



# Kinetics of the reduction of hematite ( $\text{Fe}_2\text{O}_3$ ) by methane ( $\text{CH}_4$ ) during chemical looping combustion: A global mechanism



Esmail R. Monazam<sup>b</sup>, Ronald W. Breault<sup>a,\*</sup>, Ranjani Siriwardane<sup>a</sup>, George Richards<sup>a</sup>, Stephen Carpenter<sup>c</sup>

<sup>a</sup>National Energy Technology Laboratory, US Department of Energy, 3610 Collins Ferry Rd., Morgantown, WV 26507-0880, United States

<sup>b</sup>REM Engineering Services, PLLC, 3537 Collins Ferry Rd., Morgantown, WV 26505, United States

<sup>c</sup>URS Energy & Construction, Inc., 3610 Collins Ferry Rd., Morgantown, WV 26505, United States

## HIGHLIGHTS

- TGA reduction of hematite ( $\text{Fe}_2\text{O}_3$ ) in  $\text{CH}_4$  (15–35%) was conducted at temperatures from 700 to 825 °C.
- A parallel reaction scheme was applied to the reduction data.
- One reaction is first-order and the other follows the Avrami equation for nucleation and growth.
- The reaction rates for both reactions increase with temperature and methane concentration.

## ARTICLE INFO

### Article history:

Received 18 March 2013

Received in revised form 17 July 2013

Accepted 23 July 2013

Available online 1 August 2013

### Keywords:

Chemical looping combustion

Oxygen carriers

Kinetic rates

## ABSTRACT

Chemical-looping combustion (CLC) has emerged as a promising technology for fossil fuel combustion which produces a sequestration ready concentrated  $\text{CO}_2$  stream in power production. A CLC system is composed with two reactors, an air and a fuel reactor. An oxygen carrier such as hematite ( $94\%\text{Fe}_2\text{O}_3$ ) circulates between the reactors, which transfers the oxygen necessary for the fuel combustion from the air to the fuel. An important issue for the CLC process is the selection of metal oxide as oxygen carrier, since it must retain its reactivity through many cycles. The primary objective of this work is to develop a global mechanism with respective kinetics rate parameters such that CFD simulations can be performed for large systems. In this study, thermogravimetric analysis (TGA) of the reduction of hematite ( $\text{Fe}_2\text{O}_3$ ) in a continuous stream of  $\text{CH}_4$  (15%, 20%, and 35%) was conducted at temperatures ranging from 700 to 825 °C over ten reduction cycles. The mass spectroscopy analysis of product gas indicated the presence of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at the early stage of reaction and  $\text{H}_2$  and  $\text{CO}$  at the final stage of reactions. A kinetic model based on two parallel reactions, (1) first-order irreversible rate kinetics and (2) Avrami equation describing nucleation and growth processes, was applied to the reduction data. It was found, that the reaction rates for both reactions increase with, both, temperature and the methane concentration in inlet gas.

Published by Elsevier B.V.

## 1. Introduction

The increase in the  $\text{CO}_2$  concentration, a major green house gas, in the atmosphere due to the combustion of fossil fuels such as coal, petroleum, and natural gas may lead to disastrous changes in our planet's climate. The concentration of  $\text{CO}_2$  in the atmosphere has risen to a value of  $\sim 370$  ppm today, from the preindustrial value of 280 ppm [1]. Since historic levels of  $\text{CO}_2$  have been both higher and lower than these levels, a direct link to anthropogenic actions is not possible. Even so, it is adventitious to look for ways to reduce and control the anthropogenic contribution. At present, there are a number of  $\text{CO}_2$  capture processes [2] capable of doing this, (1) precombustion, in which the hydrocarbon fuels are

decarbonized prior to combustion; (2) oxyfuel combustion, which uses pure oxygen separated from air; and (3) post combustion separation, which separates  $\text{CO}_2$  from the flues gases using different methods. All of these techniques have high costs and large energy penalty, resulting in a significant decrease (9–27%) of the overall combustion efficiency and a price increase (1.2–2.3 times) of the energy [3–5]. An alternative process such as chemical-looping combustion (CLC) has been proposed for the reduction of  $\text{CO}_2$  emissions [6,7].

Chemical looping combustion (CLC) is a novel process for heat and power production with inherent  $\text{CO}_2$  separation [8–10]. An oxygen carrier such as  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$  and  $\text{NiO}$  performs the task of transferring oxygen from air for the combustion of fuel [11]. Generally, these metal oxides are combined with an inert material such as  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{NiAl}_2\text{O}_4$ , and bentonite which acts as a porous support providing a higher surface area for

\* Corresponding author. Tel.: +1 304 285 4486; fax: +1 304 285 4403.

E-mail address: [ronald.breault@netl.doe.gov](mailto:ronald.breault@netl.doe.gov) (R.W. Breault).

reaction, and as a binder for increasing the mechanical strength and attrition resistance [12] of these oxygen carrying solids.

The CLC uses two reactors in the form of interconnected reactor beds (1) a fuel reactor where the metal oxide particles are reduced by reaction with the fuel, and (2) an air reactor where the reduced metal oxide from the fuel reactor is oxidized with air. The advantage with the technique compared to normal combustion is that the outlet gas from the fuel reactor consists of only CO<sub>2</sub> and H<sub>2</sub>O, and thus no extra energy is needed for CO<sub>2</sub> separation. Extensive research on chemical looping combustion has been performed over the past decade at Korea Institute of Energy Research [13,14], Tokyo Institute of Technology in Japan [15–20], TDA Inc. [21,22], Chalmers University of Technology in Göteborg [2], Sweden [2], CSIC in Zaragoza [2], Spain [18], US Department of Energy (DOE) [22,23], University of Cambridge [24], and University of Colorado [25].

Fuel such as coal, biomass and natural gas are being used for reduction of the metal oxides in CLC. When methane is used as a reducing agent CO<sub>2</sub> emission are less compared to other fuels and contamination emissions are negligible. Also, among the fossil fuels on the earth, methane is one of the most abundant fuels both underground and in ocean as methane hydrates. In this study, methane is used as a reducing agent.

Among the metal oxides which are used as an oxygen carrier in CLC, iron oxide (Fe<sub>2</sub>O<sub>3</sub>) is very attractive one for commercial CLC application since it is relatively inexpensive, readily available as natural mineral sand also environmentally safe compared to other metal oxide such as NiO and CuO [26]. Research on CLC has so far mainly been focused on the development and selection of suitable oxygen carrier materials and the implementation of this concept in pilot scale tests. However, few studies reported in the literature have been focused on the determination of kinetic parameters of Fe<sub>2</sub>O<sub>3</sub> based oxygen carriers. The knowledge of the kinetics data is of great importance in the design of a CLC process, because it determines the solid inventory necessary in the fuel and air reactors, as well as the recirculation rate of oxygen carriers between the reactors. Many researchers have tried to develop a universal kinetic equation for gaseous reduction of iron oxides. However, it was only possible to obtain a set of independent equations, useful for the description of the reduction process within a certain range of reaction conditions [27–29].

One of the most important parameters of the hematite reduction is the apparent activation energy as it defines the reactor dimensions and the energy consumption. Literature survey indicates that its value depends on many factors such as chemical structure of the starting raw material, nature of reducing gas, temperature range, reaction step, presence of water vapor and other gases in the gas mixture. The literature data suggests that activation energy obtained by reducing iron oxides with methane varies from 49–271 kJ/mol [30–32]. This wide range of value is due to the variation in rate controlling step assumed in developing the kinetic rates. Moreover, it is clear that the rate controlling mechanism is related to the many factors such as chemical and physical nature of starting raw material, gas composition and temperature range.

Ghose et al. [33] measured the rate reduction of porous and dense spherical pellets of iron oxide (Fe<sub>2</sub>O<sub>3</sub>) with 100% methane in the temperature range of 800–1025 °C. They suggested that the chemical reaction of Fe<sub>2</sub>O<sub>3</sub> with CH<sub>4</sub> takes place in two steps:

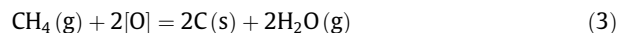
- (1) Decomposition of methane into carbon and hydrogen:



- (2) Reduction of iron oxide by hydrogen:



where [O] is the oxygen in iron oxide. Therefore, the overall reaction rate was considered as;



The apparent activation energy was obtained as 206 kJ/mol in the temperature range of 800–950 °C and 105.7 kJ/mol in the temperature range of 950–1025 °C for reaction (1) above. Furthermore, they claimed most of this apparent value was due to increase of concentration of hydrogen with increase in temperature due to enhanced cracking of CH<sub>4</sub>. The primary difference of our work from the work by Ghose [33] is that we have investigated the reaction of CH<sub>4</sub> with iron oxide at different CH<sub>4</sub> concentrations (15–35%) and also we have extended the temperature to a lower range of 700–825 °C.

The objective of this paper is to determine the kinetics parameters of the reduction reactions of Fe-based oxygen carriers, using CH<sub>4</sub>. The effects of temperature (700–825 °C), flow rate, sample size, and methane concentration (15–35%) were evaluated.

## 2. Experimental

### 2.1. Thermogravimetric Analysis (TGA) apparatus

A sketch of the reactor unit a TA Model 2050 thermo gravimetric analyzer, is shown in Fig. 1. A sample is placed on the pan which is centered in the gas feed and gas exit ports. The port at the bottom is closed. Sweep gas keeps the balance electronics in an inert environment and enters the reaction chamber at the top. A typical TGA experimental data on weight changes during reduction/oxidation for cyclic tests at a given temperature are illustrated in Fig. 2. The samples were placed in a 5-mm deep and 10-mm diameter quartz crucible. For a typical test, about 60 mg of the hematite sample was heated in a quartz bowl at a heating rate of 15 °C/min in zero-grade air to the reaction temperature. The reduction–oxidation cycles were conducted within the temperature range 700–825 °C for 10 cycles, using 15%, 20%, and 35% CH<sub>4</sub> concentrations in N<sub>2</sub> for the reduction segment and in zero-grade air for the oxidation segment. The system was flushed with ultra-high pure nitrogen for 10 min before and after each reaction segment. The concentrations of CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, CO, and O<sub>2</sub> from the exit gas stream of the reactor were analyzed using a mass spectrometer. The mass spectrometer is manufactured by Pfeiffer Omnistar

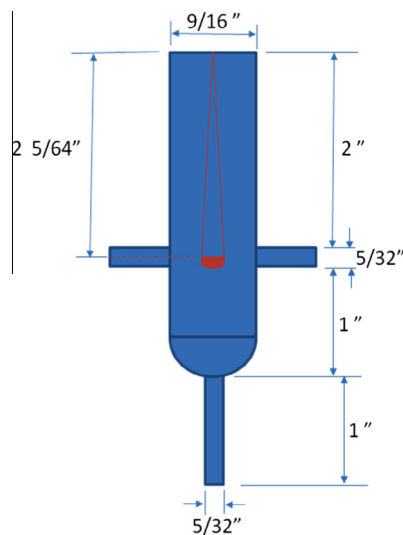


Fig. 1. Sketch of TA Model 2050 thermo gravimetric analyzer.

Download English Version:

<https://daneshyari.com/en/article/148176>

Download Persian Version:

<https://daneshyari.com/article/148176>

[Daneshyari.com](https://daneshyari.com)