



Thermodynamic analysis of the partial oxidation of coke oven gas for indirect reduction of iron oxides in a blast furnace



Wei-Hsin Chen ^{a,*}, Chih-Liang Hsu ^a, Shan-Wen Du ^b

^a Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan

^b Iron and Steel Research and Development Department, China Steel Corporation, Kaohsiung 812, Taiwan

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ABSTRACT

The partial oxidation of a COG (coke oven gas) in a blast furnace is examined in this work using thermodynamic analysis. LTIR and HTIR (Low-temperature and high-temperature indirect reduction) of iron oxides in a blast furnace are also studied. The influences of the reaction temperature, M/H (methane-to-hematite) ratio, and O/F (oxygen-to-fuel) ratio on CH₄ conversion and iron oxide reduction are examined. Within the investigated ranges of the parameters, a higher reaction temperature is conducive to CH₄ conversion, while at least 97.64% of Fe₂O₃ is reduced. In LTIR, Fe₃O₄ is the prime product, with a high level of solid carbon formation. The entire LTIR reaction is characterized by exothermic behavior, so that no additional heat is required to trigger COG partial oxidation and IR. In HTIR, increasing the reaction temperature facilitates CO-based IR and suppresses H₂-based IR. A higher temperature produces more Fe, so as to enhance the iron oxide reduction reactions; meanwhile, the FeO reduction is governed by H₂ and CH₄. When the reaction temperature is higher than 800 °C and the M/H ratio is lower than unity, a heat supply is required to drive HTIR. The O/F ratio in LTIR and HTIR should be controlled below 2 to retard carbon formation and drive iron oxide reduction.

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1. Introduction

The burning of fossil fuels releases CO₂ into the atmosphere, and this is the main driver of climate change. Therefore, the development of alternative fuels with a low carbon footprint and the modification of processes to reduce CO₂ emissions are two ways that can be used to mitigate global warming [1]. In industry, the iron and steel sector accounts for approximately 5–7 % of total anthropogenic CO₂ emissions, of which around 70% is contributed by iron production in BFs (blast furnaces) [2]. It thus follows that a significant cut in CO₂ emissions from the ironmaking process can effectively reduce the greenhouse gas emissions from the iron and steel industry, and this is the basis for the current study.

The EU (European Union) launched the ULCOS program to mitigate anthropogenic CO₂ emissions from the iron and steel industry [3,4]. ULCOS stands for Ultra-Low Carbon Dioxide Steelmaking, and is a consortium of 48 European companies and organizations from 15 European countries with the aim of drastically reducing CO₂ emissions from steel production. In ULCOS, hydrogen (H₂) is considered as

a potential reducing agent of iron ores in the reduction process, and this approach could be the core process of a new and cleaner way to produce steel with lower CO₂ emissions [5]. Another program, termed COURSE 50 (CO₂ Ultimate Reduction in Steelmaking process by innovative technology for cool Earth 50), has also been launched in Japan. COURSE 50 aims at developing technologies to reduce CO₂ emissions by approximately 30% through the suppression of CO₂ emissions from BFs, as well as the capture, separation, and recovery of CO₂ from the BFG (blast furnace gas) [6]. To accomplish this goal, the possible actions related to H₂ utilization in COURSE 50 include: (1) developing technologies for reducing iron ore using H₂ as a reducing agent, so as to decrease coke consumption in BFs; (2) developing technologies to reform coke oven gas (COG) in order to raise its H₂ content by utilizing unused waste heat; and (3) developing technologies to produce high strength and high reactivity coke for reduction with H₂. Accordingly, COG has some potential for use in the reduction of iron oxides in BFs.

In the ironmaking process coal is converted into metallurgical cokes in coke ovens, and consumed at the raceways of BFs via pulverized coal injection [7,8]. While coals are processed in coke ovens in the absence of oxygen to produce metallurgical cokes [9], COG, also called coke gas, is produced in the coke-making process

* Corresponding author. Tel.: +886 6 2004456; fax: +886 6 2389940.

E-mail address: weihsinchen@gmail.com (W.-H. Chen).

Nomenclature		P	system pressure (Pa)
a_{ik}	number of atomic weight of element k in a mole of species i (mol^{-1})	R	Universal gas constant ($=8.314 \text{ kJ kg mol}^{-1} \text{ K}^{-1}$)
f	partial fugacity (Pa)	T	temperature (K)
f^0	standard-state fugacity (Pa)	y	mole fraction
G^0	standard-state Gibbs free energy (kJ mol^{-1})	<i>Greek letters</i>	
G_{total}	total Gibbs free energy (kJ mol^{-1})	λ	Lagrange multiplier
$G_{C(s)}$	partial Gibbs free energy of solid carbon (kJ mol^{-1})	γ	Fugacity coefficient
$G_{C(g)}$	partial Gibbs free energy of gas carbon (kJ mol^{-1})	<i>Subscripts</i>	
$G_{C(g)}^0$	standard Gibbs free energy of solid carbon (kJ mol^{-1})	i	species
M	number of elements in the reacting mixture (–)	in	input
n	number of moles (mol)	k	gram-atoms of element
N	number of species (–)	out	output

when volatile coal matter is converted into COG, leaving carbon intensive coke behind [10]. The typical contents of H_2 , CH_4 , and CO in COG are in the ranges of 54–63, 23–32, and 3.6–7.6 vol%, respectively [11], revealing that COG is a naturally H_2 -rich gas mixture. Due to the amount of CH_4 contained in COG, the H_2 in the gas mixture can be further enriched if CH_4 is reformed. The product gas can then be thought of as a promising source of H_2 , and can be used in fuel cells or for indirect reduction of iron oxides in BFs [2,11].

BFs are moving bed reactors for the production of hot metal, in which layers of coke and iron ore with flux are separately fed into the reactor from the top of the furnace. Alternatively, pulverized coal accompanied by hot blast is injected into raceways through tuyeres to provide heat and reducing gases for iron ore reduction [12,8]. By virtue of the countercurrent nature of heat transfer, the temperature is lower at the top of the reactor than at the bottom. The reduction reactions of iron oxides in BFs can be catalogued into DR (direct reduction) and IR (indirect reduction), which occur at the lower and upper parts of a BF, respectively [12]. In DR, iron and CO are produced from the endothermic reactions of carbon with iron oxides at temperatures higher than 950°C [13,14]. Iron oxides or Fe_2O_3 are reduced into other iron oxides (Fe_3O_4 and FeO) and iron (Fe) by gaseous reducing agents in IR, where the temperature is usually lower than 900°C . The gas-based IR consists of three kinds of mechanisms, including CO-based [15,16], H_2 -based [17–19], and CH_4 -based [20] IR processes. The CH_4 -based IR occurs only at temperatures higher than 570°C . The three IR processes are given in Table 1.

A variety of approaches have been used to figure out the detailed mechanisms of iron oxide reduction in BFs, such as experimental studies [21–24], mathematical models [25], kinetics development

[26–28], and thermodynamic analysis [11,29], and the key works regarding this are listed in Table 2. The table indicates that IR is closely related to CO and H_2 . Prior to using COG for iron oxide reduction, the methane can be reformed via steam reforming or partial oxidation to enrich CO and H_2 in the gas [2]. However, this fuel processing increases the operating cost of hot metal production. To simplify the fuel processing and lower costs, this study examines the one-step utilization of COG via partial oxidation for iron oxide IR in a BF by means of a thermodynamic approach. The reaction mechanisms of the partial oxidation of COG are tabulated in Table 3, and the performance of this will be examined in detail later in this study. An effective IR that minimizes the heat energy in a BF has long been an aim in ironmaking. Therefore, the reaction enthalpy of COG partial oxidation in association with iron oxide IR will be evaluated in this work. Based on the results of these analyses, feasible operating conditions for iron oxide IR using one-step utilization of COG will be suggested.

2. Methodology

2.1. Minimization of Gibbs free energy

In a thermodynamic analysis, the Gibbs free energy is the most commonly used function to identify the equilibrium state of a reaction system. In a reaction system with N species, the total Gibbs free energy is expressed as

$$G_{total} = \sum_{i=1}^N n_i \left[G_i^0 + RT \ln \left(\frac{f_i}{f_i^0} \right) \right] \quad (1)$$

Table 1
A list of CO-based, H_2 -based and CH_4 -based IR processes.

Process	$\Delta H_{298}^0 (\text{kJ mol}^{-1})$	Reaction
CO-based IR processes		
$3\text{Fe}_2\text{O}_3 + \text{CO} \leftrightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$	–25.1	R1
$\text{Fe}_3\text{O}_4 + 4\text{CO} \leftrightarrow 3\text{Fe} + 4\text{CO}_2 \quad T \leq 570^\circ\text{C}$	–16.4	R2
$\text{Fe}_3\text{O}_4 + \text{CO} \leftrightarrow 3\text{FeO} + \text{CO}_2 \quad T \geq 570^\circ\text{C}$	22.3	R3
$\text{FeO} + \text{CO} \leftrightarrow \text{Fe} + \text{CO}_2 \quad T \geq 570^\circ\text{C}$	–12.9	R4
H_2 -based IR processes		
$3\text{Fe}_2\text{O}_3 + \text{H}_2 \leftrightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$	16.1	R5
$\text{Fe}_3\text{O}_4 + 4\text{H}_2 \leftrightarrow 3\text{Fe} + 4\text{H}_2\text{O} \quad T \leq 570^\circ\text{C}$	148.4	R6
$\text{Fe}_3\text{O}_4 + \text{H}_2 \leftrightarrow 3\text{FeO} + \text{H}_2\text{O} \quad T \geq 570^\circ\text{C}$	63.5	R7
$\text{FeO} + \text{H}_2 \leftrightarrow \text{Fe} + \text{H}_2\text{O} \quad T \geq 570^\circ\text{C}$	28.3	R8
CH_4 -based IR processes		
$4\text{Fe}_2\text{O}_3 + 4\text{CH}_4 \leftrightarrow 8\text{FeO} + \text{CO}_2 + 2\text{H}_2\text{O} \quad T \geq 570^\circ\text{C}$	351.283	R9
$4\text{Fe}_2\text{O}_3 + 3\text{CH}_4 \leftrightarrow 8\text{Fe} + 3\text{CO}_2 + 6\text{H}_2\text{O} \quad T \geq 570^\circ\text{C}$	884.328	R10
$12\text{Fe}_2\text{O}_3 + \text{CH}_4 \leftrightarrow 8\text{Fe}_3\text{O}_4 + \text{CO}_2 + 2\text{H}_2\text{O} \quad T \geq 800^\circ\text{C}$	126.378	R11

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