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Woody biomass waste derivatives in decarbonised blast furnace ironmaking process

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Abstract: Modern ironmaking process relies significantly on fossil-related fuels, which ultimately results in the enormous CO_2 emitted into the atmosphere. Biomass of plant origin, as a carbon-neutral energy source, has been considered as an alternative to fossil-based reducing agents such as coke. This study aims to investigate the potential of three woody biomass waste derivatives produced from biomass waste pyrolysis and gasification, namely charcoal, bio-oil, and bio-syngas, as the reducing agents in blast furnace. A model based on heat and mass balance and Gibbs free energy minimisation is proposed to simulate an ironmaking process with assistance of these derivatives. The effects of specific composition of biomass waste derivatives on process operation, CO₂ emissions, and coke replacement are explored. Also the effects of H₂-rich gas produced from biomass waste gasification on the blast furnace operation are estimated. Results indicate that reactions of woody biomass waste derivatives in blast furnace are complex and greatly dependent on composition. When charcoal has a higher carbon content, lower CO₂ concentration is found from the top gas. The higher content of hydrogen in bio-oil will inhibit further reduction in CO₂ emissions. Bio-syngas with H_2/CO ratio of 1.3 proves to have a remarkable potential to reduce CO_2 emissions. From the aspects of available biomass waste resources across the world, woody biomass waste derivatives as reducing agents are more suitable for countries with the limited pig iron production. This study provides a reference on the future of moving forward the decarbonised ironmaking by using woody biomass waste derivatives.

Keywords: Woody biomass waste derivative; Reducing agent; CO2 emissions; Blast furnace; Hydrogen

Graphical abstract



Conclusions

- Reactions of woody biomass waste derivatives in blast furnace are composition dependent.
- Woody biomass waste derivatives as reducing agents are suitable for countries with limited pig iron production.









Results

CO2 Net

Nomenclature

Abbreviations

BF	Blast furnace
BFG	Blast furnace gas
BO	Bio-oil
BOF	Basic oxygen furnace
CC	Charcoal
FC	Fixed carbon
HMB	Heat and mass balance
LHV	Lower heating value
PC	Pulverised coal
RAFT	Raceway adiabatic flame temperature
RFT	Raceway flame temperature
SDGs	Sustainable development goals
VM	Volatile matter
WGS	Water gas shift
Notations/Symbols and Units	
Cp	Specific heat, J·kg ⁻¹ ·K ⁻¹
DE	Specific direct emissions, t t ⁻¹
f	Conversion factor
Н	Enthalpy, $kJ \cdot mol^{-1}$
т	Mass flow rate, t·s ⁻¹
M	Mass, ton
MOL	Molar mass, g⋅mol ⁻¹
r	CO ₂ reduction rate
Т	Temperature, °C
Y	Annual biomass yield, kg·year-1
Greek letters	
α	Share of dry matter in wet wood
γ	Product yield
η	Efficiency
κ	Coke replacement ratio
λ	Volume fraction

φ	Mole fraction
ω	Mass fraction
Subscripts	
bio	Bio-reducers
С	Carbon
i	The <i>i</i> th input flow of the process
in	Inlet
j	The $j_{\rm th}$ output flow of the process
n	The <i>n</i> th gas component in the syngas
HM	Hot metal
out	Outlet
ref	Reference
tot	Total

1. Introduction

As one of the most energy-intensive industries, iron and steel sector ranks as the highest CO_2 emitter among heavy industries, with about 2,800 Mt CO₂ annually, accounting for 8% of total global energy system emissions [1]. The global steel demand is expected to persistently grow by more than a third to 2050, prompting iron and steel industry to urgently adopt decarbonisation technologies to meet climate protection versus change targets [2] and align with sustainable development goals (SDGs) of energy, industry, and climate action (SDGs 7, 9, 13) [3]. Along the entire steel supply chain, pig iron production remains the most important unit, and blast furnace-blast oxygen furnace (BF-BOF) route accounts for almost 80% CO₂ emissions of iron and steel industry [4, 5]. This is because fossil based coke is the main heat source and reducing agent for BF-BOF route of ironmaking, which dominates in general the modern iron production process [6]. Lots of process modifications have been developed to improve blast furnace (BF) efficiency and especially reduce CO_2 emissions [7]. These involve low-carbon transition of the BF ironmaking process by switching to a scrap-electric arc furnace or direct reduced iron route, revealing that the permanent cessation of the BF ironmaking is very high on the agenda [8, 9]. The life of the BF ironmaking is inevitably shortened, and most of process enhancement options for BF alone have reached their limits of improvement. The question of what measures can still be achieved for low-carbon BF process before 2050, which is approaching fast, has drawn attention [10]. As one of the options, the use of woody biomass waste-based reducing agents (bio-reducers) in BF maintains its momentum to reduce fossil energy dependence and CO₂ emissions [11-13].

Woody biomass waste is normally regarded as plant materials extracted from forests that lack significant commercial worth [14]. Since carbon content of woody biomass waste is lower in comparison with common fossil based reducing agents in iron and steel production processes, raw biomass waste should better be upgraded to a higher carbon content material, i.e., their derivatives or value added by-products through various technologies [15]. Thermochemical conversion technologies generally make it possible to convert biomass waste into solid, liquid and gaseous bio-reducers that can be more effectively utilised in the metallurgical and chemical industries [16]. The primary function of the reducing agents used in the BF ironmaking process is to provide reducing gases to remove the oxygen contained in the iron oxide, which can be achieved by the high carbon content included in the bio-reducers. Besides, bio-reducers can supply heat from the combustion process of carbon with hot blast [17]. Bio-reducers are usually used as an auxiliary reducing agent and cannot fully replace the top-charged coke during the ironmaking process [18]. This is because lower strength of bio-reducers at high temperature compared to that of coke provides difficulty in supporting the skeleton of BF below the melting zone [19].

The major solid bio-reducer, i.e., charcoal is derived from wood-based waste through slow pyrolysis, is highly carbonised and has properties well comparable to coke injectant and pulverised coal (PC) used in

BF [20]. Primary studies of the charcoal utilisation in the BF process focus on combustion behaviour in the raceway [21] and effect of charcoal addition on the properties of coke [22], indicating addition of charcoal can increase the burnout along the centreline of BF and the reactivity of coke with CO₂. When injecting charcoal with low ash and high basicity, slag volume and coke rate both decrease and the furnace productivity of hot metal increases [23]. Charcoal injection rate of up to 200 kg·t⁻¹_{HM} with a coke rate of around 260 kg·t⁻¹_{HM} has been achieved when charcoal has 88.26 wt.% carbon content [24], and also the injection of charcoal fines has now been used in Brazilian BF applications of ironmaking [25]. For liquid bio-reducer, bio-oil produced from fast pyrolysis of biomass is considered as one of the candidates because of its comparable properties to fossil-based heavy oil [15, 26]. The composition of bio-oil contains a mixture of oxygenated and phenolic compounds which varies largely with different nature of biomass waste [27, 28]. At a bio-oil injection rate of 140 kg·t⁻¹_{HM}, coke consumption has been estimated as 455 kg·t⁻¹_{HM} by using the mathematical modelling [29].

Gaseous bio-reducer produced through biomass waste gasification, also called as bio-syngas, is similar to hot reducing gas due to the presence of H_2 and CO, making it one of the most widely used auxiliary reducing agents [30]. The properties and profitability of bio-syngas mainly depend on their feedstock quality, gasification process operating parameters and gasification medium, gasifier type, thermodynamic operating conditions, and catalyst and sorbent [31, 32]. To increase the content of H_2 and CO in the biosyngas, particle size and moisture of biomass feedstock are controlled prior to biomass gasification [33]. Bio-syngas as an auxiliary fuel has been investigated with co-injection of coal in BF, showing that injection of bio-syngas can increase the volume-average temperature of the raceway and the endpoint burnout of PC [34]. Bio-syngas has also been compared with syngas produced from other feedstocks and gasification technologies, and bio-syngas has the advantages to reduce net CO_2 emissions [35]. The process of utilising bio-syngas is designed to produce direct reduced iron by chemical reactions based on H_2 and CO [36, 37]. The effects of H₂ and CO on the reduction behaviour of iron oxide have also been investigated, showing that H_2 plays an essential role for pure metallic iron production [38, 39]. Meanwhile, biomass waste-based H_2 gas is regarded as one of the approaches to keep H_2 production sustainable [40]. Injection of H_2 -rich gas driven from biomass into BF is studied in terms of biomass waste devolatilization, gasification and combustion characteristics [41]. Hydrogen shaft injection's influence on in-furnace phenomena and BF operational characteristics is studied by using a multi-fluid BF model [42]. Both bio-syngas, i.e., contains a mixture of CO and H₂, and H₂-rich gas produced from biomass waste gasification become important components to fulfil the applications of bio-reducers in the BF ironmaking.

To assist evaluating the validity of lignin-rich biomass waste derivatives used in BF and comparing the ability of bio-reducers to replace coke and reduce CO_2 emissions, heat and mass balance (HMB) models are essential as they can establish chemical reactions and heat transfer process in BF [43]. It is important to

determine and design the input rate of the BF operation with new and more sustainable reducing agents. Most HMB models separate the furnace into certain zones/stages based on chemical reactions of iron oxide reduction. Based on material and thermal balance, a model has been developed to predict the required raw material, BF gas (BFG) rate, and the raceway adiabatic flame temperature (RAFT) [44]. A one-dimension static HMB that divides BF into upper zone, thermal reserve zone, and lower zone, was used to study bio-reducers as BF injectant and revealed that charcoal from pyrolysis can fully replace PC, while torrefied woody biomass and wood pellets could replace PC injection by 23 wt.% and 20 wt.%, respectively [19]. The HMB model is also used to estimate BF performance with various qualities of biochar and sustainably produced liquid ethanol and biodiesel, in comparison with conventional coal types [45]. Hydrogen utilisation in BF can be estimated by the HMB model, which is easy to calculate the decreased coke consumption in BF due to the contribution of H₂ [46]. Through the overall analysis of HMB, the most favourable operation conditions of the BF process by using direct reduced iron can be provided [47].

Although the review gives a summary of the replacement of fossil-based reducing agents in ironmaking process with bio-reducers, and the use of HMB models into such scenarios, there is a dearth of analysis on how to manage large amount of inherent CO₂ emissions from bio-reducer itself. In addition, previous studies focused mostly on the effects of variations in amounts of bio-reducers and have rarely reported the effects of the specific composition of bio-reducers, such as carbon, oxygen, and hydrogen elements in the charcoal, on CO₂ emissions and coke substitution in BF, which brings us more deep thoughts on the decarbonisation in iron and steel industry. To fill the research gap, this study partially substitutes coke with bio-reducers in the BF ironmaking process by highlighting three novelties: (1) the BF ironmaking processes that operate with charcoal, bio-oil, and bio-syngas are designed to explore the effects of their specific compositions on CO₂ emissions and coke replacement rate; (2) an HMB model based on the Gibbs free energy minimisation for the BF process is proposed to simulate the processes among the reactions between bio-reducers and iron bearing materials; (3) the effect of H₂-rich gas produced from biomass waste gasification on the BF operation, reduction of iron oxide is also estimated. The study aims to figure out how to simultaneously enhance the reducing capacity and achieve low-carbon transition of the BF ironmaking process through insights on specific composition of bio-reducers. For a broader context, the availability of woody biomass waste feedstock is also evaluated and discussed based on the worldwide pig iron production and biomass waste conversion efficiency, with the aim of contributing to the future production and applications of bio-reducers for the BF ironmaking process.

2. Reactions of bio-reducers in the BF ironmaking process

The reduction reactions that remove O_2 from iron oxide occur primarily inside BF. The reaction involves a complex gas-liquid-solid three phase transformation. When coke is used as the only reducing

agent for hematite (Fe₂O₃) reduction, carbon has no immediate response with the metal, but has a Boudouard's reaction to produce CO first. Top charged coke continuously descends toward the layer of hot blast air and combusts in front of the tuyeres. The Boudouard equilibrium exists between solid carbon, CO_2 and CO, and is divided into two stages as Equation 1 and 2.

$$C + O_2 \to CO_2 \tag{1}$$

$$CO_2 + C \to 2CO \tag{2}$$

Reaction rates markedly accelerate with the increasing temperature. CO is heated up to approximate 2100 °C due to the exothermic oxidation of coke and injectants [17]. Then, CO gradually diffuses and rises through pores of ore particles due to the pressurised blast air, resulting in several steps reduction of Fe₂O₃. Phase equilibrium diagram of the Fe-O-C is shown in Figure 1a according to the Gibbs free energy of formation of each component [48]. In the presence of CO, Fe₂O₃ turns to be unstable and start its reduction to magnetite (Fe₃O₄). Curves of phase boundary reflect that Fe₂O₃ \rightarrow Fe needs at least a two-step reduction. When temperature is lower than 570 °C, direct reduction of Fe₃O₄ \rightarrow Fe proceeds easily at lower concentration of CO comparing with Fe₃O₄ \rightarrow wustite (FeO). In an opposite way, Fe₃O₄ \rightarrow FeO mostly occurs at higher temperature but needs a relatively smaller amount of CO. At the temperature over 570 °C, FeO \rightarrow Fe proceeds in the higher CO atmosphere. In the actual vertical direction of BF, iron ores continuously falling, temperature and CO concentration increase in the furnace. Therefore, the most common iron oxide reduction inside the BF processes happens as sequential three steps: $3Fe_2O_3 \rightarrow 2Fe_3O_4 \rightarrow 6FeO \rightarrow 6Fe$ [39].

In practice, all the BFs inject hydrocarbons through tuyeres to replace expensive and energy-intensive coke. Since coke layers with certain thickness also play a role of permeable route for ascending CO gas to move longitudinally across to iron ores, coke cannot be completely substituted by tuyeres injectants. Most typical used injectant is PC, and others include natural gas, fuel oil, and waste plastics [49]. It is demonstrated that reducing agents from tuyeres injection are feasible in the forms of solid, liquid, and gas. Properties of charcoal and bio-oil are similar to those of coal and fuel oil, respectively. After rapid entry with conveying gas, injected bio-reducers will react with O_2 from hot blast to form hotter CO. The reaction happening in the BF raceway between bio-reducers and O_2 can be reflected as Equation 3.

$$4C(bio - reducers) + 3O_2 \rightarrow 2CO + 2CO_2 \tag{3}$$

Reverse Boudouard's reaction, also known as disproportionation of CO, and carbonisation of CO are likely to happen simultaneously during the reduction of Fe_3O_4 . These reactions could also proceed during the reduction reactions by charcoal and bio-oil since they have a high content of fixed carbon [50], which can be represented as Equation 4 and 5.

$$2CO \to C + CO_2 \tag{4}$$

$$Fe_3O_4 + 6CO \rightarrow Fe_3C + 5CO_2 \tag{5}$$

Bio-syngas is expected to provide a reducing atmosphere using both CO and H₂. Although H₂ can be regarded as a reducing agent like CO, its reactions with iron-based chemicals are endothermic. Comparably, the reactions of Fe₂O₃ reduced by CO are exothermic. As can be seen from the Fe-H-O equilibrium diagram in Figure 1b, Fe₃O₄ is reduced by H₂ to metallic iron in a single step at the temperature lower than 570 °C. It is noted that this reaction also happens when partial pressure of H₂ is three times higher than that of H₂O, which cannot be satisfied around the magnetite reduction zone in BF. Temperature and gas composition at the upper part of BF are more suitable for the reaction of Fe₃O₄ \rightarrow FeO. In the area at 1300 °C that is close to tuyere level, the reduction behaviour of FeO \rightarrow Fe can be completed by less H₂ than CO. Rate of forward reaction of FeO \rightarrow Fe rapidly increases with more injection of H₂ through tuyere. When iron oxide reduction takes place with H₂ and CO, the gaseous mixture that contains H₂O, CO₂, H₂, and CO is easily formed in BF. The reaction called water gas shift conversion (WGS), which is temperature dependent happens among the gases is expressed as Equation 6.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{6}$$



Figure 1. The Baur-Glaessner equilibrium diagram for (a) Fe-C-O, (b) Fe-H-O.

3. System description of the BF operation with bio-reducers

3.1 Basic structure

A schematic representation of the conventional BF with different reducing agents is shown in Figure 2. The whole scheme links five blocks essential for the iron process together, i.e., BF unit, the fossil-based reducers unit, the burden unit, bio-reducers unit, and the atmosphere. Traditional fossil-based reducers, and bio-reducers both create CO_2 gases which are released from top of BF. A CO_2 loop with the return of the

much-needed carbon to woody biomass for photosynthesis would be formed among BF, the atmosphere, and woody biomass, which results in a CO_2 neutral ironmaking process by using bio-reducers. In this case, fossil-based coke and raw materials are fed into BF from the top. In contrast, the powdered charcoal, biooil, and bio-syngas are injected into BF via tuyeres, which require less mechanical strength than that of top charging.



Figure 2. Schematic diagram of the BF operation with the injection of bio-reducers.

3.2 Case studies

BF process is modelled based on mass flows which are unified as the same functional unit, i.e., one ton of iron product. The basic BF scenario operates with top-charged coke and PC injected through tuyere. Specific input data refers to a real BF operator and outlet stream results from simulation will be verified against the operator [51]. Charcoal, bio-oil, and bio-syngas are chosen as three kinds of bio-reducers in this study to replace PC and coke in BF, due to their similar properties to the fossil-based reducing agents, i.e., coke, heavy oil, and natural gas. A comparison of the ultimate and proximate analysis data of biomass waste derived charcoal and bio-oil are shown in Table 1 with characteristics of coke, PC, and fuel oil. These bioreducers differ significantly from each other because of different feedstock types and pre-treatment technologies. Herein, thirteen charcoals (CC 1 to CC 13) and seven bio-oils (BO 1 to BO 7) in Table 1 are used in the basic BF scenario.

Neme	Biomass waste	Biomass waste Proximate analysis (wt.%, dry)			Ultimate analysis (wt.%, daf)				Defense	
Name	feedstock	Ash*	VM	FC	С	0*	Н	N	S	- Reference
CC 1	Eucalyptus	0.49	18.82	80.69	88.26	8.79	2.71	0.21	0.03	[24]
CC 2	Oak	8.45	20.70	70.85	87.86	9.02	2.51	0.58	0.03	
CC 3	Olive	3.31	22.63	74.06	88.48	7.78	3.37	0.37	n.a	
CC 4 [†]	\	1.91	9.46	88.63	91.65	5.55	2.42	0.33	< 0.05	[52]
CC 5 [†]	\	4.30	13.31	82.39	86.38	10.77	2.30	0.50	< 0.05	
CC 6	\	4.60	21.80	78.20	83.70	12.00	3.10	1.10	0.10	[53]
			(daf)	(daf)						
CC 7	Radiata Pine	1.60	7.40	91.00	94.20	3.97	1.61	0.22	n.d	[54]
CC 8	Saltgrow Eucalypt	2.40	9.60	88.00	92.40	5.54	1.69	0.34	0.03	
CC 9	Scribbly Gum	2.80	4.20	93.00	95.06	3.69	0.80	0.45	n.a	
CC 10	Red Gum	2.70	18.80	78.50	84.84	12.32	2.53	0.30	0.01	
CC 11	Hardwood	4.50	24.2	71.30	80.70	15.26	3.30	0.70	0.04	[55]
CC 12	Mallee eucalypt	1.90	4.60	88.90	95.40	3.64	0.60	0.33	0.03	[56]
		(ar)	(ar)	(ar)						
CC 13	Pinus radiata	3.00	24.80	68.10	90.30	7.70	1.80	0.20	n.d	[57]
	(PT: 500 °C)	(ar)	(ar)	(ar)						
BO 1	Heterotrophic C.	n.a	n.a	n.a	76.22	11.24	11.61	0.93	n.a	[58]
	protothecoides									
BO 2	Rapeseed	n.a	n.a	n.a	74.04	11.70	10.29	3.97	n.a	
BO 3	Softwood bark	0.03	n.a	n.a	77.56	13.16	8.69	0.59	n.a	
BO 4	\	n.a	n.a	n.a	70.20	16.97	8.82	4.01	n.a	[59]
BO 5	Sugarcane	< 0.001	n.a	n.a	74.90	13.50	9.00	1.00	1.60	[60]
	bagasse									
BO 6	Oat hulls	< 0.001	n.a	n.a	74.40	13.90	8.90	1.90	0.90	
BO 7	Oat hulls	< 0.001	n.a	n.a	73.50	13.30	9.40	2.50	1.30	
Coke [†]	\	13.51	1.03	85.46	85.46	0.64	1.33	0.62	0.58	[61]
PC 1 [†]	\	11.09	20.13	68.78	79.02	3.22	4.25	1.28	1.14	
PC 2	\	9.50	27.70	72.30	86.40	6.00	4.90	2.10	0.60	[53]
			(daf)	(daf)						
PC 3	\	10.30	18.50	81.50	89.80	3.40	4.30	2.00	0.50	
			(daf)	(daf)						
Fuel oil		0.10	n.a	n.a	85.00	3.70	11.00	0.30	n.a	[15]

Table 1. Proximate and ultimate analyses of charcoal and bio-oil used as reducing agent.

CC = Charcoal; BO = Bio-oil; VM = Volatile matter; FC = Fixed carbon; C = Carbon; O = Oxygen; H = Hydrogen; N = Nitrogen; S = Sulphur; PT = Pyrolysis temperature.

Types of weight use definition from Phyllis2 Database [62]: at = as received material; dry = dry material; daf = dry and ash free material. † Ultimate analysis is dry basis.

* Calculated by difference.

The equations used to predict higher heating value (HHV) of charcoal and bio-oil have been defined with the multiple linear regressions and based on their proximate and ultimate analyses. The HHV of charcoal is calculated by Equation 7 [63].

HHV (MJ · kg⁻¹)
=
$$0.001(601.95 - 11.57Ash - 7.12VM + 341.67C + 1165.86H - 97.350$$
 (7)
- 193.37N + 110.36S) (7)

where Ash, VM, C, H, O, N, and S stand for the corresponding content of bio-reducers as shown in Table 1, expressed in wt.%. For bio-oils, the HHV is predicted using Equation 8 [64, 65]:

HHV (MJ · kg⁻¹) =
$$0.352C + 0.944H + 0.105(S - 0)$$
 (8)

According to the indicative gasification technologies based on the method of heat supply, it is assumed that the bio-syngas used in this study covers certain percentage of gases composition. Table 2 shows the properties of bio-syngas from biomass gasification and the syngas from coal gasification and CO_2 electrolysis. For using bio-syngas as a reductant, effects of H₂/CO ratio on coke rate and CO₂ emissions need to be specially considered. H₂/CO volume ratios of bio-syngas range from 0 to 1.6, which corresponds to five compositions of the syngas as shown in Table 2.

Technology	Fluidised bed gasifier		Entrained f	Solid oxide electrolysis			
Heating method	Allothermal	Autothermal	Autothermal	Autothermal	n.a		
Feedstock	Biomass	Biomass	Biomass	Coal	CO_2		
Composition		Properties (vol.%, dry)					
H ₂	40	26	39	32	0		
CO	25	20	38	55	60		
CO_2	21	35	20	8	40		
CH_4	10	13	0.1	0	0		
C_2H_4	2.5	3	0	0	0		
N_2	1.5	3	3	3	0		
H ₂ /CO	1.6	1.3	1.0	0.6	0		
LHV $(MJ \cdot m^{-3})$	14	12	10	11	n.a		

Table 2. Comparison of syngas from different technologies and fuels [35, 66, 67].

In an ideal case, the considered substitution of coke with bio-reducers in BF could range from 0 to 100%, but the necessity of coke to increase the mechanical load of BF leads to impossibility of 100% replacement of top-charged coke by bio-reducers [17]. It is suggested that a theoretical minimum coke rate of 200 kg \cdot t⁻¹_{HM} is necessary to enable the stable furnace operation in terms of the injection of other auxiliary reducers into BF [68]. Based on this constraint, substitution potentials of fossil-based reducers with three bio-reducers are investigated under two scenarios. In the first scenario, PC is fully substituted with bio-reducers through tuyere, with no substitution of coke charged from top. The second scenario has a complete substitution of PC and a partial substitution of top-charged coke with bio-reducers injected through tuyere. By changing injection rate of bio-reducers, coke replacement ratio and CO₂ mitigation rate are evaluated.

4. Methodology

4.1 Process modelling

A steady-state BF model was constructed based on the HMB by using Aspen Plus V12. The model divides the continuous melting process into five zones, where chemical reactions that drive reduction of iron oxide distribute orderly. These five zones are modelled by stoichiometric reactor RStoic and are expressed as RS1 to RS5 in Figure 3. In RS1 and RS2 which are also the upper zone of BF, indirect

reductions occur from Fe_2O_3 to Fe_3O_4 and from Fe_3O_4 to FeO, with the descent of solids, temperature of furnace increases, and the direct reduction of wustite by CO proceeds in the RS3. The fourth zone RS4 undertakes gasification of coke and PC into CO, while RS5 provides conditions of slag formation. Side reactions, such as SiO_2 reduction into Si, and MnO conversion to Mn are all considered in this area. Separators are placed between reactors to split upward vapour stream and downward product stream.



Figure 3. Schematic diagram of the chemical equation-based BF model.

In comparison with RStoic reactor which needs known stoichiometry or extent of reaction, the reactor based on Gibbs free energy minimisation namely RGibbs considers the chemical equilibrium and can identify possible products or multiple phases in which the products appear. Referring an official example that simulates iron production from Aspen Plus, a flowsheet of the linkages between RGibbs inside BF is shown in Figure 4. Similarly, Gibbs energy minimisation BF model (Gibbs-based model) divides the furnace into five major zones. It is assumed that reducing reactions in the furnace consist of multiphase equilibrium points at which the reactions are approaching to the minimisation of Gibbs free energy. Each RGibbs reactor is set up to perform at constant temperature and pressure. A heat exchanger at the top of the furnace is used to heat input burden and coke. Different from using separators in the equation-based model, assignment of outlet streams from reactors in the Gibbs-based model is dependent on the phases of the key components.



Figure 4. Schematic diagram of Gibbs free energy minimisation BF model.

Injected coke from top and PC from tuyeres are both modelled as the nonconventional solids like charcoal. Before feeding solids to the reactor and combustion oven, coke and PC need to be decomposed into their constituent elements. Thus, the processes are completed in the RYield block which is a nonstoichiometric reactor built based on yield distribution. The proximate and ultimate analyses of coke and PC are considered for decomposition and the data are shown in Table 1. Oxygen-enriched high temperature air produced in the hot blast stoves is also blown from the tuyeres. Hot blast and PC are reacted in the combustion oven to provide counter reducing gas flow with a high temperature flame (~ 2300 °C). The combustion oven is simulated by using RGibbs block. Same as with PC, charcoal and bio-oil are approached as nonconventional types and decomposed in RYield model. Injection of bio-syngas is directly modelled by inputting individual bio-syngas components, H_2 and CO, based on their volume fractions.

To validate the innovative ironmaking process models, simulation results from different models are compared with output information of a BF operator [51]. The basic design and inlet flow of commercial ironmaking plant are used as simulation parameters in the models. Main results from the models include production and composition of molten iron, slag, and top gas. The validated results are shown in Table 3. Results show good agreement of molten iron and slag between the reference and this work except the silicon (Si) content of iron product simulated by the equation-model. Also results of top gas from equation-model have larger errors, which demonstrates the RStoic reactor cannot accurately simulate interior BF reactions that possibly happen under the circumstances of different temperatures and phases of equilibrium. According to the results of Gibbs-based model, the top gas reproduces well the top gas composition of the BF operator. Thus, the Gibbs-based model offers more reliable results than the equation-model, which will be used in the following simulation.

Company		Kobe ironmaking plant					
Location		Kakogawa, Japan					
			Kobe	Equation-	Error	Gibbs-based	Error
	нм)	Outputs	[51]	based model	(%)	model	(%)
Sinter	754		Molten iron				
Pellets	387	Mass $(kg \cdot t_{HM}^{-1})$	1000	981.46	1.85	971.66	2.83
Lump ore	466	Silicon content (wt.%)	0.45	0.57	26.67	0.46	2.22
Fluxes	64			Slag			
Coke	302	Mass $(kg \cdot t_{HM}^{-1})$	282	280.60	0.50	282.9	0.32
PC	209	CaO (wt.%)	43.2	44.05	1.97	43.69	1.13
Blast air (Nm³⋅t ⁻¹ _{HM})	1177	MgO (wt.%)	6.5	6.53	0.46	6.48	0.31
O_2 enrichment (Nm ³ ·t ⁻¹ _{HM})	63	Al ₂ O ₃ (wt.%)	15.2	15.28	0.53	15.15	0.33
Blast moisture (g·Nm ³ blast air ⁻¹)	14	SiO ₂ (wt.%)	34.1	34.14	0.12	34.68	1.70
		Top gas					
		CO (vol.%)	23.9	20.37	14.77	22.81	4.56
		CO_2 (vol.%)	22.6	28.51	26.15	22.82	0.97
		H ₂ (vol.%)	4.7	3.44	26.81	4.29	8.72

Table 3. Comparison of the outputs from models in this study with ironmaking plant.

4.2 Tuyere raceway flame temperature

Raceways appear in the lower part of BF and are the regions in front of tuyeres, where PC and bioreducers combust with the injected blast air via the tuyeres. Generally, the raceways are the hottest areas in the furnace to have a high-temperature combustion and complete melting of iron and slag. In the raceway, flame temperature is defined as the temperature of the raceway output, varying with the change of blast temperature and quantities of injectants [69], so the use of different reducing agents will affect the raceway flame temperature (RFT). It can also be defined as the temperature that the raceway gas reaches when all the carbon, oxygen and water in the raceway convert to CO and H_2 [17]. To calculate RFT, an assumption of no heat transfer and loss from the raceway to the surroundings is made, which leads the RFT to a RAFT, and based on the heat balance in the raceway zone. Equation of raceway heat balance is represented as Equation 9.

$$\sum H_{i,in} = \sum H_{j,out} \tag{9}$$

where both sides are the total raceway input and the output enthalpy, respectively. Principle reactions considered in the raceway include the formation of CO and H₂O. Reference temperature of enthalpy and standard state pressure are defined as 25 °C and 101.3 kPa. Hence, enthalpy of gaseous component at 25 °C equals standard formation enthalpy $\Delta_f H_{25 \, °C}^\circ$, the enthalpy at certain temperature H_T° can be calculated as Equation 10.

$$H_{T}^{\circ} = \Delta_{f} H_{25 \circ C}^{\circ} + (H_{T}^{\circ} - H_{25 \circ C}^{\circ})$$
(10)

where the values of $(H_T^{\circ}-H_{25 \circ C}^{\circ})$ are provided by the NIST-JANAF thermochemical tables [70]. $(H_T^{\circ}-H_{25 \circ C}^{\circ})$ is also the multiplication of specific heat c_p and temperature change ΔT . By adding flame temperature T_{flame} into Equations 9 and 10, the equation could be transformed into Equation 11.

$$\sum H_{i,in} = \sum (\Delta_f H_{j,25\,^\circ\text{C}}^\circ + \int_{25}^{T_{\text{flame}}} c_{p,j} dT)$$
(11)

4.3 Evaluation methods

Exploration of injecting bio-reducers into BF is mainly found on three keywords: reduction, ratio, and efficiency. The reduction reflects in effects of reducing CO_2 emissions of ironmaking process when substituting coke or PC with bio-reducers. On-site CO_2 emissions are used to measure CO_2 emissions that exist in the top gas expelled from furnace. The index is normalised into a quantity in per unit of useful products, expressed as Equations 12.

$$DE_{\rm CO_2} = \frac{M_{\rm CO_2, tot}}{M_{\rm iron, out}} \tag{12}$$

where DE_{CO_2} is the specific direct CO₂ emissions, $M_{iron,out}$ is the amount of produced molten iron, $M_{CO_2,tot}$ is total CO₂ emissions of the BF process.

To easily compare the ability of bio-reducers to replace coke and mitigate CO_2 emissions, two indicators, i.e., coke replacement ratio and CO_2 reduction rate, are used in this study. Since all the PC from tuyeres are primarily substituted by bio-reducers in this study, calculating coke replacement ratio should deduct the amount of bio-reducers from this portion. Considering the weight of contained carbon, bioreducers equivalent to PC can be expressed as Equations 13.

$$M_{\rm bio,PC} = \frac{M_{\rm PC}\omega_{\rm C,PC}}{\omega_{\rm C,bio}}$$
(13)

where M_{PC} is originally consumed PC, $\omega_{C,PC}$ and $\omega_{C,bio}$ are mean overall carbon mass fraction of PC and bio-reducers after decomposition, respectively. Therefore, coke replacement ratio κ is elaborated as the change of the coke due to the injection of bio-reducers, which can be expressed as Equation 14.

$$\kappa = \frac{\Delta M_{\text{coke}}}{\Delta M_{\text{bio}}} = \frac{M_{\text{ref,coke}} - M_{\text{bio,coke}}}{M_{\text{bio}} - M_{\text{bio,PC}}}$$
(14)

where ΔM_{coke} is the difference between coke rate in reference case $M_{ref,coke}$ and coke rate resulting from using a certain amount of bio-reducers $M_{bio,coke}$, M_{bio} is the injection rate of bio-reducers in BF.

 CO_2 reduction rate r is defined as the mitigated CO_2 emissions in per ton of the specific bio-reducers demand, which can be evaluated as Equation 15.

$$r = \frac{\Delta M_{\rm CO_2}}{M_{\rm bio}} = \frac{M_{\rm ref, CO_2} - M_{\rm bio, CO_2}}{M_{\rm bio}} \tag{15}$$

where ΔM_{CO_2} is the difference between CO₂ emissions in reference case M_{ref,CO_2} and emissions in the case which injects a certain amount of bio-reducers M_{bio,CO_2} .

As shown in Figure 2, carbon and CO_2 originally in the bio-reducers enters BF and are released in the form of CO_2 . Furthermore, woody biomass absorbs and stores gaseous CO_2 from the atmosphere by photosynthesis during its growth. From a full system perspective that combines biomass, BF process, and atmosphere together, there is zero CO_2 emission from bio-reducers, which means that the bio-reducers are carbon neutral from growth to utilisation. The evaluation of net CO_2 emissions is necessary to clarify the emissions that cannot be avoided during the BF process. Net CO_2 emissions with charcoal and bio-oil can be expressed as Equation 16.

$$M_{\text{net,CO}_2} = M_{\text{bio,CO}_2} - M_{\text{bio}}\omega_{\text{C,bio}} \times f$$
(16)

where M_{net,CO_2} is net CO₂ emissions, *f* is a factor to convert molar mass of carbon to CO₂. For BF injection with bio-syngas, *f* is considered to convert molar mass of CO to CO₂. Mass fraction of CO in the bio-syngas $\omega_{CO,bio}$ is built based on volume fraction of gas component as shown in Table 2, which is calculated by Equation 17.

$$\omega_{\rm CO,bio} = \frac{\lambda_{CO}}{\sum_n \lambda_n MOL_n} \tag{17}$$

where λ_n and MOL_n are volume fraction and molar mass of the *n*th gas in the syngas, respectively.

The utilisation efficiency of the bio-reducers, η_{bio} is represented as the percentage of bio-reducers utilised for the reduction of the ferrous content. When the efficiency equals to one, the reducing agent is completely consumed in the whole chemical reactions. As CO is usually used as the main reducing agent,

the utilisation efficiency can be calculated by measuring the change of CO and CO_2 composition of top gas exiting the furnace, which could be expressed as Equation 18 [17].

$$\eta_{\text{bio}} = \frac{\varphi_{\text{CO}_2}}{\varphi_{\text{CO}} + \varphi_{\text{CO}_2}} \times 100\% \tag{18}$$

where φ_{CO} and φ_{CO_2} denote the mole fraction of CO and CO₂ in the top gas, respectively. For Fe₂O₃ simultaneously reduced by H₂ and CO, the utilisation efficiency of the bio-reducers, is defined as Equation 19.

$$\eta_{\rm bio} = \frac{\varphi_{\rm CO_2} + \varphi_{\rm H_2O}}{\varphi_{\rm CO} + \varphi_{\rm CO_2} + \varphi_{\rm H_2} + \varphi_{\rm H_2O}} \times 100\%$$
(19)

where φ_{H_2} and φ_{H_2O} represent the mole fraction of H₂ and H₂O in the top gas, respectively.

5. Results and discussion

5.1 Effects of tuyere injections on RAFT

Effects of carbon, CO and H₂ that are injected through tuyere on the RAFT are shown in Figure 5. The RAFT is 2312 °C when carbon, CO and H₂ have zero injection at the tuyere and the reducing agents are all charged from the top of furnace in the form of coke. It can be found that RAFTs vary with different reductants appearing in the raceway. When CO flow rate is increased to 385 kg·t⁻¹_{HM}, meanwhile top-charged carbon from coke being decreased from 436 kg·t⁻¹_{HM} to 271 kg·t⁻¹_{HM}, RAFT drops about 549 °C. Also, RAFT shows a steeper drop when injected carbon from PC increases to 165 kg·t⁻¹_{HM} without any input of CO and H₂. On the contrary, RAFT profile presents an increment of 34 °C with a higher input of H₂ in the raceway. Three different RAFT profiles indicate that change of CO in the raceway has the most significant influence on the temperature, which can be explained that more CO in the raceway causes the lower thermal energy released than the replaced coke. Furthermore, combustion of PC provides more heat than that of CO, and similar composition of PC to that of coke causes little change on the flame temperature. By adding H₂, the total input enthalpy will be greater. Therefore, the RAFT becomes higher to satisfy enough outlet enthalpy based on the assumption of enthalpy balance in the raceway.



Figure 5. Effects of the injected carbon, CO, and H₂ through tuyere on RAFT.

5.2 Effects of bio-reducers injection on CO₂ emissions

Under the basic BF scenario in Table 3, i.e., when using 209 kg·t⁻¹_{HM} PC and 302 kg·t⁻¹_{HM} top charged coke, CO₂ emissions are 778 kg·t⁻¹_{HM}. Based on this, effects of bio-reducers injection on CO₂ emissions are evaluated further. The bio-reducers firstly replace all the PC injected through the tuyere. Charcoal and bio-oil, assumed as a mixture of solid particles, have the same input quantity as the original PC injection, i.e., 209 kg·t⁻¹_{HM}. The input amount of bio-syngas will be determined by the minimum technical limit of RFAT, which is generally considered as 2000 °C [17, 35].

Figure 6 shows the trends of CO₂ emissions with the variations of carbon, hydrogen, and oxygen contents in the charcoal and bio-oil. Error bars represent the sum of the simulation errors as well as the standard deviations of the referenced compositions of bio-reducers. The higher carbon and lower oxygen in the charcoal cause less CO₂ emissions from BF. The reason can be described as that with more upward carbon, the CO₂ produced during the reduction process will continue to react with the carbon to produce CO, which results in a lower concentration of CO₂ in the top gas. The lower oxygen content constrains the amount of carbon reacted at the bottom of the furnace, so that more carbon can combine with CO₂. From Figure 6(b), it seems that hydrogen has a smaller impact on CO₂ emissions from charcoal than its effect on the emissions generated by bio-oil. When the hydrogen in the bio-oil increases from 8.69 wt.% to 11.61 wt.%, CO₂ emissions rise from 530 kg·t⁻¹_{HM} to 661 kg·t⁻¹_{HM}. The increase in CO₂ is mainly due to the WGS at the upper part of BF. An unusual point of CO₂ emissions from bio-oil happens at the reactor BO 4 that has the largest percentage of oxygen as shown in Figure 6(c). This is inferred that higher H₂O produced in the raceway because of oxygen is converted to more CO₂ at the upper zone. Nevertheless, due to the function of hydrogen in the bio-oil, the overall CO₂ emissions are lower than the emissions from charcoal.



Figure 6. CO₂ emissions of BF when charcoal and bio-oil have varied element contents: (a) carbon; (b) hydrogen; (c) oxygen.

After removing CO₂ emissions contributed by the injection of charcoal and bio-oil, results of net CO₂ emissions at various carbon contents are shown in Figure 7. Comparing with total emissions, net CO₂ emissions can be reduced by up to 643 kg·t⁻¹_{HM} and 447 kg·t⁻¹_{HM} for the cases of charcoal and bio-oil, respectively. Carbon levels of charcoal reflect direct relation with the net emissions, resulting from the higher content of carbon and the lower net CO₂ emissions. For bio-oil, trend of net CO₂ emissions with change of carbon is unapparent, and the emissions are generally higher than those from charcoal. This is mostly because hydrogen in the bio-oil plays a role in the reduction process and final emissions. Meanwhile, the unreacted carbon in the bio-oil will become the sediment into the slag, thus reducing conversion of carbon to CO₂.



Figure 7. Net CO₂ emissions with different carbon contents of charcoal and bio-oil.

 CO_2 emissions and the net CO_2 emissions from BF with bio-syngas are given in Figure 8. As discussed in Section 4.1, CO has the largest impact on the RAFT, and mass of CO in the syngas is constant as 219 $kg \cdot t_{HM}^{-1}$ which can also meet the technical limit of flame temperature. The amount of H₂ is calculated in the range from 0 to 25 kg t_{HM}^{-1} with H₂/CO ratios of syngas increasing from 0 to 1.6. The results have not shown a significant mitigation of CO_2 emissions from bio-syngas in comparison with charcoal and bio-oil. This is mainly because CO_2 in the bio-syngas is simultaneously discharged from BF. In an atmosphere of carbon, CO, and CO₂, the reverse Boudouard's reaction takes place in the raceway, where CO is converted preferentially to carbon and CO₂. As the reducing gas ascends, some CO₂ directly emit from the top if there is not enough carbon inside BF to continue reacting with CO2. More carbon is left when more H2 is in the syngas, since O_2 will first oxidise H_2 to H_2O before the rest reacts with carbon. An exception to this is in the case of H_2/CO ratio of 1.6 at which CO₂ emissions are higher than the ratio of 1.3. This is because the increase in H₂ also rises moisture in the furnace, which could accelerate the rate of WGS and the consequent CO_2 emissions. It is concluded that the optimum H₂/CO ratio for bio-syngas to reduce CO_2 emissions is 1.3. After eliminating the inherent CO₂ emissions from bio-syngas, the net CO₂ emissions are reduced by up to 697 kg·t $_{HM}^{-1}$ which is equal to the on-site CO₂ emissions from bio-syngas with H₂/CO ratio of 1.3. This suggests that the complete reduction of Fe₂O₃ to Fe can be accomplished by the joint action of H₂ and CO from bio-syngas, achieving net zero emission of BF.



Figure 8. CO₂ emissions and net CO₂ emissions with different H₂/CO ratios of bio-syngas.

Pure H₂ derived from bio-syngas is further considered as the auxiliary reducing agent into BF with unchanged coke rate of 302 kg·t⁻¹_{HM} which is same as the coke rate in the basic scenario. This scenario can be regarded as the theoretical maximum percentage of H₂ in the syngas. Consumption of H₂ for the

reduction and related CO₂ emissions from BF under different injection amounts of H₂ and CO are shown in Figure 9. Figure 9 (a) indicates that the consumed H₂ for reduction will eventually freeze at a value of 16.8 kg·t⁻¹_{HM}, which covers the amount of H₂ required for the reduction from Fe₂O₃ to FeO. This situation is achieved earlier with more injected CO to assist in the reduction process. For example, when there is no CO additionally injected through tuyere, nearly 41 kg t_{HM}^{-1} H₂ is needed to meet subsequent reactions. Comparably, the injection of H₂ is decreased to 30 kg \cdot t⁻¹_{HM} when 200 kg \cdot t⁻¹_{HM} CO is injected. This is mainly due to the fact that more CO would trigger WGS faster and then more H_2 is produced before the reduction occurs. Given that the injected H₂ is firstly combusted to H₂O in the raceway, i.e., a highly endothermic process, energy consumption can also be reduced if H_2 is injected less with the assistance of CO. The significant decrements of CO_2 emissions can be found in Figure 9 (b) when the H₂ is increased from 5 $kg \cdot t_{HM}^{-1}$ to 45 $kg \cdot t_{HM}^{-1}$. The profiles of drop in CO₂ emissions are almost parallel until H₂ is increased to 30 kg· t_{HM}^{-1} . Without injecting other auxiliary reducing agent through tuyere, CO₂ emissions are minimised to 456 kg·t⁻¹_{HM} by injecting 45 kg·t⁻¹_{HM} H₂. Although more CO leads to higher CO₂ emissions from BF, the final emissions compared to the basic case that only uses coke and PC are decreased around 170 $\rm kg\cdot t_{HM}^{-1}$ CO₂. The joint action of H₂ and CO has proven to be beneficial to mitigate of CO₂ emissions and BF operation.



Figure 9. Effects of injected H_2 and CO through tuyere on: (a) consumed H_2 for reduction; (b) CO_2 emissions.

5.3 Coke replacement ratio and CO₂ reduction rate

Top-charged coke is further to be reduced with the increased bio-reducers through tuyere. The lower limit of coke rate is set as 200 kg·t⁻¹_{HM} which ensures the stable operation of the furnace. Based on a

reduction of 102 kg· t_{HM}^{-1} coke and composition of each bio-reducer, the coke replacement ratios are calculated as Table 4. The coke replacement ratios of charcoal are in the range from 0.9 to 1.06, representing that 1 kg charcoal can replace coke from 0.9 kg to 1.06 kg. Only when the ratio is higher than one, coke in BF can be replaced by using less bio-reducers. Therefore, bio-oil is a suitable substitute for coke as the replacement ratios of bio-oil are all larger than one. In contrary, much more bio-syngas is needed to save 1 kg coke consumption, because the syngas usually contains a higher volume of other gases which simultaneously increase the total weight of syngas.

Bio-reducers	Coke replacement ratio		
Charcoal	0.90 - 1.06		
Bio-oil	1.17 - 1.30		
Bio-syngas (H ₂ /CO 0)	0.47		
Bio-syngas (H ₂ /CO 0.6)	0.73		
Bio-syngas (H ₂ /CO 1.0)	0.49		
Bio-syngas (H ₂ /CO 1.3)	0.22		
Bio-syngas (H ₂ /CO 1.6)	0.34		

Table 4. Estimated coke replacement ratios for different bio-reducers.

 CO_2 reduction rates of charcoals and bio-oils are estimated in Table 5. The highest reduction rates for charcoal and bio-oil are 0.48 and 1.19, which mean that 1 kg charcoal and 1 kg bio-oil can reduce 0.48 kg CO_2 and 1.19 kg CO_2 from BF, respectively. The reduction rates of charcoal and bio-oil are highly correlated with their element composition, the same as the relationship between CO_2 emissions and composition. The increased injection of bio-reducers replaces more coke charged from the top. However, CO_2 reduction rates decrease. This happens because bio-reducers input through tuyere has the lower specific heat enthalpy than coke charged from the top, resulting more carbon from bio-reducers being consumed towards combustion in the raceway and less carbon being available for reacting with CO_2 at the upper body of BF. Another reason for a considerable drop in reduction rates of bio-oil, for example, the reduction rate of the BO1 decreases from 0.56 to 0.16, is that hydrogen in the bio-oil increases to a large extent with the higher injection rate. In this way, the WGS can proceed rapidly to form more H₂ and CO_2 .

Figure 10 (a) shows the trends of CO₂ reduction rates for bio-syngas with the increased injection volume and the varied H₂/CO ratios. Volumes of bio-syngas change considerably under different gas compositions when the syngas is used to replace 102 kg·t⁻¹_{HM} coke. CO₂ reduction rates obtained from the on-site CO₂ emissions are mostly negative, and only positive when the syngas injection is low and with H₂/CO ratios of 1.3 and 1.6. This is obviously because the on-site CO₂ emissions include a large proportion of CO₂ contained originally in the syngas. It is necessary for syngas to consider the net CO₂ reduction rate, i.e., deducting contribution by syngas to CO₂ emissions. As seen in Figure 10 (b), the net CO₂ reduction rates decrease gradually with the higher syngas injection when H₂/CO ratios are from 0.6 to 1.6. This implies that the high volume of syngas will hinder its effectiveness in reducing CO₂ emissions, even though the final emissions are lower than the basic case, i.e., 778 kg·t⁻¹_{HM} CO₂. The main reason for this is that the syngas cannot maintain a constant capability to reduce emissions at different gas concentrations. For syngas composed of only CO and CO₂, CO₂ emissions will start to decrease when the syngas is injected more than 400 kg·t⁻¹_{HM}, reflected by the reduction rate beginning to be greater than zero. Summarily, CO₂ reduction effect of bio-syngas is more complex than that of charcoal and bio-oil. The results are varied based on different compositions and system boundaries.

Nomo		In	jection rat	te (kg·t _{HM}	()	
Iname	209	229	249	269	289	309
CC 1	0.16	0.14	0.11	0.09	0.07	0.06
CC 2	0.13	0.10	0.08	0.06	0.04	0.03
CC 3	0.18	0.15	0.12	0.10	0.08	0.07
CC 4	0.41	0.37	0.34	0.31	0.29	0.27
CC 5	0.25	0.23	0.21	0.19	0.17	0.16
CC 6	-0.05	-0.07	-0.08	-0.09	-0.10	-0.11
CC 7	0.43	0.39	0.35	0.32	0.29	0.27
CC 8	0.34	0.30	0.27	0.24	0.22	0.20
CC 9	0.47	0.42	0.38	0.35	0.32	0.29
CC 10	-0.03	-0.05	-0.06	-0.08	-0.09	-0.10
CC 11	-0.20	-0.21	-0.22	-0.23	-0.23	-0.24
CC 12	0.48	0.43	0.39	0.36	0.33	0.30
CC 13	0.22	0.19	0.16	0.14	0.11	0.10
BO 1	0.56	0.34	0.14	-0.02	-0.16	\
BO 2	0.85	0.62	0.42	0.26	0.12	\
BO 3	1.19	0.96	0.77	0.61	0.47	\
BO 4	1.06	0.82	0.61	0.43	0.28	\
BO 5	1.12	0.89	0.70	0.54	0.40	\
BO 6	1.14	0.91	0.72	0.56	0.42	\
BO 7	1.04	0.81	0.61	0.45	0.31	\

Table 5. CO₂ reduction rates of charcoals and bio-oils with different injection rates.

CC = Charcoal; BO = Bio-oil



Figure 10. Effects of injected bio-syngas on the: (a) CO_2 reduction rate; (b) net CO_2 reduction rate.

5.4 Utilisation efficiency of bio-reducers

The relations between utilisation efficiencies of bio-reducers and BFG temperature are shown in Figure 11, together with the variation in BFG composition. Since CO and H₂ both work for reduction in the cases of bio-oil and bio-syngas, Figures 11(b) and 11(c) also show the ratios of H₂O and H₂ in the BFG. For BF operation with the selected charcoals, bio-oils, and bio-syngas, the utilisation efficiencies range from 0.41 to 0.53, 0.50 to 0.54, and 0.50 to 0.88, respectively. Except for the charcoal, bio-oil and bio-syngas in BF are utilised to a greater extent than 50% utilisation efficiency of coke and PC in BF. This suggests that bio-oil and bio-syngas have the greater impact on Fe₂O₃ reduction in BF. The lower utilisation of charcoal is because charcoal that has a higher carbon content transforms more CO₂ into CO, leading to a greater concentration of CO remaining in the BFG. It is evident that the utilisation efficiencies of the bio-reducers are well aligned with the change of CO₂ fraction in the top gas.

Temperatures of BFG show different increment curves for three bio-reducers. For charcoal and bio-oil, BFG temperature increases from 122 °C to 129 °C and from 137 °C to 141 °C with the increment in utilisation efficiency, respectively. The injection of bio-oil with a higher hydrogen causes a rise of H₂ gas fraction in the BFG, resulting in a higher BFG temperature than when BF is injected with charcoal. As shown in Figure 11(c), the similar change of BFG temperature can also be reflected when BF is operated with bio-syngas, where BFG temperature increases from 142 °C to 195 °C with CO fraction increases from

0.04 vol.% to 0.30 vol.%. It is demonstrated that injection of bio-syngas into BF can provide more heat to the reducing gases as most of CO sourced from syngas is not reacted, and therefore more sensible heat can be obtained from the BFG. To sum up, bio-syngas compared to charcoal and bio-oil in BF provides more heat and reduces final CO₂ concentration in the BFG.



Figure 11. Gas fraction of BFG and bio-reducers utilisation efficiency as a function of BFG temperature when BF is injected with: (a) charcoal; (b) bio-oil; (c) bio-syngas.

5.5 Comparison of bio-reducers

Table 6 summarises the performances of three bio-reducers and compares their abilities to reduce CO_2 emissions and replace coke usage in ironmaking process. From the perspective of conversion technology of bio-reducers, although the thermal energy required for producing charcoal and bio-oil is lower than the best practice for coke production, i.e., 2080 kJ·kg⁻¹ coke [71], their yields are less than that of coke which exceeds 70 wt.% [72]. High-temperature, energy-intensive gasification of biomass undoubtedly also presents a challenge to utilise bio-syngas in the BF ironmaking process. One possible consideration for solving this is to recover waste heat from iron and steel plant for the biomass pyrolysis and gasification, as both coke oven gas and coke or BG slag cover a large amount of waste heat which could compensate the energy needed for bio-reducers production. Meanwhile, on-site production of bio-reducers avoids long-distance transportation, which would reduce the operating and transportation cost.

Uncertainty in composition of bio-reducers due to different biomass waste feedstock, conversion temperature and process poses another challenge to injecting bio-reducers into BF and presents limitation in this study. As summarised effects of bio-reducers' composition on CO_2 emissions from BF, achieving the optimal performance in reducing CO_2 emissions requires a higher content in charcoal, a higher hydrogen content in bio-oil, and a certain ratio of H₂/CO for bio-syngas. By screening feedstock and temperatures, the optimise properties can eventually be tailored. While the bio-reducers are capable of CO_2 emissions reduction, whether they can meet the requirement of heat supply for ironmaking process remains a question. Figure 12 compares HHVs of charcoal and bio-oil to those of commonly used coke and PC in metallurgical

process. It can be seen that charcoal and bio-oil have a higher heating value than coke, which provides an advantage for use in BF. According to Figure 5, the increment in carbon in the raceway through injecting charcoal and bio-oil would lower the RAFT but within a manageable range, i.e., above 2000 °C. For bio-syngas, its heating value cannot directly satisfy the heat demand of the raceway. Therefore, additional steam or hot blast is needed to support bio-syngas as a reducing agent in BF. Although technologies for producing bio-reducers from biomass waste have been practiced, their use in BF has only been demonstrated for the injection of charcoal in small-scale BF. The techno-economic feasibility of utilising bio-reducers in BF needs to be further explored, as competitive cost and sustainable structure for manufacture of bio-reducers would be key factors for them to be used in BF.

Bio-reducer	Charcoal	Bio-oil	Bio-syngas
Conversion technology	Slow pyrolysis	Fast pyrolysis	Gasification
Yield	32.8 wt.% -53.8 wt.% with pyrolysis temperature from 300 °C -500 °C [57]	60 wt.% on dry feed basis [15]	1.2 - 2.3 kg product of per kg of feed with H ₂ /CO ratios from $1 - 3$ [73]
Energy demand for	1400 kJ·kg ⁻¹ of dry biomass	1094 kJ heat required for	3230 kJ heat needed for
producing bio-reducers	feed pyrolysis process [74]	pyrolysis reaction of per kg of biomass feed [75]	per kg of biomass feed gasification [76]
CO ₂ reduction rate	Average level of 0.15	Average level of 0.60	Mostly lower than 0
Effects of composition on reducing CO ₂ emissions	 Carbon content in charcoal dictates CO₂ emissions More CO₂ emissions are reduced with a higher carbon and lower oxygen content in charcoal 	 Hydrogen content in bio-oil has major influence on CO₂ emissions CO₂ emissions increase with higher hydrogen in bio-oil 	 CO₂ included in bio- syngas causes higher CO₂ emissions than charcoal and bio-oil H₂/CO ratio of 1.3 has optimal performance in reducing CO₂ emissions
Ability to replace coke	1 kg charcoal can replace coke from 0.9 – 1.06 kg	1 kg bio-oil can replace coke from 1.17 – 1.30 kg	1 kg bio-syngas can replace coke from 0.22 – 0.73 kg
Effects in BF operation	High reactivity to CO ₂ . Heat supply effect is higher than the reducing agent effect	Act more as reducing agent than heat supply	Higher temperature in BFG is produced by bio- syngas. H_2 in the bio- syngas plays major role in Fe ₂ O ₃ reduction

Table 6. Summary of three bio-reducers.



Figure 12. Comparison of HHVs among charcoal, bio-oil, and commonly used coke and PC.

6. Biomass waste resources for BF operation

Bio-reducers utilisation in the ironmaking process is greatly impacted by the amount of available woody biomass waste, as woody biomass resources are always limited by their long growth and processing cycle. In this section, woody biomass waste available for the BF ironmaking is evaluated based on the world pig iron production and woody biomass waste conversion efficiency, which aims to provide more insights from a worldwide perspective.

Figure 13 firstly gives world distribution of pig iron annual production quantities (million tonnes). Displaying the deepest shadow and the largest circle radius with 908 Mt pig iron, China undoubtedly scores the largest iron producer, followed by India (68 Mt), Japan (62 Mt), Russia (52 Mt), and South Korea (45 Mt). Many countries located in Europe and America have not much iron production, except for Germany, Ukraine, Brazil, and the United States. Assuming that pig iron is produced entirely by the BF process, demands for the auxiliary bio-reducers are calculated according to the injection rates in Section 4.2, i.e., 209 kg·t⁻¹_{HM} for charcoal and bio-oil, and 989 kg·t⁻¹_{HM} for bio-syngas with H₂/CO ratio of 1.3. Figure 14 shows the total bio-reducers demand for the partial replacement of coke and PC in BF, which amounts to 280 Mt, 280 Mt, and 1327 Mt for charcoal, bio-oil, and bio-syngas, respectively.



Figure 13. World pig iron production in 2020 (data from [77], copyright of map: Australian Bureau of Statistics, GeoNames, Microsoft, Navinfo, OpenStreetMap, TomTom, Zenrin, powered by Bing,).

Potential demand of woody biomass waste is evaluated by Equation 20 [78]:

$$Y = \frac{M_{\text{bio-reducers}}}{\alpha \cdot \gamma} \tag{20}$$

where *Y* is annual biomass waste requirement, $M_{bio-reducers}$ is mass of thermochemically produced bioreducers, α is the share of dry matter in wet wood, γ is the product yield of bio-reducers from biomass. The slow pyrolysis yield of charcoal uses an efficiency of about 35 wt.% at a pyrolysis temperature of 500 °C [57], while the fast pyrolysis yield of bio-oil is chosen to be 60 wt.% on the dry feed basis [15]. The product yield of bio-syngas with 1.3 H₂/CO ratio through the gasification of 1 kg dry based woody biomass waste gasification is around 1.2 kg [73]. Therefore, as shown in Figure 14, the demands for the biomass waste feedstock to produce bio-reducers, i.e., charcoal, bio-oil, and bio-syngas, are given as 800 Mt, 470 Mt, and 1100 Mt, respectively.

To explore whether the biomass waste resources in each country are sufficient for the production of pig iron, the status of bio-energy used to supply industrial energy is collected from public data in references [79-83]. Quantities of biomass waste used for the industry will diminish the amount of biomass requested for producing bio-reducers used in the BF process, and the resulting excess biomass resources is shown in Figure 15. Positive results depict that the woody biomass waste resources in these counties are surplus after the production of bio-reducers. Brazil has the most abundant resources, followed by the United States, Mexico, and India, which indicates that these countries are better suited to switch fossil fuel by bio-reducers in BF. Countries such as Finland, Sweden, Poland, Canada, and Argentina are also better choices for using bio-reducers due to their relatively low pig iron production. For Russia, it is known that forest waste resources would have more surplus suitable to produce bio-oil, as well as the complexity of assessment of Russia's woody biomass waste resources, resulting in an inaccuracy of assessing available resources [84]. The negative figures show insufficient biomass waste resources to produce bio-reducers, with China having the severest shortage of the forest biomass waste, suggesting that China is not a good candidate to use bio-reducers in the BF ironmaking, but can choose other end-use measures such as CO₂ capture to achieve reducing CO₂ emissions. Japan and South Korea are also not ideal countries for using bio-reducers. Some countries such as Germany, France, and the United Kingdom can shift their partial pig iron production to bio-reducers-assisted ways, and they can also rely on imported woody biomass waste from the countries with excess woody biomass resources, e.g., Brazil, Canada to meet their production demands.

The estimation of woody biomass waste feedstock availability in this study is based on the assumption that the feedstock will be used primarily for the production of bio-reducers for ironmaking process. While in the actual situation, bio-reducers may face competitive disadvantages compared to other usage of woody biomass waste resources. For instance, in many countries, woody biomass waste resources have higher use in electricity generation, heating, fuel supply, and biogas/biomethane production. This may be determined by supply conditions from contractors, the conversion technologies of biomass waste, and the production costs of bio-reducers, which can cause higher price of bio-reducers than that of fossil-based reducing agents. To increase the competitiveness of bio-reducers in the market, one possible measure has been proposed by improving utilisation rate of biomass waste feedstock, such as the pyrolysis off-gas from charcoal production could serve as a feedstock for biomethane production [85]. In addition, the higher cost of bioreducers is associated with immature markets for charcoal, bio-oil, and bio-syngas since a complete supply chain from handling of their feedstock to transportation and storage of products has not been established. Therefore, integrating bio-reducers production with other chemical industries, as well as iron and steel plant presents priority to achieve more economic benefits and reduce CO₂ emissions on a larger scale. The development of commercially viable bio-reducers products is essential for their adoption in decarbonised the BF ironmaking process.



Figure 14. Demands for bio-reducers and feedstock used in pig iron production.



Figure 15. Surplus woody biomass waste resources after producing bio-reducers in different countries.

7. Conclusions

This study explores the potential of three woody biomass waste derivatives as reducing agents in the BF ironmaking process. Effects of the specific compositions of charcoal, bio-oil, and bio-syngas on the BF operation, CO₂ emissions, and coke replacement are investigated by using an HMB model based on Gibbs free energy minimisation. The effects of H₂-rich gas produced from biomass waste gasification on the BF operation is estimated. Moreover, availability study of woody biomass waste feedstock in various countries is conducted to evaluate future production and applications of auxiliary bio-reducers in the BF operation.

The main findings regarding the effects of bio-reducers' composition on CO_2 emission reduction are summarised as following: (1) high reactivity of charcoal with CO_2 due to carbon enrichment in the charcoal allows more CO_2 to react with carbon to form CO, and therefore reduces CO_2 concentration of the top gas; (2) while the higher hydrogen content in bio-oil cannot improve its ability to reduce CO_2 emissions because more CO_2 is generated as a result of WGS reaction, bio-oil ultimately has lower CO_2 emissions than charcoal due to hydrogen; (3) bio-syngas that has H₂/CO ratio of 1.3 proves to be the best choice for the BF injection. These can be concluded that the mechanism of using bio-reducers in BF to reduce CO_2 emissions is complex and is significantly relevant to composition, as manifested by carbon element in charcoal, hydrogen element in bio-oil, and H₂/CO ratio of bio-syngas.

The estimation of woody biomass waste feedstock availability in various countries reveals that the implementation characteristics in bio-reducers make them more suitable for countries where pig iron production is small and woody biomass waste resources are abundant. The actual situation demonstrates that coupling industries and commercialised bio-reducers market are required to increase the competitiveness of bio-reducers in biomass waste feedstock assignment. Even if importing biomass waste resources is an option to promote bio-reducers for some countries, a trade-off between cost and sustainability is necessary, and avoiding excessive deforestation is always an issue to be considered.

The limitations in this study are presented as the uncertainty in composition of bio-reducers due to different feedstock and conversion technologies. Since the various compositions collected were average values after multiple times of tests, the errors of their compositions are not given in the references. The sensitive analysis should be explored in the further study to evaluate the impacts of feedstock properties and conversion technologies on the BF operation from a holistic picture. Along with the wide use of bio-reducers in the near future, the potential of bio-reducers would play a more significant role in CO₂ mitigation for iron and steel industry. This study brings more inspiration to produce decarbonised iron by considering bio-reducers.

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