

A Review of Biomass-Based Reducing Agent Utilization for Sustainable Iron and Steelmaking Process

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Abstract. Since iron and steelmaking industry is one of the most intensive fossil carbonaceous material consumptions which have a direct impact on CO₂ emission, it is therefore significantly important to decrease these consumptions. Several kinds of biomass could be applied as a reducing agent and fuel to replace coal and coke in iron and steelmaking process. The aim of this review work is to investigate the importance of biomass which is carbon neutral resource in the sustainable development of the iron and steelmaking process. The review carried out an exploration of biomass-based products as alternative reducing agents and the possibilities of biomass use in iron and steelmaking processes. The paper also puts forward relevant theories of iron and steelmaking. Finally, the development of biomass-based reducing agents for future research was discussed.

Keywords: Iron and steelmaking industry, CO₂ reduction, Biomass-based reducing agent, Carbon neutral, Sustainable development

1. Introduction

Steel industry uses fossil fuel which is associated with CO₂ emission. A previous research study [1] revealed that the industry is contributing 5-7% of the global CO₂ emissions. Therefore, technical solutions to eliminate emissions from fossil-based iron and steelmaking are necessary. [2, 3] According to the Kyoto protocol, steel manufacturer is in the highly regulated industries. CO₂ reduction is an ongoing challenge faced by steel plants. In spite of strict regulation, there are opportunities to improve their practices and respond effectively to the awareness of environment protection. Several research studies in greenhouse emissions, control, and Reduction were conducted. [4] Carbon neutral materials such as biomass should be positively considered as alternative sources to replace part of fossil-based reducing agents in the iron and steelmaking industry. [5, 6] Biomass-based reducing agents are any biological origin of materials that are not fossilized. Biomass can be used as an original form as fuel, or be refined to different states such as solid, liquid, or gaseous biofuels. [7] Wood as charcoal source is used for more than 52 million tons annually in cooking and iron and steelmaking process. Charcoal can use to replace as reducing agent of coal and coke in iron and steelmaking process. [8] Several new and alternative technologies such as the COREX process, the FINEX process, the coal-based HYL process, the coal-based MIDREX process, fine ore reduction in a circulating fluidized bed and the use of biomass iron ore composite agglomerates are under development to decrease the environmental issues of steel industry. [9, 10] The aim of this review is to investigate the importance of biomass and theories of iron and steelmaking. In addition, the biomass-based products as alternative reducing agents and the possibilities of biomass use in iron and steelmaking processes will be explored. Furthermore, the future research works in the field of iron and steelmaking with the use of biomass in Thailand will be discussed.

2. Theoretical analysis

2.1 Integrated of iron and steelmaking process

The most common route for steel production today involves 2 stages, the production of hot metal in Blast Furnace (BF) and liquid steel in Basic Oxygen Furnace (BOF). [11] Some researchers [2] classify the steel production into 4 main routes, namely Blast Furnace (BF) - Basic Oxygen Furnace (BOF), Direct Reduction (DR) process - Electric Arc Furnace (EAF), Smelting Reduction (SR) - Basic Oxygen Furnace (BOF) and melting of scarp in Electric Arc Furnace (EAF) as shown in Fig. 1.

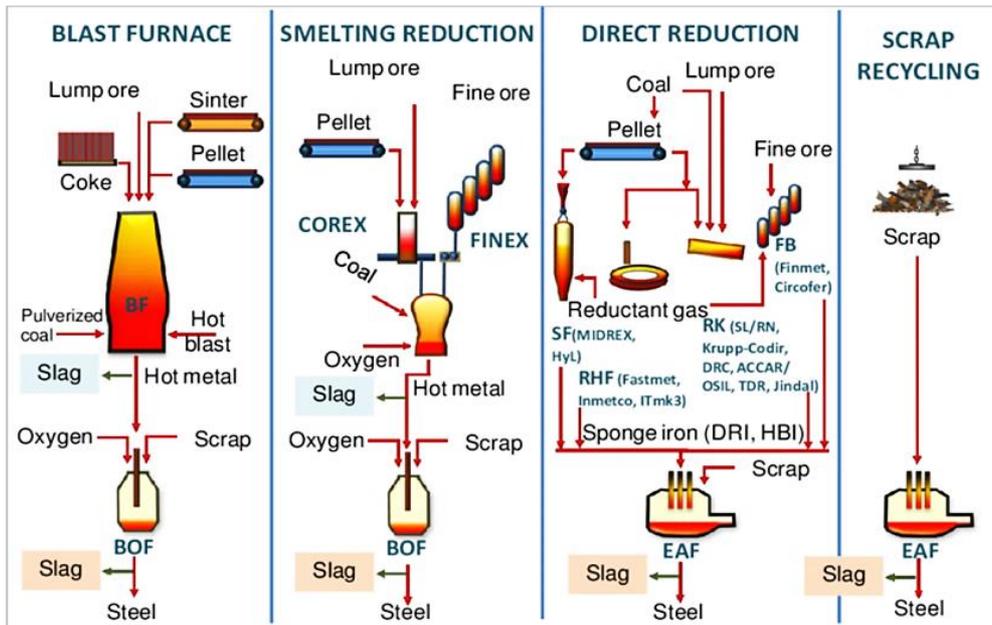


Fig. 1 Typical Integrated Steelmaking Process [2, 12].

Steel production starts with iron ore mining process and the agglomeration processes such as sintering and pelletizing, follows by the reduction of the iron ore to iron by removing oxygen. Iron is then further converted to steel by lowering the carbon content, adding alloys and removing impurities. [3] Generally, integrated steel mills use BF-BOF route in steel production which represents about 70% of the world steel production. [2] BF-BOF route is considered the most important route for steel production in which coal and coke as energy and reducing agents are applied in the process. During the process, iron ore and coke which prepared from pyrolysis of coal are charged into the blast furnace. Simultaneously, Pulverize Coal (PC) is injected in modern BF. Hence, iron ore is chemically reduced and physically melted to the hot metal. The hot metal produced is transferred from BF to BOF for lowering carbon content and converting into steel. Recycled steel scraps can be used by either charging into BOF or EAF to increase the steel throughput of the steel mill. The produced liquid steel is further refined in the steel ladle for fine adjustment of the temperature and chemistry at secondary steelmaking prior to the casting. [13] The recycling and melting of steel scarp is done in the EAF which represents the second important route for steel production. EAF route is accounted for 25% of world steel production. [2]

An alternative route of iron and steel production is Direct Reduction (DR) process which mainly uses natural gas as a source of energy and reducing agents, produces approximately 5% of the world steel production. [2] In this process, iron ore is reduced directly in solid state by adding methane as a reducing agent, for example, a shaft furnace or rotating kiln. The product is called "sponge iron" due to its porous structure. Sponge iron is further processed to steel in an EAF and BOF, where the iron is melted and the carbon content is reduced in steelmaking process. The SR-BOF route is another alternative route based on the combustion of coal for the reduction of iron ores without agglomeration. This route represents only 0.4% of the world steel production. [2, 3, 14]

2.2 Iron and steelmaking fuels

Fuels used in iron and steelmaking are mainly fossil and byproduct as solid, liquid and gaseous states. These fuels release energy by combustion reaction of carbon and/or hydrogen with oxygen. Fossils have been transformed by biochemistry and geology into such fuels as coal, natural gas, petroleum, etc. Fuels can be classified into primary and secondary fuels. Primary fuels are such as coal and wood, while secondary fuels are such as coke, charcoal, byproduct and waste fuels. [13] There are two main approaches to decrease CO₂ emissions in steel industry. The first approach is done by making fundamental changes on the existing processes to eliminate or mitigate fossil fuels. For instance, hydrogen produced by electrolysis may be applied directly in the process. The core existing process is kept in the second approach. Greenhouse gas emissions are managed via the combination of Carbon Capture and Storage/Utilization (CCS/U) in which CO₂ is separated from industrial off-gas and underground storage. [15]

The recent research study [16] on the development of low-emission Integrated Steelmaking Process (ISP) showed the conceptual flowsheet for ISP which is defined as the low emission in iron and steelmaking process. The ISP combines of (1) sustainable supply of biomass and its processing to produce charcoal, bio-oil and other renewable energy (2) utilization of charcoal as partial replacement for coal and coke products in ironmaking and steelmaking (3) recovery of high-grade waste heat from molten slag and (4) conversion of molten BF slag into a Portland cement substitute as shown in Fig. 2.

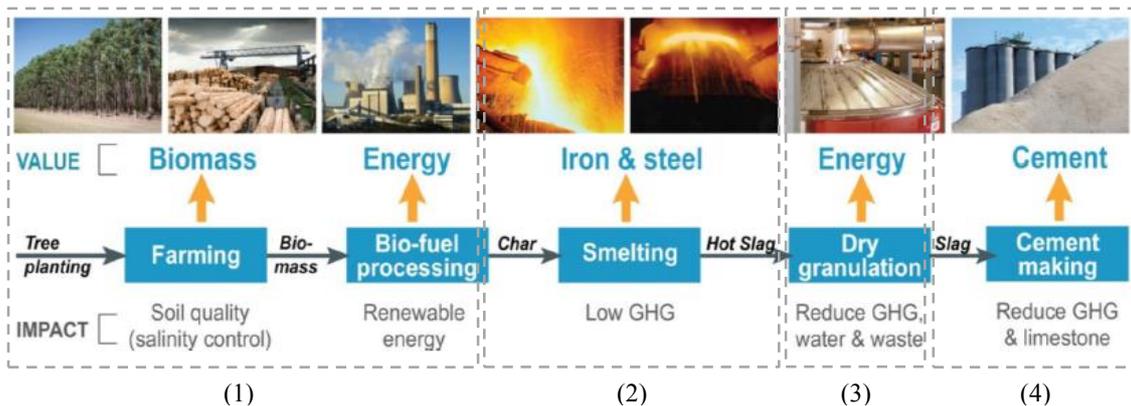


Fig. 2 The conceptual flowsheet across the value chain for the low-emission Integrated Steelmaking Process (ISP) [16].

2.3 Reduction kinetics of the conventional iron ore pellet

To understand how the rate of reduction of iron oxide varies under different conditions such as temperature, pressure and type of reducing agents, it is essential to have an idea of the thermodynamics and kinetics of iron oxide reduction. [17] Generally, the rate controlling step (bottle neck) or the rate determining step of the conventional iron ore pellet reduction can be categorized into 3 main types. First, Boundary layers control, the rate depends on the heat and mass transfer across the gas-flow boundary at the outer surface of the pellet. This type of reaction control can take place in the condition without strong gas flow through the pellet such as in the rotary hearth furnace. However it can be neglected in some conditions, for example, a large amount of gas with high flow rate in a BF can diffuse through the surface of pellet. Second, Gaseous diffusion control, the diffusion rate of reducing gas through the product layer of material controls the total rate of iron ore reduction. Third, interfacial reaction control, the chemical reaction at the wüstite-iron interface controls the overall reaction rate. [18]

2.4 Reduction mechanism and behavior of Self-Reducing Pellets (SRP)

The reduction reaction kinetics for conventional pellets and sintered ore is controlled by reduction gas diffusion from outside. On the other hand, the reaction of carbon composite

agglomerates which are the mixture of iron ore and coal as reducing agents can be occurred inside the agglomerates themselves as shown in Fig. 3. [19] Once the agglomerates are heated, Carbon monoxide (CO) is generated inside them. This reaction is commonly known as the Boudouard reaction; $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ (endothermic). CO is promoted from the reaction and is used in the reduction of iron oxide; $\text{Fe}_x\text{O}_y + y\text{CO} \rightarrow x\text{Fe} + y\text{CO}_2$ (exothermic). This reduction reaction proceeds rapidly in the carbon composite agglomerates because coal accounts for about half of the volume of each agglomeration, thereby making the agglomerates become porous. [18]

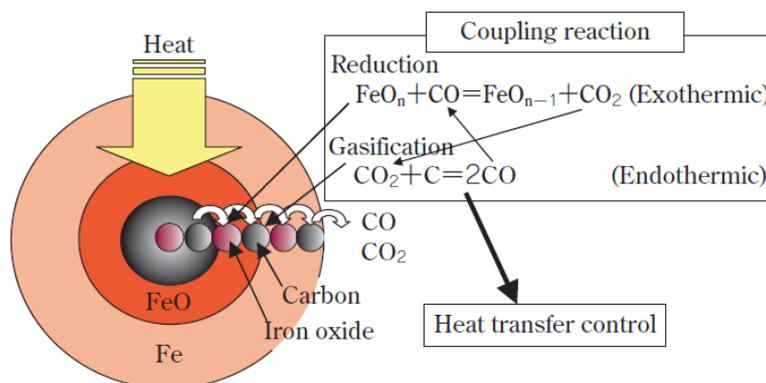


Fig. 3 Reduction mechanism of carbon composite pellet [19].

The reduction of any iron oxide by carbon embedded begins with ferric oxide, the highest oxide of iron, takes place in three stages at temperature above 570°C. It proceeds along the sequence hematite (Fe_2O_3) → magnetite (Fe_3O_4) → wüstite (FeO) → (iron) Fe. [17, 20] The reduction of FeO to metallic iron was found to be slower than the reduction of Fe_2O_3 to Fe_3O_4 and that of Fe_3O_4 to wüstite. It was also reported [20] that the rate of gas-solid reactions depends significantly upon the evolution of the pore network in porous solids during the reaction. The reduction rate of embedded reducing agent in SRP has been investigated. [21] It was discovered that the reduction rate was very fast at the temperature 900 to 1200°C and under argon atmosphere. Coconut charcoal showed the highest reactivity compared to that of coal char, coke and graphite. [22] Increasing of the amount of carbon as reducing agents in SRP increases the reduction rate. Furthermore, the research [23] has found that the rate of reduction increases with decreased carbon particle size. Moreover, the reduction rate depends on the rate of film mass transfer or pore diffusion of gaseous reduction through the product layer.

Previous researches [24, 25] investigated the effect of volatile matter reduction in SRP at the temperature up to 900°C. The result showed that reduction from volatile gases is faster than that of fixed carbon in SRP. There is no significant difference in the reduction degree between the reduction behaviors of ore-coal and ore-charcoal composite in non-isothermal reduction of composite pellet from room temperature up to 1000°C under argon gas atmosphere. However, the compressive strength after reduction of ore-coal composite is better than the ore-charcoal composite pellet. This is possibly due to the pyrolysis and transient plasticity in coal at some temperature range which provide additional high-temperature strength to the bonds. [26] The reductions of the ore-coal composite using different kinds of iron ore resources have been investigated. [27] The samples were reduced non-isothermally up to 1573 K with heating rate of 0.33 K/s under inert atmosphere. The results of microstructure changing during reduction of the hematite-coal composite are shown in Fig. 4. The white zone is metallic iron, grey zone is FeO, dark grey zone is slag and black zone is porosity.

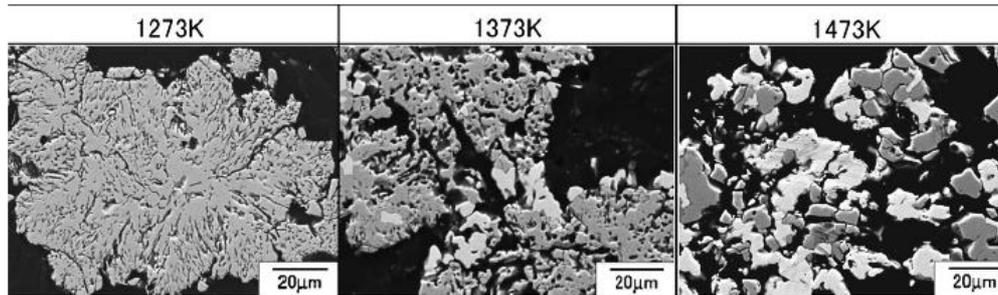


Fig. 4 Microstructure changing during reduction of the hematite-coal composite during non-isothermal reduction [27].

The reduction kinetics of SRP made from the dust collected from BF off-gas in the temperature range of 1348-1573 K in 93%N₂-7%CO₂ gas atmosphere has been studied [28]. The reduction mechanism is shown in Fig. 5. The results showed that the rate determining step is the interfacial reaction control with the activation energy 111.66 kJ/mol. The reduction rate was expressed by apply the total mass change fraction with the McKewen equation; $1 - (1 - R)^{1/3} = kt$

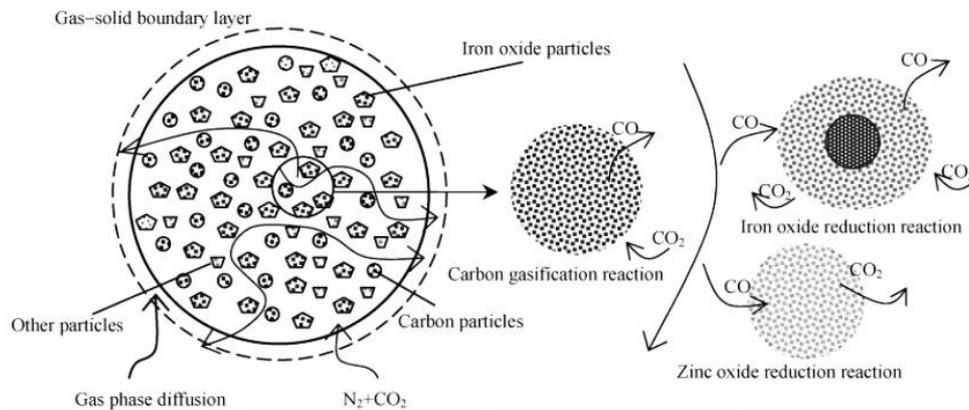


Fig. 5 Schematic of reduction mechanism of carbon containing dust pellets [28].

However, such analysis using only one total kinetics equation may be insufficient to represent the reduction kinetics of SRP since its mass change during reduction contains both change from oxide reduction and carbon gasification. The better way to analyze the reduction kinetics of SRP is the use of reaction kinetics model which contain separately equations for each chemical reactions, devolatilization, gas generation, gas consumption and gas exchange. [18] The mathematical modeling of reduction rate has been carried out. In addition, a review and critically analysis of coal gasification and devolatilization in the iron ore/coal composite under self-generated or neutral atmosphere like N₂ or Argon gas has been conducted. [29] The possible rate-controlling steps in reduction kinetics can be heat transfer of surface-chemical reactions such as FeO reduction and Boudouard reaction. The result showed that the time course of the reduction can be simulated without developing detailed mechanisms for the chemical reactions and heat and mass transfer. However, if the specifics of gas production of other conditions are required, a more detailed model must be developed.

A kinetics model for the isothermal reduction of SRP with embedded charcoal under the CO-CO₂-N₂ gas atmosphere has been developed. [30] Fig. 6 shows the concept of the proposed reduction kinetics model of the SRP and the involved chemical reactions with an assumption that there is no distribution of pressure, gas composition and temperature inside pellet. The CO and CO₂ gas are generated and consumed through the involved chemical reactions and devolatilization. The generated gas and the gas from the atmosphere outside of SRP are exchanged in the vacancy inside the SRP.

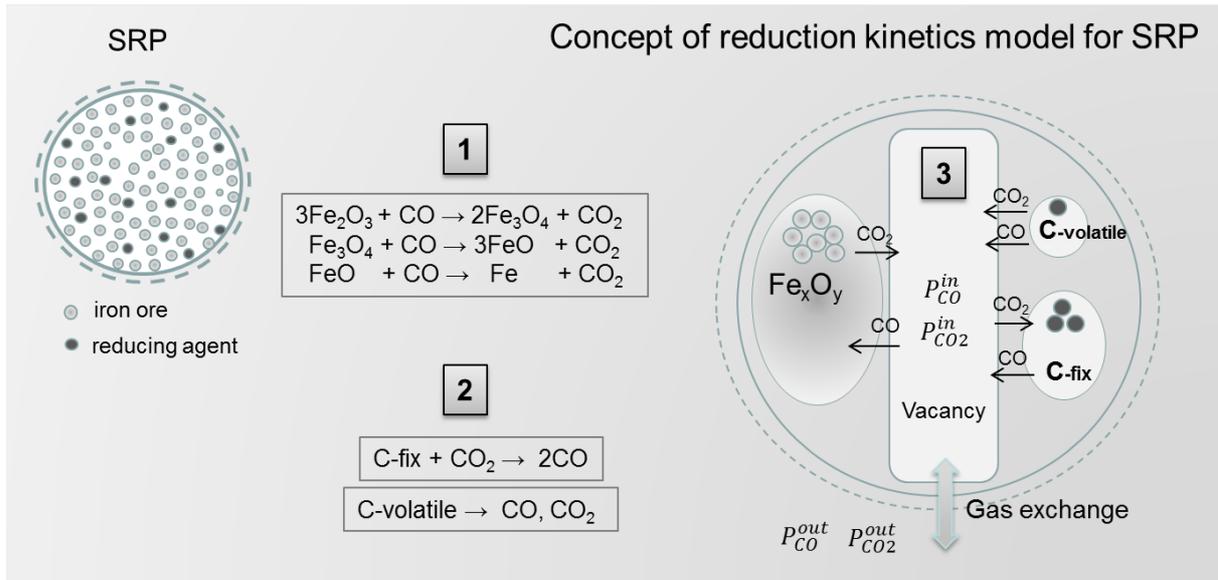
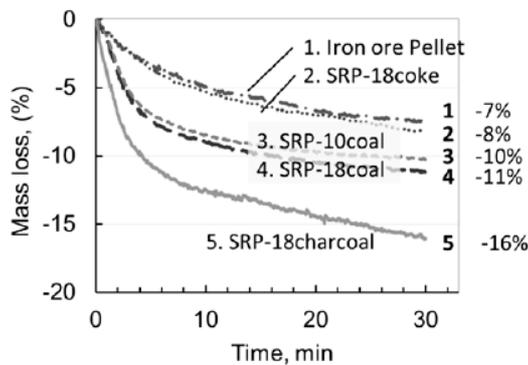
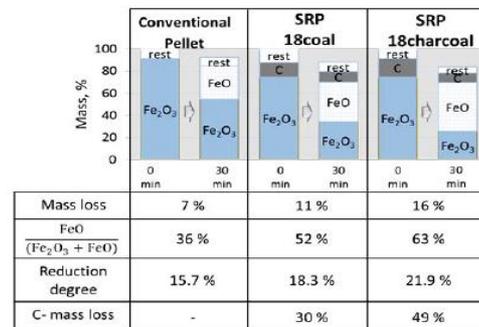


Fig. 6 Schematic of reduction mechanism of SRP with embedded charcoal and the involved chemical reactions [30].

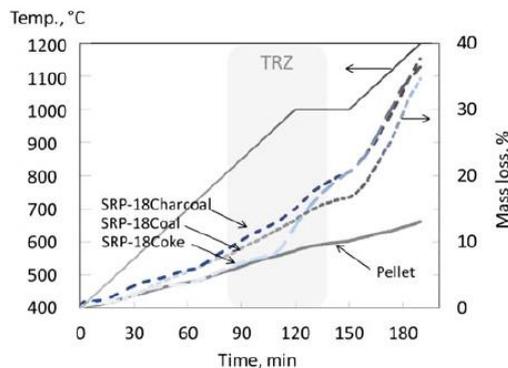
Furthermore, the experiment results using the thermogravimetric method and chemical composition analysis [30] showed that the reduction degree of SRP with embedded charcoal is relative higher than conventional iron ore pellets for the isothermal condition at 900°C. In case of non-isothermal condition, the reduction degree of SRP with charcoal is more than twice higher than the conventional iron ore pellets as shown in Fig. 7.



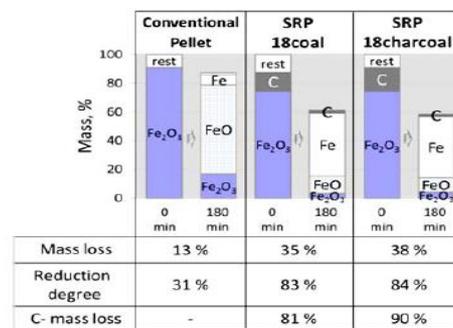
(a) Mass loss of SRPs during isothermal reduction in the thermogravimetric method



(b) Mass loss, chemical analysis and reduction degree after isothermal reduction for 30 minutes



(c) Mass loss of pellets during non-isothermal reduction, grey zone: BF-thermal reserve zone (TRZ) simulated-condition



(d) Summarized results of non-isothermal tests

Fig. 7 The experiment results from using the thermogravimetric method [30].

The research [31] shows comparison of the gasification behavior and the reactivity of three different carbon types, namely charcoal, coke, and graphite. Mass loss as well as differential mass loss with respect to time is plotted as a function of time and temperature as shown in Fig. 8. Charcoal is the most reactive carbonaceous material, as its gasification starts at 760°C, while for coke and graphite gasification start at 860 and 940°C, respectively.

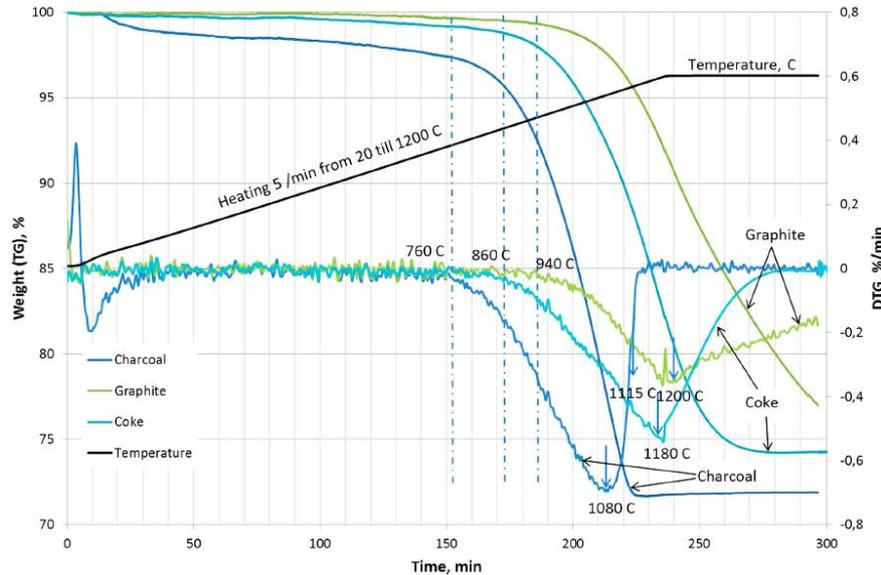


Fig. 8 The gasification behavior of carbon materials being heated up to 1200°C with a heating rate of 5°C min⁻¹ under CO₂ [31].

The research [32] shows the investigation of the reduction degree investigation by using off-gas analysis. Sinter and sinter-nut coke mixture under different gas compositions (O₂, N₂, CO, CO₂), flow rate and temperatures using muffle reduction furnaces has been carried out. The off gas obtained from an online gas analyzer. The total oxygen weight loss from iron burden materials and also total carbon solution loss from coke were calculated by measuring the weight loss after the reduction processes. The reduction degree was calculated as shown in Eq.1;

$$R (\%) = (A * \Delta t) / z \tag{1}$$

with $A = 0.714 v^\circ N_2^\circ (CO/N_2 - CO^\circ/N_2^\circ) + 2(CO_2/N_2 - CO^\circ/N_2^\circ)$

and $B = [0.427 (\% Fe) - 0.111(\%FeO)] W$

where

CO[°], CO₂[°], N₂[°]: Volume percentage of CO, CO₂, and N₂ in inlet gas (vol %)

CO, CO₂, N₂: Volume percentage of CO, CO₂, and N₂ in outlet gas (vol %)

v[°]: Total gas flow rate of inlet gas (8.0 L / min)

%Fe, %FeO: Mass concentration of Fe and FeO in sinter or pellets (wt%)

W: Weight of sinter or pellets (g)

Δt: Reduction time (s)

3. The role of biomass use in iron and steelmaking process

Biomass has been identified as one possible raw material to replace part of fossil based reducing agents in the iron and steelmaking industry. It has been found that charcoal properties can be usefully optimized. [33] The attractive outcomes from source of energy and reducing agents in iron and steel industry by using biomass to replace fossil can decrease production cost and CO₂

emission. An iron and steelmaking process was proposed [34] to use renewable energy in the form of wood charcoal to produce hot metal.

Main opportunities for the use of biomass in the integrated route for iron and steelmaking production can be summarized as shown in Table 1.

Table 1 A summary of the main opportunities for the use of biomass.

Process	Replacement		The use of biomass in the process
	Partial	Full	
Coke making	✓		As a reducing agent and fuel in coke making or BF [35, 36, 37]
Sintering / Pelletizing	✓	✓	As solid fuel (coke or anthracite) [35, 37]
Ferrous burden	✓	✓	Mixed within the ferrous burden layers [35]
Carbon-ore composite pellet / SRP	✓	✓	As carbon-ore composite pellets [37]
PC injected	✓	✓	As a tuyere injectant (most commonly used) [33,36, 37]
EAF / Re-carburizer in steelmaking		✓	As coal / coke [37, 38, 39]

3.1 Biomass use in coke making and sintering process

To understand the importance of mitigating the CO₂ emission and environmental impacts of the coke making in BF system, substitution of fossil fuel with biomass sources such as charcoal from wood, woody agricultural product, wastes, etc. is proposed. [40] Biomass is a carbon source in which the CO₂ is released from its combustion. This reaction does not increase GHG concentration in the atmosphere due to carbon neutral which refers to the balance of carbon emission with carbon removal. Biomass-based reducing agents can be used as coke prepared by substituting a portion of the coal blend and as an auxiliary fuel injected directly into the furnace as shown in Fig. 9.

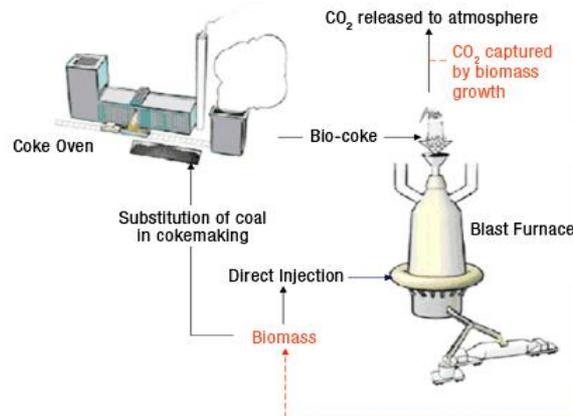


Fig. 9 Illustration of biomass used in blast furnace [40].

The substitution of charcoal as an alternative fuel for coke breeze in a simulated Japanese Steel Mills sinter blend was investigated. [41] The sinter mixtures containing charcoal were clearly less dense and formed. Therefore, the sintering productivity was maintained as the charcoal substitution rate increased from 0 to 25%.

3.2 Biomass use in BF via Pulverize Coal Injection (PCI) and ferrous burden

Theoretically, biomass charcoal properties are close to Pulverize Coal (PC) which is injected in modern BF. Hence, PC can be substituted by charcoal without any effect from alkali problem. [42] Biomass charcoal can rapidly react and reduce iron ore (~1.5 times) at a lower temperature because it has a higher reactivity due to its porous structure and high surface area compared to the PC and coke. [43] The replacement of PC as the BF tuyere injectant is the application with high potential for CO₂ emission reduction. [44] Charcoal is the most effective biomass charcoal for direct injection in terms of GHG mitigation. Previous research [40] has shown that complete substitution of fossil fuel injection by biomass could reduce the GHG emission of steelmaking by 25%.

The use of the “carbon-neutral” material such as biomass is one of alternative options which can reduce the CO₂ emission from the ironmaking process. Biomass is considered to be carbon neutral because it releases the same amount of carbon during combustion, as it absorbs CO₂ while growing. However, feedstock production also absorbs carbon during growth and then released O₂. [45-48] Whereas, fossil fuels such as coal, oil and natural gas, etc. pollute the environment by adding extra CO₂ to the atmosphere. [18] The carbon-neutral revolution for ironmaking production from biomass crops is demonstrated in Fig. 10

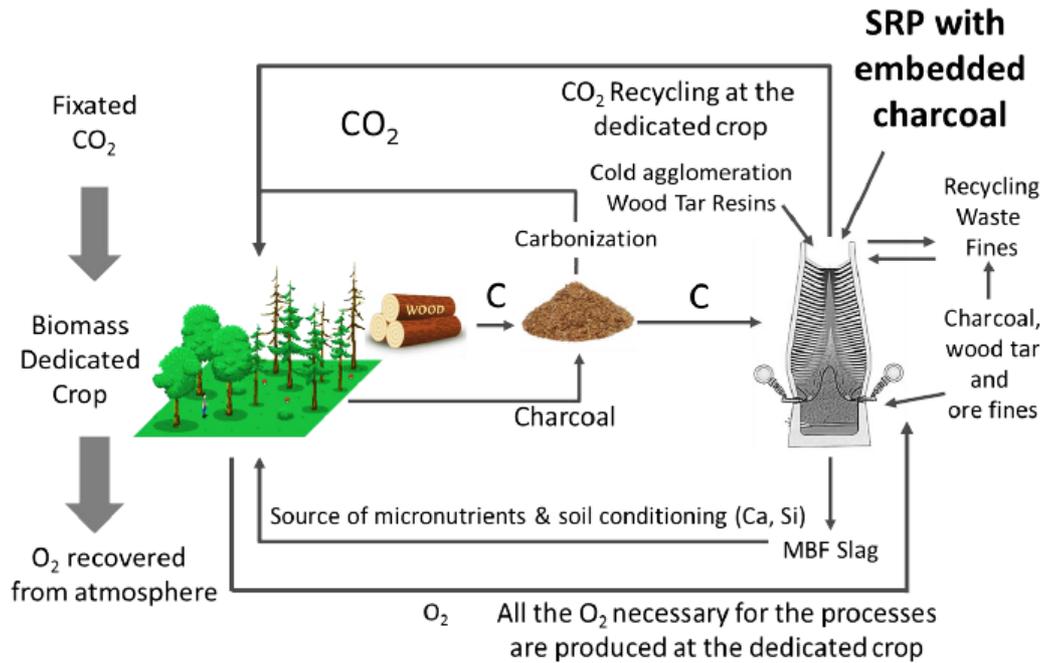


Fig. 10 Illustration of the closed cycle for iron production from biomass crops, including the combination of biomass into SRP as BF charge [18].

Biomass is embedded in SRP and applied in PC injection into BF to generate reduction gas as shown in Fig. 10. [49] For instance, there are several mini steel mills, especially in Brazil, which are operated and charged with lump charcoal and Charcoal Powder Injection (CPI) from eucalypts instead of coke. [50, 51] However, the use of charcoal-SRP is likely unsuitable in larger BF due to the lower strength of charcoal compared to coke. [46] Therefore, commercial blast furnaces that use wood charcoal have a capacity of only 300,000 ton/year. [52]

3.3 Biomass use in alternative ironmaking process (DRI DR, SR)

Direct reduction (DR) of iron process is the conversion of iron ore to metallic iron in solid state by using a reducing gas or syngas, which produced from natural gas reforming. Gasification from biomass has been concerned as an alternative for ironmaking process that could contribute to a sustainable iron and steel industry. [53] Generally, chemical and physical properties of biomass charcoals are similar to that of coal and coke. Although the chemical similarity is relatively easy to achieve, in practical, the physical properties such as density, mechanical strength and reactivity might be required considerable amounts of processing to improve. It is usually conceded that the replacement of biomass charcoal with high mechanical strength that is similar to that of BF lump coke structure is prohibitively expensive. [47]

Recently, the developments of the new technology for the agglomeration of fine concentrate have been carried out. [54, 55] The ironmaking process using oxidized pellets as a raw material including the production of metallized pellets are used further process such as DR and EAF. [56, 57] The technology of briquetting can be applied for the recycling of fine iron and wastes such as sludge, dusts, fines, etc. The possibility to apply Stiff Vacuum Extrusion (SVE) for the

agglomeration of the natural and fine materials generated during ironmaking has been studied. [54] The products of Extrusion Briquettes (BREX) from SVE process were subjected to the high temperature reduction. BREX before and after the reduction process are shown in Fig. 11. [58]

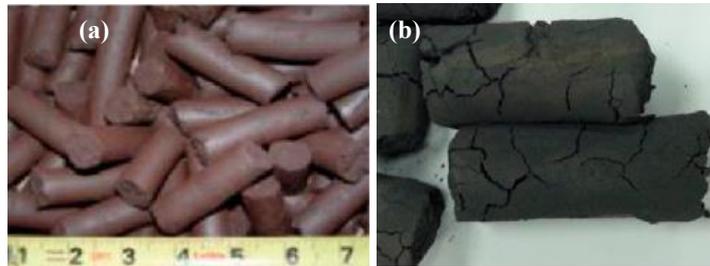


Fig. 11 Raw BREX (a) and Reduced BREX (b) [58].

Previous research [59] has shown that the iron ore and coal BREX could be considered as the alternative to the iron and coal pellets for the reduction process in furnaces such as the Rotary Hearth Furnace (RHF). Full-scale testing of the experimental of BREX behavior has been conducted [54, 56] in the industrial Midrex reactor operated by J.C. Steele & Sons, Inc. The results of the preliminary analysis reveal that the recycling of BREX would help to increase the levels of steel productivity and release significant area occupied by dumped wastes.

Normally, coal and charcoal are used for carbonization especially in pre-reduction of iron oxide pellets for smelting reduction process [60, 61]. From the carbonization data [58], it was proposed that novel carbon composite iron oxide pellets using semi-charcoal and the residual volatile matter (VM) in charcoal could be effectively used. Data analyses of the carbonization gases from coal and woody biomass have been carried out to evaluate their chemical and thermal possibility. These possibilities of biomass uses are defined by various properties such as moisture content, volatile matter, fixed carbon content, ash content, etc. [62]

3.4 Biomass use in Steelmaking process

Steelmaking process produces steel by melting steel scrap in an EAF. Direct reduced iron (DRI) with low carbon content is sometimes used when steel scrap is in short supply. Carbonaceous material is added to the EAF process for three purposes: (1) to provide reduced atmosphere during melting, (2) to perform slag foaming by injecting of carbon which can protect the heat loss of the arc and save electrical energy costs and (3) to produce specific steel grades by adding re-carburizer of carbon to the ladle after tapping from the EAF. [57] The three purposes demonstrate opportunities for substitution of biomass with carbonaceous materials in the EAF process. [35] Steel re-carburizer is normally a coal-based char and is added into the ladle during tapping and at the ladle furnace. Charcoal has been shown to be suitable for steelmaking process. [38, 63] Moreover, charcoal strength has no significant effect in EAF process due to the size of the furnaces and the fine charcoal mixed with hot blast. [64]

4. Charcoal production

Speaking of raw biomass, it is inefficient for the application of iron and steelmaking production due to its high moisture content which results in a relatively low calorific value of the fuel, low carbon content and low specific energy. [16] It should be transformed to charcoal via a pyrolysis process before use because of its original properties. [65] Charcoal making process is demonstrated in Fig. 12. In this scenario, woody biomass is transported into a storage shed. From there, it is conveyed to a hopper. Raw feed materials are broken into chips by a chipping unit. The chipper produces particles of generally uniform size within a specified acceptable range. Some classification and sorting of particles is required at this stage. The wet chips are conveyed to a bed dryer unit by the hot air. The dry biomass chips are sent to the pyrolysis unit. Some of the combustible gases generated from pyrolysis of biomass are burnt to run the process. The remaining water in the biomass exits from the unit as vapor. The remaining gases are condensed to form bio-

oil that can be used on-site or supplied to other processes as thermal fuel. The main product from this process is charcoal which is discharged from the bottom of the pyrolysis unit. [16] There are three types of primary fuels that could be produced from biomass as follows: [48]

1. Liquid fuels (ethanol, biodiesel, methanol, vegetable oil and pyrolysis oil)
2. Gaseous fuels (biogas (CH_4 , CO_2), producer gas (CO , H_2 , CH_4 , CO_2 , and H_2O), syngas (CO , H_2), and substitute natural gas (CH_4))
3. Solid fuels (charcoal, torrefied biomass, biocoke, biochar)

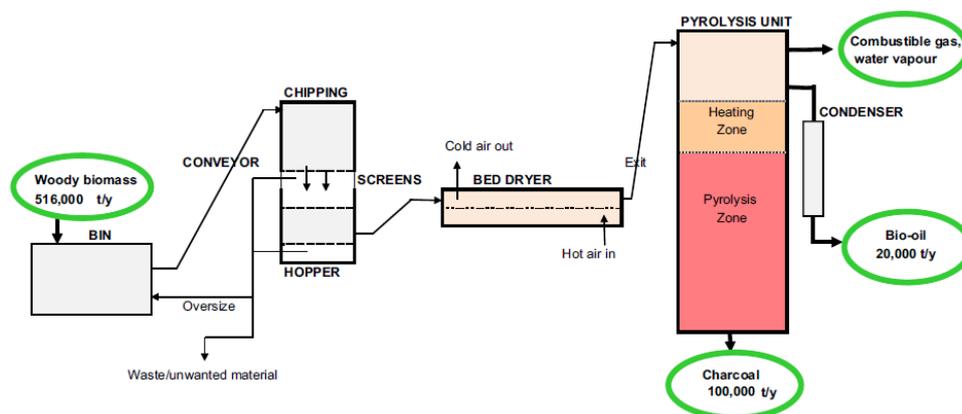


Fig. 12 Conceptual flowsheet of a charcoal plant in the state of New South Wales, Australia with an annual capacity of 100,000 t/y charcoal plant [16].

4.1 Pyrolysis process

The pyrolysis process is a process in which biomass is decomposed into gas, liquid and solid by rapidly heating biomass above 300-400°C. Large hydrocarbon biomass molecules are broken down into smaller molecules. Liquid fuel or bio-oil products are produced by fast pyrolysis, whereas slow pyrolysis produces some gas and solid charcoal. [48] Woody materials have special characteristics when carbonized at high temperature. [62, 66] The carbonization was completed after increasing temperature until arriving at a maximum carbonization temperature and released some Volatile Matter (VM). [62]

4.2 Torrefaction process

Torrefaction process is being considered for effective utilization of biomass as a clean and applicable solid fuel. In this process, the biomass is slowly heated to 200-300°C under controlled atmosphere condition. Torrefaction modifies the chemical structure of biomass hydrocarbon to increase its carbon content while reducing its oxygen. Moreover, torrefaction increases the energy density of the biomass and absorb moisture from the air. [48]

4.3 Gasification

The chemical reactions take place inside the biomass gasifier. Sequentially, the following physicochemical reactions are (1) Drying (>150°C), (2) Pyrolysis (devolatilization) (150-700°C), (3) Combustion (700-1500°C) and (4) Reduction (800-1100°C). The chemical reactions of drying, pyrolysis and reduction are endothermic reaction which absorbs heat. Moisture of the fuel is removed in drying process. Non-condensable gases, liquids and water vapor are removed in the pyrolysis process leaving behind charcoal. [67] Whereas, combustion is an exothermic reaction where the fuel is oxidized. [68]

5. Biomass charcoal upgrading for ironmaking process

The most studied biomass-based reducing agent is charcoal, which usually has low ash content and low amount of harmful components. [69] Pretreatment of the biomass before using is considered in a pyrolysis process where the carbon content and heating value are raised and the

oxygen content is lowered which is beneficial for the ironmaking process. Physicochemical properties of charcoal can be upgraded into a more efficient form but at the cost of a yield decrease. [65, 70] The biomass conversion routes can be summarized in Fig. 13. [48] The conversion can be achieved through either biochemical conversion (fermentation) or thermochemical conversion (pyrolysis, gasification). In biochemical route, large biomass molecules are broken down into smaller molecules by bacteria or enzymes which occur very slowly without requiring high energy. The main products of biochemical conversion are methane, carbon dioxide and solid carbon residue. In thermochemical route, the production of thermal energy is the main driver for thermochemical process by which physicochemical reactions can be achieved through pyrolysis / torrefaction, gasification, liquefaction and/or combustion, sequentially. The necessary conditions for thermochemical route are given in Table 2. [2, 48]

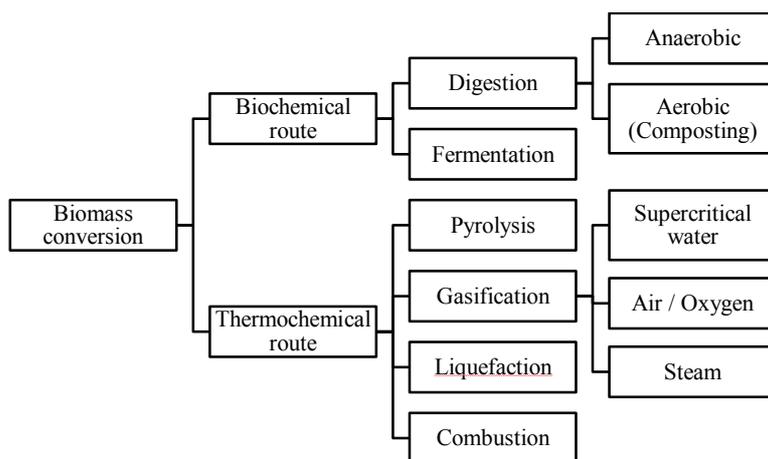


Fig. 13 Different options for conversion of biomass into fuel gases or chemicals [48].

Table 2 Conditions for biomass thermochemical conversion [48].

Process	Temperature (°C)	Pressure (Mpa)	Catalyst	Drying
Liquefaction	250 - 330	5 - 2	Essential	Not required
Pyrolysis	300 - 600	0.1 - 0.5	Not required	Necessary
Combustion	700 - 1400	~ 0.1	Not required	Not essential but may help
Gasification	500 - 1300	~ 0.1	Not essential	Necessary
Torrefaction	200 - 300	0.1	Not required	Necessary

The available biomass upgrading technologies for charcoal production include pelletization, pyrolysis, torrefaction, steam explosion, hydro-thermal carbonization and lignoboost as can be summarized in Fig. 14. [36]

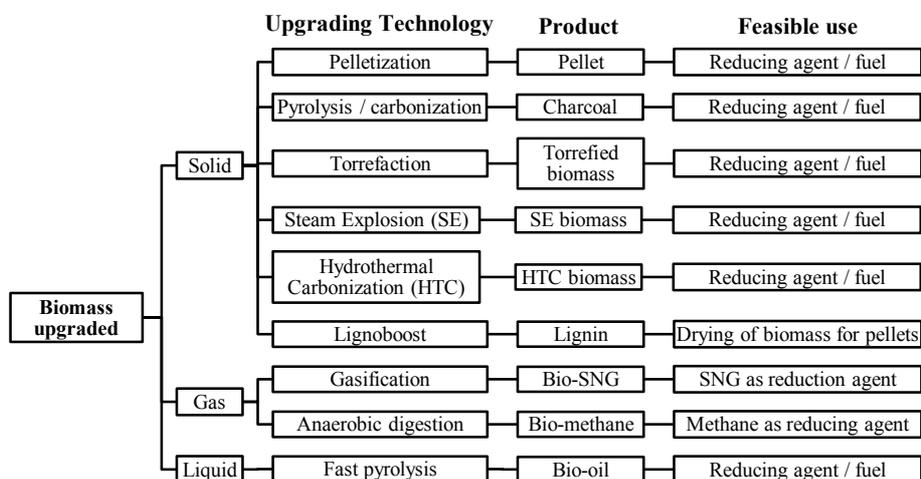


Fig. 14 Biomass upgrading technologies according to product types [36].

The physical and chemical properties of different kinds of biomass charcoal compared to coal and coke are given in Table 3. [36, 61, 64, 71, 72] Charcoal is an ideal reducing agent for ironmaking process because there is no sulphur and contains very little ash (< 3% wt.). [64] Its bulk density and energy density are considerably different from coal and coke. Different physical properties between charcoal and fossil fuels can be seen through their microstructures. Coal and coke are dense and compact whereas charcoals are highly porous. [49] For instance, black pine charcoal has higher porosity than coke around 3 times. The porosity measurements have been studied and can be compared with visual observations by the Mercury Intrusion Porosimetry (MIP) method as shown in Fig. 15. [73]

Table 3 Physical and chemical characteristics of charcoal and coke [36, 61, 64, 71, 72].

Parameter	Unit (db = Dry Basic)	Material					
		Wood chip [36, 71, 72]	Wood pellet [36, 71, 72]	Torrefied wood pellet [36, 71, 72]	Charcoal [64]	Coal [36, 71, 72]	Coke [64]
Fixed carbon	%wt ^{db}	16-25	16-25	22-35	>70	50-55	85-88
Volatile matter	%wt ^{db}	75-84	75-84	55-65	20-25	15-30	1-3
Moisture	%wt ^{db}	30-55	7-10	1-5	~10	10-15	~2-4
Ash	%wt ^{db}	0.4-2.0	0.2-0.4	0.5	~3	~10	>10
Sulphur	%wt ^{db}	n/a	n/a	n/a	~0	0.5-3.1	0.7-1.2
Phosphorus (P ₂ O ₅)	%wt ^{db}	n/a	n/a	n/a	0.08	n/a	0.01-0.03
Crushing strength	kg/cm ³	n/a	n/a	n/a	30-40	n/a	100-150
Bulk Density	kg/m ³	200-300	550-650	650-800	230-260	800-850	400-500
Calorific value	kcal/kg	1672-2866	3582-4060	4298-5731	6800-7200	5492-6686	6500-7200
Biological degradation	-	Fast	Moderate	Slow	Slow	None	None
Transport cost	-	High	Medium	Low	Medium	Medium	Low

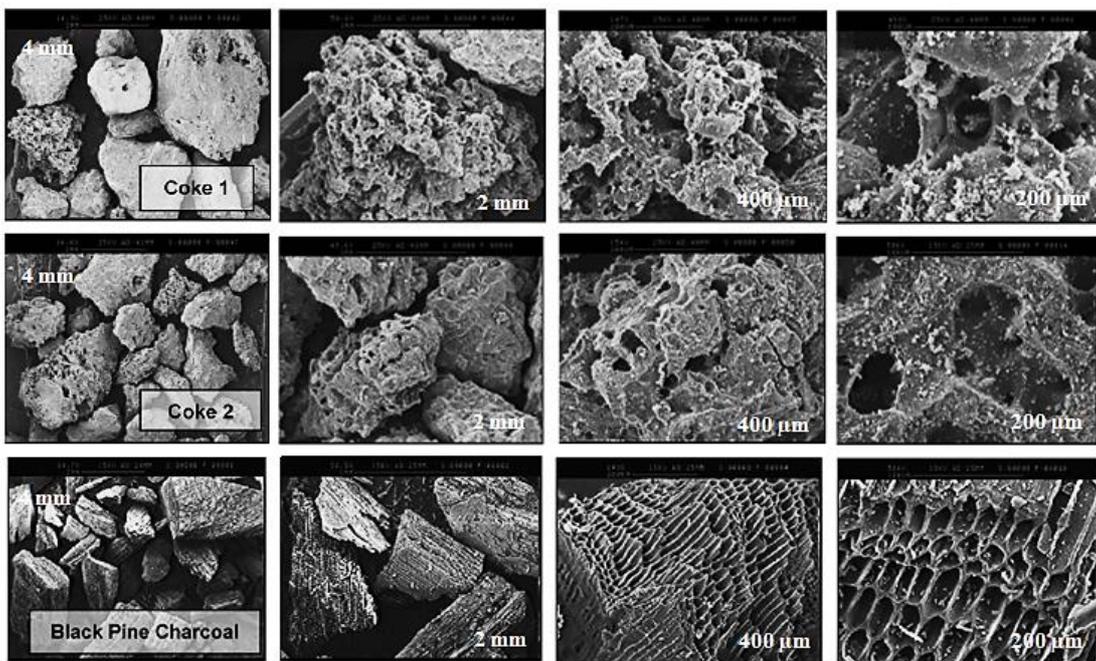


Fig. 15 Porosity measurements by using Mercury Intrusion Porosimetry (MIP) of charcoal and coke [73].

6. Environmental performance of biomass in an integrated iron and steelmaking process

Substitution of fossil fuels by biomass charcoal in an integrated steel plant is complex due to the technical restrictions. [74, 75] The most conventional use of biomass within the BF-BOF route is in the form of charcoal, which requires upgrading using pyrolysis process. [1] Evidence [39] has shown that biomass products have potential to reduce approximately at 32-58% of CO₂ emissions in the BF-BOF route as shown in Table 4. Several research [76, 77] have studied that unreduced carbon-ore composite pellets or briquettes can be charged in ironmaking process. However, charcoal is unsuitable for use as a full replacement of the lump coke charged to medium and large BF due to its insufficient strength. Nevertheless, it has been replaced some or all of the nut coke by mixing with the ferrous burden layers. [39] Charcoal Powder Injection (CPI) is already practiced in mini BF in Brazil [50] with an injection rate around 100-190 kg/t HM (ton of hot metal). [78] Other research [79] has estimated that charcoal injection rates of 200-225 kg/t-HM may be feasible for large BF.

Table 4 Proposed applications for charcoal in a typical Australian integrated iron and steelmaking operation [39].

Application	Basic	Net emission reduction	
		t-CO ₂ /t-crude steel	% of CO ₂ emissions
Sintering solid fuel	50 - 100% replacement of coke breeze or anthracite at 45-60 kg-coke/anthracite / t-sinter (and 1.7 t-sinter/t-HM)	0.12 - 0.32	05-15
Cokemaking blend component	2 - 10% of coking coal blend, with coke used at 300 - 350 kg-coke / t-HM	0.02 - 0.11	1-5
BF tuyere injectant	100% replacement of injected coal (PCI) at 150 - 200 kg-coal / t-HM	0.41 - 0.55	19 - 25
BF nut coke replacement	50 - 100% replacement of 45 kg-nuts / t-HM	0.08 - 0.16	3 - 7
BF carbon/ore composites or BOF pre-reduced feed	5 - 10% of iron in charcoal/ore pellets to BF or charcoal-based pre-reduced feed to BF or BOF	0.08 - 0.15	4 - 7
Steelmaking re-carburizer	100% replacement of 0.25 kg-char / t-crude steel	0.001	0.04
Note:	- HM is hot metal (i.e. liquid iron from the BF)		
Totals		0.70 - 1.26	32- 58

- PCI is Pulverized Coal Injection assumed to be 75% C
- Coke, coke breeze, anthracite and re-carburizer are assumed to be 85% C
- It was assumed that the plant's output of HM and crude steel were equal
- Results assumption are based on direct materials substitution only

The EAF process has used steel scrap rather than iron ore, as a result, the overall CO₂ emissions per tonne of crude steel are typically lower than the integrated route for around 0.5 ton. Table 5 shows that the opportunity for Australian EAF steelmakers to mitigate CO₂ is approximately 5.9-11.5%. [39]

Table 5 Proposed applications for charcoals in a typical Australian EAF steelmaking operation [39].

Application	Basic	Net emission reduction	
		t-CO ₂ /t-crude steel	% of CO ₂ emissions
Charge carbon	50 – 100% replacement of 12 kg-coke / t-crude steel	0.019 - 0.037	3.8-75
Raw materials, electrodes, etc.	0% replacement of 4.5 kg-C / t-crude steel	0.02 - 0.11	0 (of 3.5)
Natural gas heating	0% of 3 Nm ³ /t-crude steel (0.54 t-C / t-crude steel)	0.41 - 0.55	0 (of 0.5)
Slag foaming agent	50 – 100% replacement of 5 kg-coke / t-crude steel	0.08 - 0.16	1.6 – 3.1
Steel re-carburizer	50 – 100% replacement of 1.4 kg-char / t-crude steel	0.002 – 0.004	0.5 – 0.9
Note:	- Coke, foaming agent and re-carburizer assumed to be 85% C		
Totals		0.71 - 1.26	32- 58

- No improvements in electrical usage were considered here.
- Results assumption are based on direct materials substitution only

Carbon life cycle in conventional BF ironmaking was examined for the purpose of establishing a base case for comparison as shown in Fig. 16(a). [80] The Pulverized Coal Injection (PCI) rate of the process was assumed to be 140 kg/t HM. The carbon life cycle in ironmaking system consists of

4 sub-systems, namely (1) coal mining, (2) coal transportation, (3) cokemaking process and (4) ironmaking process.

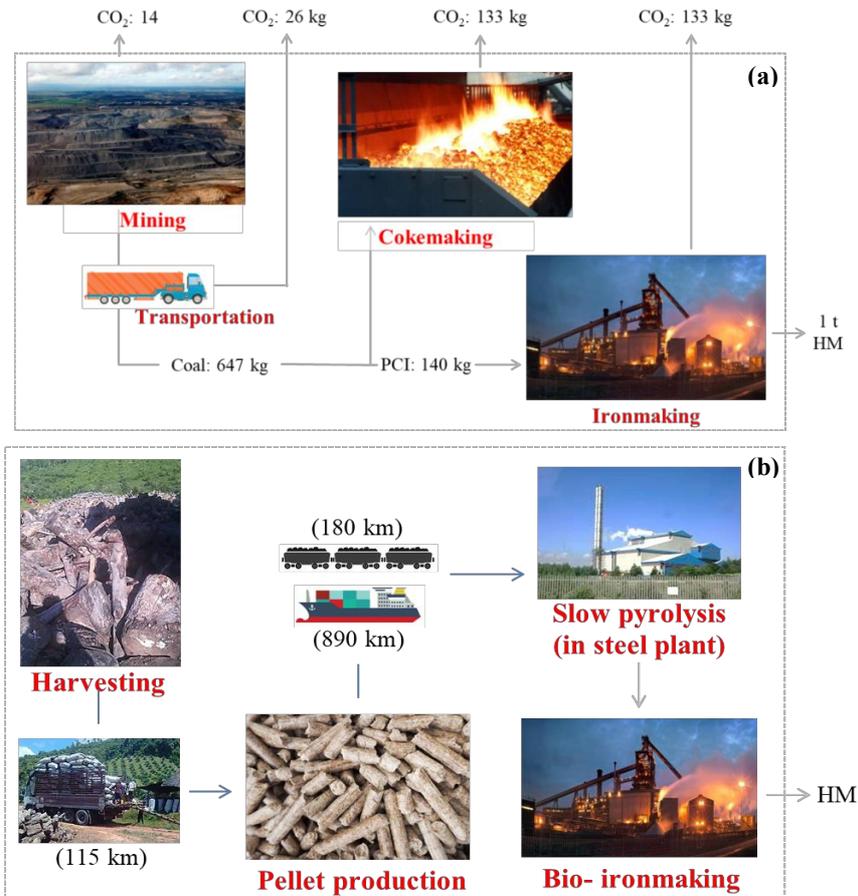


Fig. 16 Carbon life cycle in (a) conventional ironmaking and (b) wood pellets for bio-ironmaking.

Emission contribution of each sub-system was calculated as shown in Table 6. The total emission in the carbon life cycle associated with one ton of hot metal produced by the conventional BF process is totally 1,552 kg CO_{2eq}/t HM. Biomass-based ironmaking route involved the collection of forestry residues as raw materials and their conversion into charcoal prior to long-range transportation. The biomass residues from forestry operation as raw materials lead to emissions associated with their growth and harvesting. However, this is part of regular forestry operations, these emissions are excluded from the calculation. Moreover, the transportation of high-carbon density charcoal has also lowers emission related to long-range transportation of materials. As a result, CO₂ emission of biomass-based ironmaking processes including wood pellet bio-ironmaking and charcoal bio-ironmaking as shown in Fig. 16(b) are significantly reduced to 261.8 kg CO_{2eq}/t HM and 62.8 kg CO_{2eq}/t HM respectively.[80]

Table 6 Comparison of Emissions in Different Ironmaking Pathways [80].

Conventional ironmaking	Emission (kg CO _{2eq} /t HM)	Wood pellet bio-ironmaking	Emission (kg CO _{2eq} /t HM)	Charcoal bio-ironmaking	Emission (kg CO _{2eq} /t HM)
Coal mining	14	Harvesting and transportation (115 km)	144.2	Residues collection and transportation (80 km)	20.3
Coal Transportation (46 km rail, 434 km barge)	26	Pellet Transportation (Rail 180 km, Vessel 890 km)	39.1	Charcoal Transportation (Truck 1200 km)	41
Cokemaking	133	Pellet production and pyrolysis	78.5	Charcoal making	1.5
Ironmaking	1379	Ironmaking	0	Ironmaking	0
Total	1,552	Total	261.8	Total	62.8

7. Discussion and future prospects

Biomass offer attractive and affordable cost, high source of energy as reducing agents in iron and steelmaking process. This is one of the high potential improvement ways to decrease CO₂ emissions. As a result, the steel industry could turn to use biomass to replace fossil in order to reduce the fossil CO₂ emission, production costs as well as exploit bio-waste materials as a raw material in iron and steel making process. [81-86] Charcoal is a manufactured product that its physical and chemical properties can be modified or upgraded to optimise each process of iron and steelmaking process. The production of charcoal with specified properties requires careful control of the pyrolysis process. [37] The sustainable biomass utilization in iron and steelmaking process research has been studied for both the integrated BF-BOF and EAF steelmaking process routes. Biomass applications remain prospective in steel plant operations

The use of biomass charcoal for iron and steelmaking in Thailand will be further studied. Several types of renewable carbon sources such as oil palm, palm kernel shell, coconut shell, rubber wood, bamboo, etc. as shown in Fig. 17 [87-90], which have slow of biological and thermal degradation of charcoal, are locally available. Our future research will work on the thermal gravimetric analysis (TGA) device to investigate the reduction behavior of SRP with various kinds of embedded reducing agent. An online gas analyzer at KMUTNB will be used to quantify the offgas composition during reduction process. Then, the evaluation of the kinetics parameters will be calculated by numerical modelling.



Fig. 17 Biomass residues: a) oil palm, b) palm kernel shell, c) coconut shells, d) rubber wood and g) bamboo.

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