



Research article

Direct reduction of oxidized iron ore pellets using biomass syngas as the reducer



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ABSTRACT

The syngas derived from a pyrolysis and gasification process was used as a reducing agent to produce iron ore pellets. The reduction temperature was kept between 1123 K and 1323 K, and the time was set 30 min. Results showed that the reducibility increased from 88.1% at 1123 K to 99.95% at 1323 K. The reduction rate increased with increasing reduction temperature. Further, the reaction rate in the early stage was higher than that in the later stage.

The X-ray diffraction (XRD) and metallographic microscope analyses of the oxidized pellets and direct reduced iron (DRI) products showed that, the reduction process followed the reaction scheme: $\text{Fe}_2\text{O}_3 \rightarrow \text{FeO} \rightarrow \text{Fe}$. A kinetics analysis indicated that, the reduction rate was controlled by an interfacial chemical reaction with syngas and that the activation energy was 104.76 kJ/mol. The effect of syngas as the reducing gas on the reduction of iron ore pellets was similar to that of natural gas. The use of biomass during DRI production can eliminate CO_2 emissions, energy crisis, and climate change.

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1. Introduction

Iron production plays a fundamental and important role in the modern steel industry, which is closely related to the overall development and economy of society [1]. Blast furnace iron production is the prevailing technology for iron-making with approximately 1,188,379 thousand tons of iron in the year 2012, accounts for 94.6% of the world production [2]. In this technology metallurgical coke or coal is used as a common reducing agent in different processes. However, increasing strict environmental requirements, especially CO_2 emissions, may hinder the development of blast furnace iron-making technology [3]. The DRI process is one of the leading methods of non-blast furnace iron-making. The DRI, as a significant substitute for steel scrap, is an ideal alternative raw material for electric steelmaking [4]. Because of high resulting purity and stability, DRI has become the foundation for the development of fast steel production processes. Depending on the type of

reducing agent, DRI production can be divided into two categories: coal-based reductions and gas-based reductions. Compared to other iron-making processes, the gas-based shaft furnace method has the advantages of high yield, low energy consumption, and low emissions. According to statistical analysis, about 90% of DRI production throughout the world is gas-based direct reduction processes. The global DRI industry has continuously grown in recent years to peak in 2013, reaching 75.2 million tons annually. Direct reduced iron from Midrex and HYL/Energion, where the typical gas-based shaft furnace methods are applied, account for approximately 78.6% of global DRI production [5]. However, traditional gas-based reduction methods require rich natural gas resources, which are derived primarily from fossil fuel.

There is growing international concern regarding global climate change, especially in the context of ever-increasing greenhouse gas emissions [6,7]. The CO_2 emissions in China are the highest in the world [8]. In this regard, it is difficult to further use natural gas as a raw material for gas-based direct reduction processes in China. To reduce the dependency of iron-making industry on fossil fuels, technical breakthroughs toward cleaner DRI production and CO_2 emissions reduction, as well as seeking a renewable reducing fuel and a green iron-making process, are of strategic significance for the Chinese national economy.

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There are several methods which can be used in iron and steel industries to minimize CO₂ emissions. A promising solution is the use renewable energy resources, such as biomass as the reducing agent in the existing iron production process to replace fossil fuels such as coke and coal [9]. Biomass is a widely distributed, abundant, renewable, and environment friendly reducing agent that has attracted the attention of international scientific community. Extensive research has been carried out on the use of biomass instead of coal as a DRI solid reductant. Strezov [10] mixed biomass with iron ore at different ratios and found that, the iron ore was successfully reduced to the metallic iron phase when up to 30% by weight of biomass was introduced. Emmerich and Luengo [11] studied the physical and chemical properties of babassu coconut following heat treatment at different temperatures up to 1273 K. Compressive strength, density, craniometry, heat of combustion, and ash content testing suggested that babassu charcoal from unbroken coconuts can be used as a substitute for metallurgical coke as a reducing agent in blast furnaces. However, a large amount of biomass addition to iron ore results in pelletizing difficulties and insufficient rigidity, so it is not suitable for industrial applications. Biomass gasification, as one of the thermo-chemical methods, has been perceived as an attractive process for producing syngas which is rich in reducing gases, such as H₂, CO, and CH₄ fewer C₂ hydrocarbons. Organic substances, such as wood, bamboo processing waste, garden waste, straw husk and rice husk, can be crushed and used to produce the reductive gases through gasification. The reducing gases can be injected to a direct reduction furnace to reduce iron ore pellets. During the DRI production process, CO₂ and H₂O produced within the direct reduction furnace diffuse into the atmosphere. Through photosynthesis, plants absorb CO₂ and H₂O and generate organic matters, which can in turn be used as reduction materials in the future. In this way, the DRI production process can be carried out with no net CO₂ emission. Kaewpanha et al. [12] investigated steam co-gasification of brown seaweed and land-based biomass. The authors found that, the hydrogen-rich gas was produced and the yield of hydrogen increased with an increase in the amount of steam. Udomsirichakorn et al. [13] observed that the steam gasification of biomass with the presence of CaO resulted in higher hydrogen production (maximum H₂ yield of 451.11 ml/g biomass) and *in situ* CO₂ capture and tar reduction. Entrained flow gasification of torrefied wood residues was carried out by Weiland et al. [14], who showed the molar percentage of H₂ and CO could reach 28.0% and 60.3% within the temperature range of 1483–1523 K. Similar results were also reported by Duman et al. [15], who found that steam gasification is one of the promising methods to produce H₂ from safflower seed cake, especially in the presence of CeO₂-Fe₂O₃ catalysts, the highest H₂ yield was obtained with 1492 cm³/g at 973 K.

In this study, biomass syngas was used as the reductant during the DRI production process. Using biomass to produce syngas for the reduction can compensate the utilization of some amounts of natural gas or coal as the reducer, decreasing the consumption of fossil fuels and thus the emissions of CO₂. The biomass reserves are abundant in the world and have a great potential for future development. For example, the total amount of biomass reserves in China is 38.410 × 10⁸ and 40.073 × 10⁸ tce in 2004 and 2009, respectively, while the accordingly available amount is 4.813 × 10⁸ and 5.340 × 10⁸ tce, respectively [16]. There are three advantages of using biomass syngas as the reductant. First, the resulting pellets are pure and stable. Second, CO₂ emissions are reduced during the DRI production process, which can satisfy the technical requirements of the sustainable development of the steel industry. Third, it is an effective way to reduce the dependence on fossil fuels.

The objective of this study was to investigate the feasibility of using biomass syngas as the reducer for the direct reduction of iron ore oxidized pellets. The effects of reduction time and temperature on the direct reduction of iron ore oxidized pellets were measured. The kinetics analysis of the direct reduction by biomass syngas was conducted, and the corresponding reaction rate *k* was determined.

2. Materials and methods

2.1. Materials and facilities

Iron ore powder was supplied by Wuhan Iron and Steel Corporation, Wuhan, China. The bentonite was supplied by Wuhan Iron and Steel Group, Ezhou Iron and Steel Corporation, Ezhou, China. The chemical compositions of the bentonite and iron ore powder are shown in Table 1. The properties of the sawdust, the biomass used in this study are presented in Table 2. The sawdust was collected from the furniture factory of the Huazhong University of Science and Technology, Wuhan, China. The iron ore powder, bentonite, and the sawdust were crushed to pass through a 0.20-mm sieve.

The iron ore pellets consisted 98% iron ore powder and 2% bentonite on weight basis. The pellets were rolled and pelletized on a disc balling machine of 1.0 m dia. After pelletization, the resulting green pellets having 10 to 15 mm dia were used as the test samples. The pellets were heated in an oven at 378 K for 24 h to remove excess moisture. The dried pellets were then roasted in an electric furnace under oxygen-enriched atmosphere at 1523 K for 25 min to obtain oxidized pellets. The chemical composition of the oxidized pellets is shown in Table 3.

2.2. Experimental apparatus and methods

The schematic diagram of the experimental apparatus used for the reduction of the composite pellets is shown in Fig. 1. The lab-scale DRI system was comprised a biomass gasification and reduction system.

The biomass gasification system was heated to the reaction temperature required to obtain a stable flow of reducing gas, which helped to eject the initial gas out of the system through a gas switch controller.

Biomass steam gasification with the assistance of catalysts was conducted. The biomass steam gasification temperature in the furnace was set at 1073 K. Sawdusts were used as raw materials. They were stocked in a hopper and fed into the reactor *via* a screw feeder at a rate of 20 kg/h, when the desired temperature was reached. Then, the steam in water boiler was provided *via* a steam flowmeter at a velocity of 12 kg/h. The synthetic gases consist of CO, 25.79%; H₂, 45.15%; CH₄, 11.38%; CO₂, 17.28%; C₂ hydrocarbons, 0.4%.

Afterwards, 50 pellets were placed in a swing pipe which was hanging inside the reduction furnace tube, and the furnace was heated. The furnace was allowed to reach at the required reaction temperature, and was maintained at 1123, 1173, 1223, 1273 and 1323 K, respectively. Throughout the process, N₂ was injected as a protective gas to prevent the pellets from reaction. As the reducing gas reached at a stable flow of 7.0 cm³/s, the gas controller switch was switched to introduce the reducing gas in the reduction system to trigger the reduction reaction. During the reduction process, the pellets weight was recorded automatically by an electronic weight balance and the computer. The reduction of the pellets began at a high temperature in a reductive atmosphere. The weight of the pellets was continuously decreased and was recorded by a computer until the experimental run was completed. After 30 min of reduction, N₂ was introduced in the reactor until it was cooled to room temperature to avoid reoxidation of the pellets. Each trial was maintained for a period of 30 min, and several repeat runs were carried out under identical conditions to ensure the repeatability of the process.

The Sample was fixed in the metallographic specimen inlaying machine using thermosetting resin. And then it was cut in half and then was passed from five passes of coarse grinding, fining grinding, polishing,

Table 1
Chemical compositions (%) of iron ore and bentonite.

	Fe	Si	Al	Mn	Ca	Mg	Ti	S	K	LOI
Iron ore	67.72	5.39	2.02	0.30	9.39	14.49	0.33	0.27	–	0.09
Bentonite	3.25	68.41	18.37	0.04	3.77	3.88	0.69	–	1.55	0.04

LOI: Loss on ignition.

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