3.5	26–34	30
	By-products	2.1	30–38	34
	Total agriculture	5.6	56–72	64
Forestry		48.9	72–84	78
Organic waste		1.7	6–10	8
Total		56.2	134–166	150

Fuel	C	H	N	O	S	Ash	HHV (MJ/kg)	Ref.
Eucalyptus	51.22	5.86	<0.3	41.72	NA	0.57	NA	[45]
Whole tree chips	51.8	6.1	0.3	41.19	0.01	0.6	19.6	[46,47]
Stem wood chips	48–52	5.4–6	0.3–0.5	diff.	<0.05	1–3	18.5–20	[46,47]
Forest residue	51.3	6.1	0.3	40.8	0.02	1.33	20.4	[46,47]
Stump chips	47–54	5.6–6.5	0.1–1.1	diff.	<0.05	1–3	19.3	[46,47]
Pine sawdust	51.0	6.0	0.08	42.8	0	<0.5	ND	[48,49]
Pine Bark	52.5	5.7	0.4	39.7	0.03	1.7	20.95	[48,49]
Spruce bark	49.9	5.9	0.4	41.4	0.03	2.3	19.83	[48,49]
Kraft lignin (Indulin AT)	64.46	5.45	1.01	24.72	1.85	2.43	29.1	[50]
Kraft-lignin (Lignoboost)	67.35	5.57	<0.5	22.35	2.81	1.36	28.7	[50]
Pine Kraft-lignin	64.7	5.7	0.9	26.3	1.5	2.5	NA	[51]

Fuel	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	SO ₃	P ₂ O ₅	Ref.
Birch bark	3.0	NA	1.0	60.3	5.9	4.1	0.7	NA	4.8	3.5	[46]
Birch	3.8	NA	NA	57.8	7.7	11.5	7.7	NA	3.8	7.7	[46]
Pine sawdust	8.3	2.0	1.8	41.8	11.8	12.3	0.3	0.12	1.9	5.2	[48,49]
Pine Bark	1.3	5.3	0.3	40.6	4.5	7.6	0.5	0.12	2.0	4.8	[48,49]
Spruce bark	6.13	0.68	1.9	72.39	4.97	7.22	2.02	0.12	1.88	2.69	[48,49]
Forest residue	20.63	2.99	1.42	47.55	7.20	10.23	1.60	0.40	2.91	5.05	[49]
Pine Kraft lignin	3.0	1.2	0.3	1.0	1.0	4.7	38.5	NA	NA	NA	[51]

Dryer	Band dryer	Rotary dryer	Steam rotary dryer	Pressurized fluid-bed dryer	Pneumatic steam dryer
Feed	Sawdust, wood shavings, wood chips	Sawdust, wood chips, bark	Sawdust, wood processing residues	Wood chips	Sawdust, bark, forest residues
Feed flow, t h ⁻¹ (dry)	8–9	6–7	5–6	9	25
Moisture inlet, wt. %	5–60	50–60	50–60	50–60	50–60
Moisture outlet, wt. %	10–15	10–15	10–15	10–15	10–15
Drying medium	Air, flue gas (90–120 °C)	Air, flue gas (250–400 °C)	Steam (ambient pressure)	Recycled LP steam (0.3–0.4 MPa)	Recycled LP steam (0.3–0.4 MPa)
Heating medium	Hot air	Flue gas	HP steam (0.6–1 MPa)	HP steam (2.6 MPa)	HP steam (0.7–2.6 MPa)
Evaporation capacity, t h ⁻¹ H ₂ O	10	7–8	6–7	5–40	25
Evaporation energy demand, MJ kg ⁻¹ H ₂ O	4–5	4–5	3–4 0.8–1 (energy recovery)		2–3 0.5–0.7 (energy recovery)

Conversion technology	Description
Torrefaction	<p>Operation conditions: 200–300 °C for 15–30 minutes without the presence of air</p> <p>Major product: slightly carbonized solid residue, called torrefied biomass</p> <p>Development stage: several demonstration plants in operation</p>
Hydrothermal carbonization	<p>Operation conditions: mixed with saturated water-steam at 150–250 °C from few minutes to few hours</p> <p>Major product: slightly carbonized solid residue, called HTC biomass</p> <p>Development stage: several demonstration plants in operation</p> <p>Note: Suitable for wet biomass; water-soluble inorganic elements are removed with water</p>
Slow pyrolysis	<p>Operation conditions: slow heating to 300–600 °C and kept for 15–30 minutes to several hours without the presence of air</p> <p>Major product: highly carbonized solid residues, called biochar or charcoal</p> <p>Development stage: existing since early age of human civilization</p> <p>Note: Process heat often supplied by partial combustion of biomass or volatile products; particles larger than a few cm</p>
Fast pyrolysis	<p>Operation conditions: high heating rate to 400–600 °C for a few seconds without the presence of air</p> <p>Major product: Mixture of water and organic compounds including oxygenates and phenolic compounds, called bio-oil</p> <p>Development stage: a few commercial plants in operation</p> <p>Note: Process heat by excess heat from a power station or partial combustion of char; particles need to be milled less than a few mm.</p>
Gasification	<p>Operation conditions: 600 °C to 1400 °C with oxidizing agent (typically, 30–50% of oxygen or air required for stoichiometric combustion with steam or CO₂)</p> <p>Major product: Syngas (mixture of H₂, CO and CO₂ with small amount of CH₄)</p> <p>Development stage: several pilot and demonstration plants in operation (coal gasification plants in commercial operation)</p>
Combustion	<p>Operation conditions: complete combustion with excess air</p> <p>Major product: High-temperature heat</p> <p>Development stage: widely utilized for power generation and heat for process industries world-wide</p>

Conversion method	FT synthesis*	Methanol synthesis*	Mixed alcohol synthesis*	Fermentation
Temp (°C)	200–500	220–275	260–425	20–40
Pressure (bar)	10–40	50–100	50–300	1–2
H ₂ /CO ratio	0.6–2.0	Unimportant	1–1.2	Not sensitive
(H ₂ -CO ₂)/(CO+CO ₂) ratio	Unimportant	0.7–slightly >2	Unimportant	Unimportant
CO ₂	<5%	4–8%	<5%	Aids initial growth rate
H ₂ O	Low	Low	Low	Most reactors use an aqueous solution
Tar, ppm	<0.1	<0.1	<0.1	unknown
Particulate matter, ppm	<0.1	<0.1	<0.1	must be removed
Alkali max, ppb	<10	<10	<10	unknown
S components (H ₂ S, SO ₂ , CS ₂), ppb	<100	<100	<100	some tolerance
N-components (NH ₃ + HCN) ppb	<20	<10	<10	might have appositve effect
HCl, ppb	<10	<10	<10	should be removed
Alkali metals, ppb	<10	<10	<10	Unknown

*The concentrations allowed might slightly differ depending on catalysts used

Component (vol.%)	BFG	COG	BOFG	TGR-BFG
H ₂	3	66	4	9
CO	20	6	58	46.7
CH ₄	0	21	0	0
C ₂ H ₆	0	3	0	0
CO ₂	24	2	20	37.7
N ₂	53	3	18	6.6
LHV (MJ/Nm ³)	2.85	17.5	7.6	NA

Program	Technologies	Maturity of the technology	Source
ULCOS (Europe)	Top-gas recycling blast furnace with CCS	Laboratory, pilot trials, industrialization 2020 onwards	[5]
	Bath smelting (Hlsarna)	Laboratory, pilot trials, industrialization 2030 onwards	[5]
	Direct reduction (ULCORED)	Laboratory, industrialization 2030	[5]
	Electrolysis (ULCOWIN)	Laboratory, industrialization 2040	[5]
COURSE50 (Japan)	H ₂ -based reducing agents in BF	Laboratory, pilot trials, industrialization 2030 onwards	[243]
	CO ₂ sequestration from BF gas	Laboratory, pilot trials, industrialization 2030 onwards	[243]
POSCO CO ₂ breakthrough framework (Korea)	Pre-reduction and heat recovery of hot sinter	Heat recovery system installed	[244]
	CO ₂ absorption using ammonia solution	Laboratory, pilot trials	[244]
	Bio-slag utilization for the restoration of marine environments	Commercial	[244]
	Hydrogen production using COG and wastes	Laboratory, pilot	[245]
	Iron ore reduction using hydrogen-enriched syngas	Not mentioned	[245]
	Carbon-lean FINEX process	Commercial	[244]
AISI CO ₂ Breakthrough Program	Ironmaking by molten oxide electrolysis	Laboratory	[246]
	Ironmaking by hydrogen flash smelting	Laboratory	[246]
Australian programme	Use of biomass-derived chars as substitutes for coal and coke	Laboratory, pilot, also industrial trials	[247]
	Dry slag granulation, waste heat recovery	Laboratory, pilot	[247]

Technology	Description of the technology	CO ₂ emission reduction potential	Energy demand	Advantages	Disadvantages
BF-based technologies					
Base-line BF	Coke and PC are used as reducing agents, agglomerated iron charge.	BF-based CO ₂ emissions are around 1.22 tCO ₂ /tHM [15], plant site emissions 1.8–2.2 tCO ₂ /t HRC [257], Life cycle emissions 2.2–2.5 tCO ₂ /t HRC [10].	The energy demand of BF is around 12–13 GJ/tHM [15]. Cumulative energy demand for BF-BOF-based steel is around 20–30 GJ/tCS.	Production of HM in BF for steel production is the most cost-efficient technology today.	The most advanced BFs are operated near their limits, which means that further CO ₂ reduction is difficult.
Charcoal injection	Biomass-derived char replaces injected coal by 100%.	Up to 30 % reduction in BF CO ₂ emissions [61]. Higher (>50%) if applied also e.g. in coking, sintering and heating furnaces [179,185].	Energy demand is quite similar.	Charcoal application in BF could be quite straightforward. Major investments in infrastructure in IS plant could be avoided.	Charcoal is more expensive compared to PC. Global charcoal markets are non-existing. Handling, transportation, storage is more difficult compared to coal.
TGR-BF (with CCS)	Upgraded BF top-gas replaces part of the injected coal and top-charged coke. CCS can be used to avoid the release of CO ₂ emissions to the atmosphere.	24% reduction in BF CO ₂ emissions, 15% reduction at IS plant-scale without CCS, 60% reduction at IS plant-scale with CCS [250].	Slightly higher compared to base-line BF [258].	TGR-BF enables the CCS.	Technology still under development. Market penetration will take decades if realized. Heavy investment costs. CO ₂ avoidance cost > 50 €/tCO ₂ [258].
Microbiological process gas treatment	Microbiological fermentation is used to transform process and flue gases into fuels and chemicals.	Emission reduction due to the “binding” of process gases into chemicals ^{a)} . Difficult to evaluate CO ₂ emission reduction.	Not evaluated.	By utilizing the by-products gases from IS plant in ethanol production, the use of fossil-based fuels in other industries could be reduced. It is claimed that ethanol production from BOF gases is economically viable [241].	Carbon will ultimately be released in burning.
H ₂ injection	A small share of the coal or coke is replaced with hydrogen injected to the BF.	Coke rate decrease by 33 kg/tHM with 13 kg/tHM H ₂ injection [259]. Direct CO ₂ emission reduction in BF ~ 108.8 kgCO ₂ /tHM.	Not evaluated.		H ₂ production is quite expensive with current technologies.
Direct reduction					
Fluidized bed reactors	Circored and Finmet are gas-based and Circofer coal-based fine ore direct reduction technology. Combination of circulating fluidized bed and bubbling fluidized bed [260].	20–30% reduction with Circofer-Hismelt-BOF or Circofer-EAF route compared to agglomeration-BF-BOF route [257]. 50–90% reduction with Circored-EAF route with H ₂ used as reducing agent compared to BF-BOF route [252].	Circofer 11.7 GJ/t HBI [261], Circored-EAF 18.3–20.0 GJ/tCS [262].	Produces a pure CO ₂ stream for CCS [257]. No need for raw material agglomeration. Can use H ₂ as reducing agent.	Technology has not gained wide popularity.
Shaft furnaces with coal or NG	MIDREX and HYL/Energiron are pellet/lump ore direct reduction processes. Reducing gases used in the process are produced from coal, NG, etc.	Steel production with Energiron-EAF produces about 50% of the CO ₂ emissions compared BF-BOF route without CO ₂ removal [251].	9.4–11.2 GJ/t DRI [261].	No coke, coke ovens or sinter plant required. Lower specific capital cost than an integrated steel plant [260]. Several NG-based DRI plants existing (Midrex and HYL).	Price of natural gas is high in many regions in the world. Oxidation of DRI in presence if stored or transported. Production capacities still small compared to BF.
Shaft furnace with H ₂	Hydrogen produced with water electrolysis used as reducing	The CO ₂ emissions depend on the electricity grid mix, 180 kgCO ₂ /tCS at the	13.1 GJ/tCS [253].	Almost zero emissions from reduction process.	Hydrogen production is expensive and requires lots of electrical energy. Safety

issues with H ₂ .				
Smelting reduction				
Smelting reduction	agent in a shaft furnace (like Midrex).	lowest [253]		
	COREX is based on the combination of pre-reduction shaft furnace and melter-gasifier.	Life cycle CO ₂ emissions at similar level compared to BF-based steelmaking, if the plants would be located in Europe [261].	Net energy consumption 18.9–21.7 GJ/tHM [261].	No need for BF coke, some amount of lower quality nut coke is required [261]. Restrictions for non-coking coal quality (VM content should be maintained at around 25%). There should be a user for export gas to ensure the economic viability of the process [260].
	FINEX is based on the combination of fluidized bed reactors and melter-gasifier.	Life cycle CO ₂ emissions at similar level compared to BF-based steelmaking, if the plants would be located in Europe [261].	Not evaluated.	No need for pelletizing, sintering or agglomeration of iron-bearing materials. Utilizes non-coking coal as reducing agent. Lower CAPEX and production cost compared to BF route [260]. Technology not wide-spread.
Other	Hlsarna is a bath-smelting technology that combines coal preheating and partial pyrolysis in a reactor [263].	80% CO ₂ reduction compared to average BF with CCS, 20% without CCS [263].	20% reduction in primary energy consumption compared to BF process [264].	Technology at demonstration stage [263].
	Electrowinning	The CO ₂ emissions depend on the electricity grid mix, 180 kgCO ₂ /tCS at the lowest [253].	9.3 GJ/tCS [253].	Technology under development.

^{a)} Ethanol produced from the steel mill basic oxygen furnace process gas with LanzaTech's technology has 67% lower GHG emissions compared to petroleum gasoline [265].