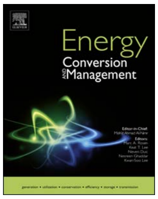
Energy Conversion and Management 158 (2018) 1–8

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman



Study on intrinsic reaction behavior and kinetics during reduction of iron ore pellets by utilization of biochar

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ARTICLE INFO

Keywords:
Iron ore-biochar pellets
Char gasification
Indirect reduction
Behavior
Kinetics

ABSTRACT

Biochar, as an important renewable and carbon-natural energy, shows plentiful prospects to be used in the ironmaking industry. In this study, the effect of iron ore content and temperature on the reduction of iron ore-biochar pellets in nitrogen atmosphere were investigated. Results indicated that with the decrease of carbon to iron ratio, the iron ore indirect reduction was promoted more than char conversion which resulted in an decrease value of CO:CO_2. Pellets reduction at 900 °C found that 60% iron ore in pellet exhibited considerable carbon conversion and the highest iron ore reduction amount. With the increase of reaction temperature, the char gasification reaction was promoted prior to the iron ore reduction, resulting in an increase of CO:CO_2 ratio. The wustite and metallic Fe gradually increased, while hematite and magnetite gradually decreased, with the increase of temperature. Kinetics study found that carbon conversion was controlled by one-dimensional diffusion, while the iron phase reduction reaction was controlled by three-dimensional diffusion, and the increasing activation energy as the reaction proceeded restricted the iron reduction process. The intrinsic reaction behavior, thermal kinetics, and technical analysis may guide the application of bioenergy in the ironmaking industry.

1. Introduction

In recent times, climate change caused by greenhouse gas (GHG) emissions has become a major global challenge. It is agreed that CO_2 plays a key role in GHG emissions that result in global warming, and the combustion of fossil fuels, such as coal, petroleum and natural gas, are the main contributors to CO_2 emissions [1,2]. Energy consumption in iron and steel industry is estimated to be about 20% of the annual industrial fossil fuel utilization, and accounts for approximately 6.7% of total world CO_2 emissions [3]. Therefore, reduction of the fossil energy consumption and CO_2 emissions are the top priorities of the iron industry [4]. Fortunately, biochar has been proposed as a climate-mitigation material/energy resource due to its renewable and carbon neutral properties [5,6]. Biochar, with the merits of high calorific value, high carbon content, porosity, and good reducing capacity [7,8], shows the potential to be used in the iron and steelmaking industry to partially replace fossil fuels and mitigate the CO_2 burden. Consequently, it is of great significance to explore efficient technologies for the conversion, management and application of biochar in ironmaking processes.

Biochar, obtained from the anoxic thermal cracking of biomass, can be an energy provider and reductant when reacts with iron ore. Iron ore acts as an oxygen carrier for the chemical looping conversion of biochar to produce heat and reducing gas [9]. Compared with conventional fossil derived coke, biochar has higher reactivity and better porous structure. It thus contributes to the high reduction rate and possibly lowers the reaction temperature; this consequently saves energy and promotes the production [10,11]. Furthermore, raw biomass has a high volatile content, which is released at relatively low temperatures, compared with the temperature required for iron ore reduction. The escaped volatiles then might change the temperature profile, gas distribution, and heat transfer within the blast furnace [3]. Biochar, from the pyrolysis of biomass with polygeneration of biogas and bio-oil, therefore, has outstanding economic, technical, and environmental advantages when compared to those of fossil coke and raw biomass, for utilization in ironmaking blast furnace or direct reduction furnace.

Currently, the use of biomass/biochar in ironmaking industry has been demonstrated and investigated extensively for bio-material application, pollutant control and CO_2 mitigation [3,11–14]. In Brazil, about 8 Mt of pig iron is produced every year using biomass-derived feedstock in a mini-blast furnace [15]. A project funded by the American Iron and Steel Institute conducted a study on hot metal making in a rotary hearth furnace by wood charcoal, and found that the reduced

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https://doi.org/10.1016/j.enconman.2017.12.037
Received 11 October 2017; Received in revised form 24 November 2017; Accepted 12 December 2017

iron contained low gangue and sulfur, because of the low sulfur content and high reactivity of biomass charcoal [16]. Cheng et al. [11] investigated the substitution of fossil coke by bio-charcoal for iron ore sintering, and found that the duration time of melting temperature and the sintering quantity were the best when the substitution rate of biomass charcoal was 60%. Chen et al. [17] pointed out that torrefaction at a relatively low temperature of 300 °C could transform biomass into a material resembling high-volatile bituminous coal used in blast furnaces. Mousa et al. [3] reviewed the current application situation for bioenergy in the ironmaking industry and stated that biomass/biochar utilization for ironmaking was still limited and suffered many challenges in the technical and economic aspects.

Hence, more research is required to investigate the reaction behavior, conversion kinetics of the reduction of iron ore by bioenergy, in order to achieve a higher efficiency production technology. It has been proved that the reduction conditions (temperature, time, and reduction agents), iron ore composition and reduction methods (direct, indirect, and multi-step) influence the iron ore reduction results differently [18–20]. Rashid et al. [21] investigated the reduction of iron ore using palm kernel shell, and showed that 20 wt% of biomass used in iron ore reduction transformed iron oxide into magnetite and wustite with 18.69% CO_2 mitigation and 19.78% saving of fossil carbon. Guo et al. [18,22] studied the direct reduction of iron oxide by bio-syngas, and found that biomass-derived syngas could reduce Fe^{3+} with well reducibility. The reduction process followed the chemical interfacial reaction mechanism with an activation energy of 104.76 kJ/mol. We et al. [23,24] pointed out that chemical looping gasification of biomass using iron ore as an oxygen carrier was a novel approach for biomass conversion and application, and iron ore reduction by biomass could be divided into two stages: reduction by volatile and followed by reduction by char. Srivastava et al. [25] studied the firing of iron oxide and biomass pellets at different temperatures for different residence times, and investigated the iron loss in slag and metallization characters of the products, results showed that pellet fired at 1450 °C for 20 min had metallization of 98.10%. Obviously, both of volatile and char, the two products from pyrolysis of biomass, can react with iron ore and result in the reduced iron phases. While the reaction of char with iron ore is the rate-limiting step because volatile gases (CO and H_2) can directly react with iron ore in a much higher rate than that of solid biochar [24,26]. So the reduction of iron ore by biochar is extremely different to that of biomass. The efficient utilization of biochar in ironmaking process is of great significance for energy saving and CO_2 mitigation. Fu et al. [27] investigated the metallization degree and crushing strength of the biochar and iron ore mixed composite after reduction in argon atmosphere, results showed that the metallization degree was as well as ground-up coke and the crushing strength was increased by adding 2.5% bentonite as binder. Xu et al. [28] explained that biochar particles could facilitate the microbial reduction of hematite through the electron shuttling process. Huang et al. [29,30] investigated the chemical looping conversion of biochar using iron ore and demonstrated that iron ore acted as a good oxygen carrier which could be recycled for char gasification. However, the reports on the reaction of biochar with iron ore, especially for the reaction process, composition evolution and reaction mechanism of the reduction of iron ore by biochar are very limit. Moreover, the intrinsic reaction between biochar and iron ore will be stood out in nitrogen atmosphere without the interference of other reactive gases such as H_2O, CO or CO_2. The knowledge of the intrinsic reaction behavior and thermal kinetics may be useful for better understanding the reduction of iron ore by biochar and facilitating the application of bioenergy in the ironmaking industry.

In this study, the intrinsic reaction behavior during reduction of iron ore-biochar pellets was investigated. The effect of iron ore content and temperature on the reduction process was explored to reveal the reduction behavior and composition transformation of iron ore-biochar pellets at various conditions. The kinetics of the two isothermal conversions, carbon conversion and extent of iron reduction, were evaluated separately based on the nucleation and growth gas–solid reaction model, then have a deep insight into the mechanism of reduction of iron ore-biochar pellets.

Table 1
Properties of biochar and iron ore fines.

Sample	Properties				
Biochar	Proximate analysis, dry, wt.%				
	Ash	Volatile	Fixed carbon	LHV (MJ/kg)	
	1.67	20.57	77.76	22.42	
	Elemental analysis, dry, wt.%				
	C	H	N	S	O (by difference)
	87.56	2.81	0.18	0.21	7.57
	Specified inorganic species[a], wt.%				
	Na	K	Ca	Mg	Fe
	0.01386	0.12874	0.61322	0.08702	0.09321
Iron ore	Chemical composition[b] (%)				
	Fe	Si	Ca	Mn	Cr
	84.64	13.52	1.40	0.39	0.05

[a] Analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (ELAN DRC-e, PerkinElmer, USA).

[b] Investigated by X-ray fluorescence (XRF) (EAGLE III, EDAX Inc., USA) analyzer.

2. Materials and methods

2.1. Materials

Woody shavings, sourced from a local furniture factory, were used as the raw biomass materials in this study. And woody char was obtained by pyrolysis at 550 °C in a fixed-bed reactor with a flow of nitrogen (99.99%, 0.4 L/min) for the pyrolysis time of 30 min [31,32]. After grinding for 3 min in a blade mill (XY-1000A, Songqing Hardware Company, China), the collected residual char was used as the biochar samples in this study. Iron ore fines, received from Wuhan Steel Group Co., Ltd, China, was screened to remove the impurities and then used as the iron ore in this study.

Table 1 shows the properties of biochar and fresh iron ore fines used in this study. Compared with raw biomass, biochar had reduced volatile, hydrogen and oxygen content with higher calorific value, fixed carbon and carbon content. And the specified inorganics such as Na, K, Ca, Mg and Fe were both less than 1 wt% in biochar which were ignored subsequently. The X-ray fluorescence (XRF) analysis indicates that Fe (84.64 wt%) and Si (13.52 wt%) were the metallic elements identified in overwhelming majority, with minor amounts of Ca, Mn, and Cr found in fresh iron ore fines. And hematite, magnetite, and quartz were the main crystal components in the fresh iron ore fines from X-ray diffraction (XRD) (X'Pert PRO, PANalytical B.V., Netherlands) result (Fig. S1).

2.2. Iron ore-biochar pellets preparation

Iron ore-biochar pellets were prepared using a universal material testing machine (CMT5205, MTS, China) fitted with a load sensor and displacement transducer, with resolutions of ± 0.01 N and ± 0.1 μm, respectively [7,31]. Before densification, the iron ore fines, biochar and deionized water were thoroughly stirred and sufficiently mixed. The mass ratio of iron ore in the total solid densified materials was varied from 50% to 90% and the mass of deionized water was 10 wt% of total solid materials. In each run, proportional amounts of iron ore fines, biochar, and water was densified to form a cylindrical iron ore-biochar pellet of 1.5 g (dry mass), 8 mm in diameter, and 9–20 mm in height. The pellets were then dried for 24 h and used for the following reaction. Then the calculated mole ratio of carbon to iron (Ω) in pellets were 4.83, 3.22, 2.07, 1.21, 0.54, respectively, when mass content of iron ore in pellets increased from 50% to 90%.