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Iron ore reduction by methane partial oxidation in a porous media

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ABSTRACT

In this work, iron ore reduction by the gaseous products of methane partial oxidation in a porous media (H_2 and CO) is studied numerically and experimentally. A new fixed-bed reactor was designed to perform the reduction tests, along with the development of a mathematical model that considers reduction reactions, mass balance and energy equations for both gas and solid phases. The experimental results show a low reduction degree at equivalence ratio (φ) of 1.2 and allow model parameterization. The model was applied to sensitivity analyses regarding to operation parameters such as equivalence ratio and iron ore pellets size. The performed analysis predicts favorable metallization degree for high equivalence ratios (or high H_2 and CO concentrations) and smaller pellets.

Introduction

Direct reduced iron (DRI) industry has grown steadily during the last 40 years, contributing around 7% of the world's total iron-making capacity. This growth was stimulated by a desire or necessity to use lower grade ores and fuels that are unsuitable for blast furnaces [1]. In parallel with this situation, environmental friendly technologies are highly valued by society and industry, which makes necessary finding combustion processes that are more efficient than conventional ones, among which combustion in porous media arises as a very attractive alternative. This technology is characterized by being capable to burn an excessively rich or lean fuel mixture, due to the intense heat exchange between the solid media and the premixed gas fuel. Because of the heat recirculation inside the porous media, which produces an excess of enthalpy in the reaction zone, these burners have a wide range of combustion, while conventional burners do not. The transient system involves a traveling wave representing unsteady combustion zone freely propagating in either downstream or upstream direction inside the porous media. The wave velocity measurements are based on displacement of thermal profile along the reactor length. The relatively high thermal emissions with low emissions of CO and NO_x in lean mixtures

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and excellent flame stability are basic requirements to generate industrial applications. One of the main uses of this technology is the partial oxidation of fuels utilizing a highly rich mixture [2,3]; this is done to obtain syngas ($H_2 + CO$) in the combustion products, which are the same reducing gases that DRI processes use in order to reduce the iron ore.

There are few proposed models for fixed-bed iron ore reduction reactors. Aguilar et al. [4] proposed a model of this kind based on unsteady state condition. Parisi and Laborde [5] proposed a model for a countercurrent moving bed reactor. The model considers global reduction reactions and it was validated with data available from two DRI plants. Takenaka et al. [6] proposed a shaft furnace model where reaction rate equations were derived from the three-interface model, including heat and mass balances. Alamsari et al. [7] proposed a model for a countercurrent moving bed reactor, where the three-interface model was also considered. Methane reforming and water gas shift reactions were included as the reactions that occur in the gaseous phase. The model also included heat and mass balances. Mondal et al. [8] proposed a kinetic model using CO as the reducing agent. Kinetics constants were derived based on Arrhenious equation and cementite formation reaction was considered. Valipour [9] proposed a non-isothermal model based upon a special application of the grain model, where each grain is reduced according to the unreacted shrinking core model at three-interfaces simultaneously, and included heat and mass balances. Nouri et al. [10] proposed grain model that considers the global reduction reaction by CO and H_2. The countercurrent moving bed reactor was modeled under steady state conditions. The results were contrasted with available data from a DRI plant. The kinetics of the reduction reactions is very important to develop a mathematical model of the reduction zone. Unreacted shrinking core model (USCM) proposed by Levenspiel [11] is vastly used for kinetics model of iron ore reduction in which the reaction occurs first at the outer surface of the particle. According to the model, the reaction zone then moves towards the center of the solid, leaving behind converted material and inert solid (ash). Therefore, at any time, there exists an unreacted core of reactant solid that is shrinking in size during the reaction.

The aim of this work is to perform an experimental and numerical study of the reduction of iron ore by the product gases of partial combustion of a methane-air mixture in a porous media burner, where the combustion front propagates through the iron ore bed. While porous media burners have been used in the past to produce syngas efficiently, it has not been studied its application in mineral reduction. A porous media burner is considered a fixed-bed reactor for this purpose, while most DRI industrial applications consider moving-bed reactors. In addition, when used to produce syngas, porous media burners have the capability to control the combustion wave speed adjusting the equivalence ratio.

In order to do this, a new porous media reactor was designed and built to perform the experimental tests. For the development of the mathematical model, mass balance and energy equations were taken into account, and the global reduction reactions were considered. The model was parameterized with experimental data obtained.

Experimental apparatus and procedure

Experiments on iron reduction were conducted using the setup shown in Fig. 1. The system consisted of a combustion tube filled with a porous medium, natural gas and air supply systems, a temperature measurement system, and a gas chromatograph. There were two configurations of the porous medium: In the first case, the reactor was filled with alumina spheres only, this was done with the purpose of establishing a baseline. In the second case, the porous medium was composed of two sections of alumina spheres and a section of iron ore pellets. The configuration was the following: from the reactor top to bottom, a 100 mm section filled with alumina spheres, to ensure stable initiation of upstream waves; an intermediate section filled with 120 mm of iron ore pellets. This section constitutes the reduction zone; a 40 mm section filled with alumina spheres, from the bottom of the reduction zone to the reactor bottom.

The irregular geometry of iron ore pellets was approximated by a sphere with 5 mm diameter. The specified volumes of 5.6 mm solid alumina balls and 5 mm iron ore pellets resulted in two packed beds with a porosity of ~40%. Combustion tube was made of quartz with an inner diameter of 41 mm, a wall thickness of 2 mm, and length of 30.2 cm. To avoid heat losses, to achieve quasi-uniform system temperature profiles, and to protect quartz tube, the inner surface of the combustion tube was covered with a 3 mm layer of Fiberfrax insulation and 6 mm thick high-temperature insulation was applied on the external diameter of the reactor. Combustible mixtures of natural gas with air were set up by a continuous flow method where the fuel and air flows were metered using a set of Aalborg mass flow controllers. The composition of the natural gas was 94.1% CH_4, 4.8% C_2H_6 and 1.1% of other gases. Before the reactants enter the combustion tube, they were premixed in a mixing chamber to ensure uniform gas composition. Then, the mixture was introduced through a distribution grid at the reactor bottom. The exit of the reactor was open to atmosphere. During the experiments, the upstream propagating combustion wave was initiated at the reactor exit. The upstream propagation was recorded. As the wave reached the bottom alumina section, the flame was turned off.

A ceramic shell of 0.5 cm in diameter was positioned axially in the combustion tube. It contained 0.08 cm diameter holes with three S-type (platinum/rhodium) thermocouples fabricated by OMEGA. The voltages measured by the thermocouples were recorded by an OMB DAQ 54 acquisition module and converted by the Personal DaqView Software. The thermocouple junctions were spaced 6 cm apart along the length of the shell. The first one was located at 7 cm below the reactor exit. The thermocouples were completely covered by the ceramic shell allowing to record temperatures very close to solid phase temperatures. The axial position of the thermocouples provided minimal disturbances to the gas flow and heat fluxes in the reaction zone. The experimental error in the temperature measurements was estimated as ~50 K and the error in the flow measurements was ~10%. To measure the exhaust gas composition a PerkinElmer gas chromatograph, model CLARUS 500, was used. The gas samples were taken