

# Thermodynamic analysis of a methane carbon cycling reforming system integrated iron direct reduction<sup>#</sup>

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## ABSTRACT

The use of hydrogen instead of coke for iron reduction, known as hydrometallurgy, is a potential route to reduce carbon emissions in the iron and steel industry. Hydrogen is used as a heat source and reactant, which is governed by both chemical equilibrium and heat supply. Current processes face the challenge of high energy consumption arising from the heat demand and gas consumption. To alleviate this challenge, we used different H<sub>2</sub>/CO at different stages of iron oxide reduction to utilize the heat of reaction to drive endothermic reactions. In this way, it is possible to achieve auto-thermal process or less energy consumption. Based on this idea, we proposed a methane carbon cycling reforming system integrated iron direct reduction. This system yields H<sub>2</sub> and CO separately, and reducing gas can be directly delivered to the ironmaking system in special proportions. The energy consumption is 8.73 GJ/t<sub>DRI</sub>. This study provides a promising way for the construction and integration of efficient and low-carbon emission hydrogen ironmaking systems.

**Keywords:** methane carbon cycling reforming, hydrogen, direct reduced iron

## NONMENCLATURE

### Abbreviations

CMD	Catalyst methane decomposition
RB	Reverse boudouard
DRI	Direct reduced iron
MCCR	Methane carbon cycling reforming
GOD	Gas oxidation degree

### Symbols

X	Conversion rate
$\eta_{total}$	Total energy efficiency

## 1. INTRODUCTION

Energy crisis and environmental problems caused by massive burning and rough utilization of fossil fuels more and more prominent. It has become an important consensus for various industries to develop new energy technologies and seek sustainable development. The general ironmaking method using coke to smelting in high temperature. The ironmaking process accounts for 70% energy consumption among iron and steel industry in China[1]. This industry is characterized by high carbon emissions. In order to achieve the goal of carbon neutrality, the iron and steel industry is faced with the challenges of energy reserves and reducing carbon emissions.

Substitute coke for hydrogen to ironmaking, also known as hydrometallurgy, is one of promising way to reduce CO<sub>2</sub> emission. Gas-based hydrogen direct iron reduction is applied in many countries, using hydrogen and carbon monoxide as the reducing gas. The reducing gases plays the role of both reaction feedstock for the iron reduction reaction and heat carriers for the reaction in the shaft furnace. As a result, it is characterized by large quantities and high temperatures, which leads to increased energy consumption. The H<sub>2</sub>/CO ratio of reducing gas is related to associated with the gas consumption and energy consumption[2]. Nevertheless, the H<sub>2</sub>/CO ratio of reducing gas is introduced to the shaft furnace in a certain ratio and cannot be adjusted flexibly.

In fact, the reduction of iron oxides is not a one-step reaction, according to metallurgical thermodynamics, and the reduction of iron oxides is divided into three stages, presenting three phase stability zones, which provides the possibility of segmented reduction. Supplying the iron reduction system with specific ratios of hydrogen and carbon monoxide based on endothermic or exothermic conditions in different stages

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provides a new way to improve the utilization of reducing gas.

However, this approach acquires different proportions of hydrogen and carbon monoxide to meet various demands. Methane carbon cycling reforming (MCCR) is a novel method to produce hydrogen and carbon monoxide separately, which uses methane and carbon dioxide as materials. It was first proposed by Takenaka et al.[3], More[4] further investigated, and Mantripragada[5] studied from different process configurations. By this way, hydrogen and carbon monoxide produced by two sequential reactions. The product gas can be regulated to meet the requirements of reduction reactions.

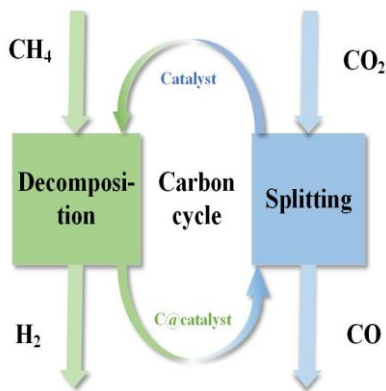


Fig. 1 Schematic of MCCR

Combining the production and utilization of reducing gas, we proposed a new methane carbon cycling reforming system integrated three-steps iron direct reduction. Through MCCR, hydrogen and carbon monoxide are produced separately. Then, hydrogen and carbon monoxide with special proportions are introduced to various periods of iron oxides reduction. In

this way, the H<sub>2</sub>/CO ratio can be adjusted and no heating of the reducing gas is required.

## 2. MODEL AND EVALUATION CRITERIA

### 2.1 Schematic of system

The system mainly consists of two parts, the reducing gas production subsystem and the three-step direct reduced iron (DRI) subsystem. The schematic diagram is shown in Fig. 2. We do not show heat exchangers. The reducing gas produced by the MCCR subsystem can be used as a feedstock input to the DRI subsystem, as storage fuel or as a raw material for other industrial processes.

#### 2.8.1 MCCR subsystem

The MCCR subsystem consists of CMD and RB reactions, which are capable of producing high purity H<sub>2</sub> and CO, respectively. Reducing gas can be used as a feedstock input for the iron reduction system, or can be used as storage fuel or as feedstock for other industrial processes.

Firstly, methane decomposes in the reactor to produce hydrogen and the coke remains at the catalyst. Secondly, carbon dioxide is delivered to eliminate those coke at the catalyst and as well produce carbon monoxide. During the process, hydrogen and carbon monoxide are produced by two sequential reactions:

CMD:



RB:



The CMD and RB reactions produce H<sub>2</sub> and CO in stepwise. For practical production, a continuous supply of reducing gas is required. However, continuous

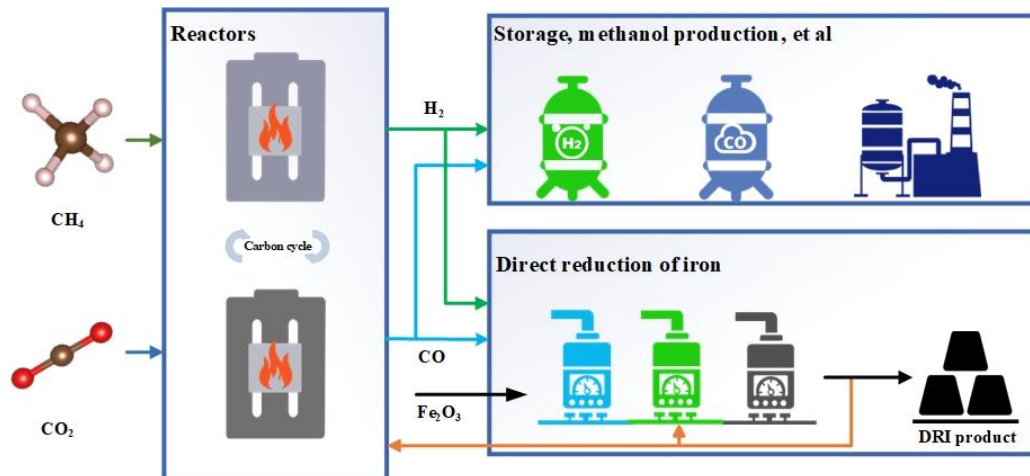


Fig. 2 Schematic of the proposed system

production of reducing gas can be achieved by switching reaction period between two reactors.

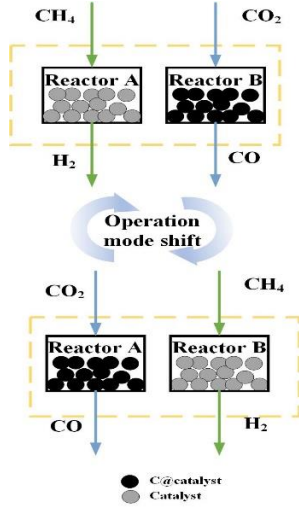


Fig. 3 Operation mode in dual reactors

### 2.8.2 3-step DRI subsystem

According to the metallurgical thermodynamics, the reduction of  $Fe_2O_3$  goes through three reduction steps at the temperature higher than  $570\text{ }^\circ\text{C}$ , rather than direct reduction to metallic iron. The reduction process is  $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$ . Based on the different reaction features of those three stages, feeding with  $H_2$  and  $CO$  in specific ratios can achieve auto-thermal process of the reaction process or improve the utilization of energy. At the same time, the reducing gas contained in the exhaust gas of the iron reduction system can be used as energy source for the MCCR subsystem and heat supply to iron reduction reactors. The operating parameters of the iron reduction system are shown in Table 1.

Table 1. Parameters of DRI subsystem

Parameters	Unit	Value
Inlet reducing gas temperature	$^\circ\text{C}$	800
Iron reduction temperature	$^\circ\text{C}$	800
Required solid feed	t/h	28.1
DRI production	t/h	26.4[6]
Metallization	%	94[7]

### 2.2 Evaluation criteria

The reducing gas produced by MCCR is delivered to the DRI subsystem, and the conversion of methane and

carbon dioxide is associated with further reaction. The conversion rate is calculated by:

$$X = 1 - \frac{n_{out}}{n_{in}} \quad (3)$$

Gas oxidation degree (GOD) shows the reaction behaviors of reducing gas with iron oxide:

$$GOD = \frac{H_2O}{H_2 + H_2O} \text{ or } \frac{CO_2}{CO + CO_2} \quad (4)$$

The analysis target is to evaluate the total energy efficiency of the system. It is calculated by:

$$\eta_{total} = \frac{\sum F_{fuel} \times HHV + E_{DRI}}{F_{CH_4} \times HHV_{CH_4}} \quad (5)$$

where  $F$  represents the mole flowrate, HHV represents the High Heat Value, and  $E_{DRI}$  is the global energy consumption to generate DRI.

## 3. RESULTS AND DISCUSSION

### 3.1 Reducing gas produced by MCCR

The MCCR subsystem is driven by the heat generated by the combustion of the exhaust gases of the DRI subsystem. In the CMD reaction, the methane conversion is 92.54%, while the  $CO_2$  conversion of RB reaction is 78.71%. The conversion of  $CO_2$  is lower than  $CH_4$ . It is caused by two reasons. Firstly, the RB reaction relies on the carbon deposit generated by the CMD reaction. However, the carbon deposit at the catalyst is less than the  $CO_2$  in the case of a molar ratio  $CH_4$  to  $CO_2$  is 1:1 feed in the subsystem, which means an excess of  $CO_2$ . Secondly, the RB reaction behavior is slow inherently because of its reaction kinetics. The hydrogen product contains residual methane, and as well the carbon monoxide product contains  $CO_2$ .

The production of  $H_2$  and  $CO$  from MCCR was carried out in a fixed-bed reactor at  $800\text{ }^\circ\text{C}$  using 0.2 g of 50 wt% commercial  $Ni/Al_2O_3$  catalyst. Prior to reaction, the catalyst underwent a reducing pretreatment under a flow of 10 vol%  $H_2$  in an argon atmosphere at  $800\text{ }^\circ\text{C}$  for 1 h. In the CMD reaction, 10 mL/min of  $CH_4$  and 90 mL/min of Ar were introduced to react for 15 minutes. Subsequently, argon gas was used to purge the residual  $CH_4$  and  $H_2$ . Finally, the RB reaction was conducted by delivering 10 mL/min of  $CO_2$  and 90 mL/min of Ar for 15 minutes. At  $800\text{ }^\circ\text{C}$ , the methane conversion rate is 82.29%, while  $CO_2$  conversion is 65.35%. The simulation is based on the principle of minimizing Gibbs free energy,

without taking reaction kinetics into account. So, the experimental result is lower than the simulation result.

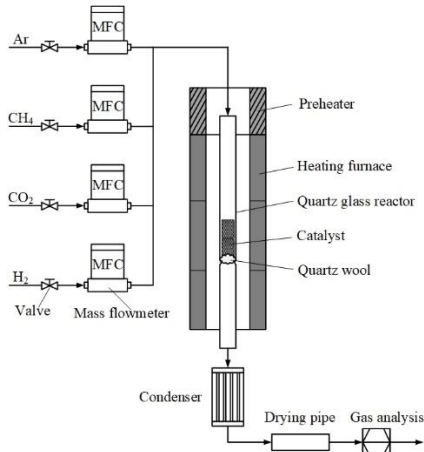


Fig. 4 Schematic of experimental platform

### 3.2 3-step iron direct reduction

At 800 °C, hydrogen and carbon monoxide behaviors similarly in reactions. In Fig. 5, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> are rapidly and irreversibly reduced by hydrogen. But the reduction of FeO is influenced by the presence of oxidizing gas, and FeO is only reduced when GOD drops to a lower value. This implies that the reduction of FeO is the limiting step in the DRI subsystem.

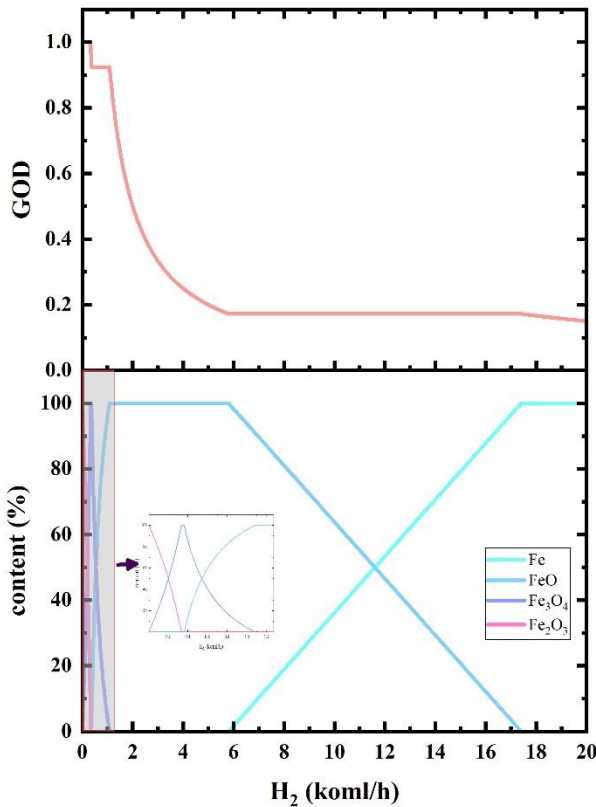


Fig. 5 Relationship between iron oxides and H<sub>2</sub>

In the first stage of the iron reduction, hydrogen is introduced into the reactor to reduce Fe<sub>2</sub>O<sub>3</sub>, and the exhaust gas is composed mainly of water, with a small portion of carbon dioxide.

In the second stage of the reduction, approximately 29:1 molar ratio of CO to H<sub>2</sub> are introduced to the reactor to reduce the Fe<sub>3</sub>O<sub>4</sub> produced in the first step. The reduction potential is reduced due to the presence of CO<sub>2</sub> in the reducing gas, resulting in a higher ratio of CO to H<sub>2</sub> compared to the 19:1 ratio when pure CO and H<sub>2</sub> are introduced.

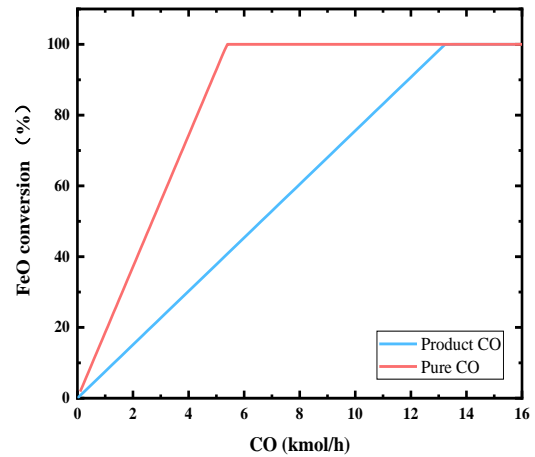


Fig. 6 The conversion of FeO reduced by CO

In the third reaction step, FeO reacts with the reducing gas at a lower rate. In Fig. 6, the conversion rate of FeO to equal-molar reducing gas is less than 20%. As an example, for CO reduction, about 3 times more CO is required for each 1 kmol/h of FeO reduction. Introducing a large volume of reducing gas to improve its conversion rate is essential. However, the reaction between Fe<sub>3</sub>O<sub>4</sub> and FeO is reversible, influenced by the oxidizing gas, and the GOD of CO produced by the MCCR system is 0.12, which further increases the need for reducing gas.

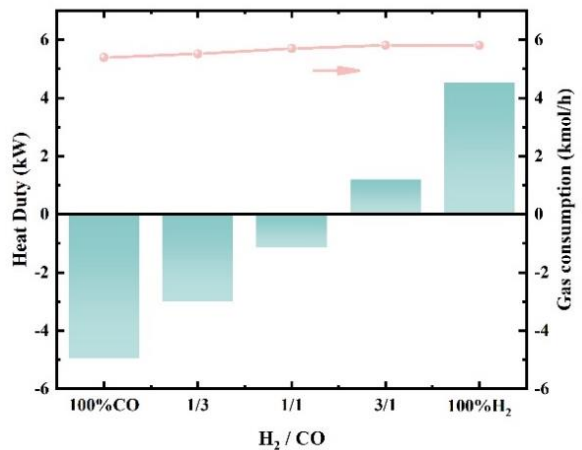


Fig. 7 Heat duty influenced by H<sub>2</sub>/CO

In Fig. 7, with the increase of the proportion of H<sub>2</sub>, the heat duty increases. When the ratio H<sub>2</sub>/CO is 1:1, the heat released from an exothermic reaction is close to the heat absorbed from an endothermic reaction. During the third reduction step, hydrogen and carbon monoxide are introduced into the reactor in a 1:1 molar ratio to reduce FeO.

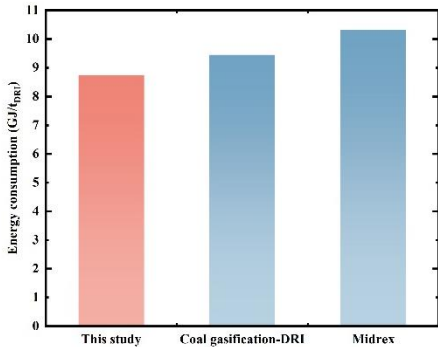


Fig. 8 Energy consumption[8]

In addition to adjusting the H<sub>2</sub>/CO ratio to take advantage of the heat generated by the exothermic reaction during the iron reduction process, the system also utilizes the waste heat from the exhaust gas to preheat the iron ore, thereby further reducing energy consumption. The produced reducing gas can be delivered directly to the DRI system in specific proportions, enabling isothermal production and utilization of the reducing gas and reducing irreversible losses. The reducing gas does not require heating to high temperatures that require extra energy. Using the strategy of adjusting the hydrocarbon ratio of the reducing gas at different stages of the iron reduction system, the energy consumption per ton of DRI is 8.73 GJ, which is 15.42% and 6.7% lower than the other two processes currently available, and a significant reduction in energy consumption in comparison with some hydrometallurgical methods.

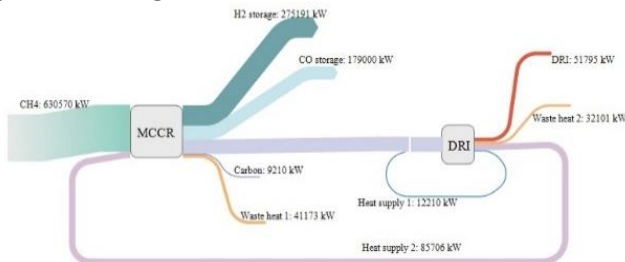


Fig. 9 Energy Sankey diagram of the proposed system

The reducing gas produced in the MCCR subsystem is not entirely utilized by the DRI subsystem, and the remaining reducing gas can be stored as a fuel or used as a feedstock for other industrial processes, e.g., for

further processing into methanol via Fischer-Tropsch synthesis. The proposed novel coupling of iron reduction with a methane reforming system achieves a total utilization efficiency of 80.83%.

#### 4 CONCLUSIONS

We propose a system that combines the generation and utilization of reducing gases. Different from traditional ironmaking methods, the reduction of iron oxides goes through three steps and reacts with specific H<sub>2</sub>/CO ratios of reducing gas to make use of the reaction heat to reduce energy consumption. In this proposed system, the reducing gas produced by MCCR can be supplied to different reduction stages of iron oxides with specific ratios, or it can be stored as fuel. The study findings can be summarized as:

(1) A new methane carbon cycling reforming system integrating a three-steps iron direct reduction system is proposed. We developed a model to analyze this system, and investigated the operation parameters to achieve auto-thermal or reduce energy consumption.

(2) The MCCR system was experimentally verified to produce H<sub>2</sub>/CO respectively. The conversion rates are 82.29% and 65.35% for CH<sub>4</sub> and CO<sub>2</sub>, respectively, which are lower than the simulation results.

(3) Utilizing the reaction heat between the iron oxide and the reducing gas, auto-thermal equilibrium or less energy input process is achieved. The total energy efficiency of the system is 80.24% and the energy consumption is 8.73 GJ/t<sub>DRI</sub>, which is 15.42% and 6.7% lower than the other two current processes.

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