



Identifying iron-based oxygen carrier reduction during biomass chemical looping gasification on a thermogravimetric fixed-bed reactor

Jimin Zeng, Rui Xiao*, Shuai Zhang, Huiyan Zhang, Dewang Zeng, Yu Qiu, Zhong Ma

Key Laboratory of Energy Thermal Conversion and Control, Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, PR China

HIGHLIGHTS

- Controlling the oxygen release was proposed in chemical looping gasification.
- The phase transfer of iron oxide was identified in the experiment.
- A self-designed thermogravimetric fixed-bed reactor was constructed.

ARTICLE INFO

Keywords:

The reduction extent of iron-based oxygen carrier
Thermogravimetric fixed-bed reactor
Biomass chemical looping gasification
Phase transfer

ABSTRACT

Establishing a direct relationship between the mass change of iron-based oxygen carrier and gas production is crucial for the efficient operation and the control of the lattice oxygen release in biomass chemical looping gasification. In this study, a thermogravimetric fixed-bed reactor was designed to achieve the simultaneous measurement of the mass change and gas composition in the reduction of the oxygen carrier. Three oxygen carriers of pure iron (III) oxide, natural hematite, and red mud were used as candidates. The phase transfer of the oxygen carrier along with the biomass pyrolysis/gasification was studied. The mass loss rates and the gas composition were matched by three significant phase transition stages. The phase transitions from Fe_2O_3 to Fe_3O_4 , Fe_3O_4 to FeO , and FeO to Fe occurred when CO appeared, $\text{CO}/\text{CO}_2 = 0.97$, and $\text{CO}/\text{CO}_2 = 2.61$, respectively. The extent of oxygen carrier reduction was 28.61% of pure iron (III) oxide, whereas the oxygen carrier reduction molar ratio was 74.50% of red mud. X-ray diffraction (XRD) spectrums showed the oxygen carrier was reduced to the metallic iron phase. Sintering and agglomeration were found in the reacted oxygen carriers of the scanning electron microscope (SEM) images.

1. Introduction

Biomass gasification is a thermo-chemical process for producing syngas, pure hydrogen or other liquid fuel and meeting the industrial application [1,2]. However, the low syngas quality is one of the major problems in conventional biomass gasification [3,4]. Chemical looping gasification (CLG) is popular in recent years because of the flexible process control during gasification [5]. Instead of using molecular oxygen as the oxygen source, the lattice oxygen derived from iron-based oxygen carrier (IR-OC) is used to gasify biomass [6,7]. Therefore, CLG of biomass is beneficial for controlling the oxygen release [8] and improving the hydrogen concentration in the product gas [9].

In the CLG process, the reduction of IR-OC plays a key role for the quality of syngas production [10]. On one hand, high ratios of hydrogen/steam ($\text{H}_2/\text{H}_2\text{O}$) [11] and carbon monoxide/carbon dioxide (CO/CO_2) [12] have a close relationship with the phase transfer of a

metal oxide in phase diagram [13]. On the other hand, the reduced OC generally shows the catalytic effects for reforming reactions to increase hydrogen in syngas [14,15] (Fig. 1). Once the reduction extent of IR-OC is controlled by the release of lattice oxygen, the high-quality syngas with the expected H_2/CO can be obtained [16]. Therefore, understanding the reduction extent of IR-OC is one approach for the process optimization.

In decades, researchers did much considerable work for this attempt. Huang and He et al. investigated biomass gasification using lattice oxygen (BGLO) [17,18] in a fluidized bed reactor, and evaluated the efficiency of the process. Similar experimental designs were also based on a fixed/fluidized bed reactor for the investigation of iron-steam reaction [19,20]. The limitation of the experimental design was from the data collection on the reactor: lattice oxygen loss was based on the gas concentration change [21] without a direct observation on the solid. The other approach was the solid mass change in a

* Corresponding author.

E-mail address: ruixiao@seu.edu.cn (R. Xiao).

Nomenclature

CLG	chemical looping gasification
OC	oxygen carrier
IR-OC	iron-based oxygen carrier
FR	fuel reactor
AR	air reactor
\dot{n}_{in,N_2}	total inlet nitrogen gas molar flow rate, mol/min
\dot{n}_{out}	total outlet dry product gas molar flow rate, mol/min
x_i	the volume fraction of gas i ($i = H_2, CO, CO_2, CH_4$), %
c_i	the relative composition of gas i ($i = H_2, CO, CO_2, CH_4$), %
n_i	amount of substance of gas i ($i = H_2, CO, CO_2, CH_4$), mole

m_{Total}	total mass loss recorded by the reactor, g
$m_{pyrolysis}$	mass loss of biomass pyrolysis, g
φ_{OC}	the extent of OC reduction, %
N_i	cumulative molar gas production ($i = H_2, CO, CO_2, CH_4$), mole
n_i	product molar gas per second ($i = H_2, CO, CO_2, CH_4$), mol/s
γ_{OC}	OC reduction molar ratio, %
n_{BTO}	biomass to CO and CO ₂ gas detected by gas analyzer, mole
$n_{pyrolysis}$	biomass to the gas detected by gas analyzer in pyrolysis, mole
n_{FC}	amount of substance of fixed carbon in biomass, mole

thermogravimetric analyzer (TGA). Riley and Siriwardane et al. [22,23] investigated the char and OC system for the OC reduction in a thermogravimetric analyzer and mass spectrometric (TGA-MS) system. Chen et al. [24] studied the direct solid-solid reaction for the char and OC system. This method determined the OC mass change by the record of the mass loss and detected gas species on a MS, but there were two issues: (1) both the mass amount and the gas flow rate were too small, and the result caused the experiments being possibly not representative for industrial application [25]; (2) the gas molecules had fragments in the MS measurement [26,27]. Consequently, the reactor and experimental design for the research should reach both requirements of specific gas production [28] and representative solid OC change [29]. The direct relationship between the OC reduction and the gas production could be established based on the advanced design. The understanding of thermodynamics [30] and the hydrogen production [31] would be clear. High efficiency of energy conversion would be achieved [32].

In this context, a thermogravimetric fixed-bed reactor was designed for tracking the change of the solid mass and the gas compositions in real time. The data collected determined the amount of lattice oxygen transfer in CLG, as well as the typical syngas concentration. Mass changes were calculated by the principle of mass conservation. The performance of three different IR-OCs were investigated on this reactor. The extent of OC reduction and the OC reduction molar ratio were analyzed in terms of the on-line solid mass changes and the gas compositions. The direct relationship from solid to gas were established. The experimental phase transition of iron oxide was also discussed. The fresh and reacted OCs were characterized via X-ray diffraction (XRD) spectra and Scanning Electron Microscope (SEM). The reactor design provided with a method for the experimental relationship set-up between OC phase transfer and different gas compositions.

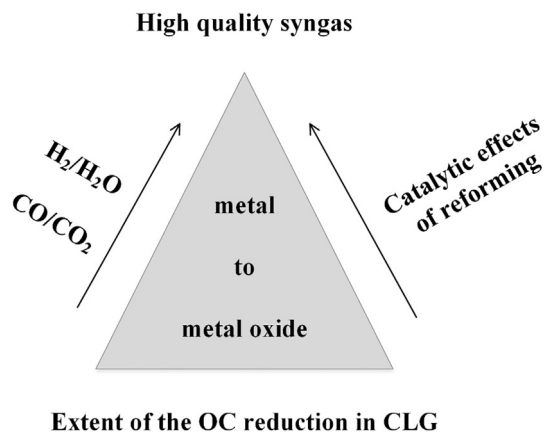


Fig. 1. The function of the OC for high quality syngas production in CLG.

2. Experimental

2.1. Material

Pine sawdust obtained from Jiangsu province of China was used as the fuel sample. The particles were crushed and sieved to the range from 100 μm to 200 μm , then dried at 105 $^{\circ}\text{C}$ for 12 h in an oven. The proximate and ultimate analyses of the dried sawdust were shown in Table 1.

Three kinds of IR-OCs were used in this study: pure iron (III) oxide, natural hematite, and red mud. Pure iron (III) oxide represented a performance criterion. Natural hematite and red mud were both low-cost and easily available, and they were potential OC candidates for the future industrial application. Both natural hematite [33] and red mud [34] were verified to be the good candidates in some typical studies. Pure iron (III) oxide was bought from Sinopharm Chemical Reagent Co. Ltd. Natural hematite was imported from Brazil. Red mud was provided from University of Kentucky Center for Applied Energy Research (United State). The sample was prepared as two steps. First, the solid sample was calcined at 950 $^{\circ}\text{C}$ for two hours. After that, the sample was crushed and sieved to the particles (100–300 μm). Table 2 showed the result of X-ray Fluorescence (XRF, ARL-9800, Switzerland) analysis for three IR-OCs.

2.2. Apparatus and procedure

A series of experiments were conducted in a thermogravimetric fixed-bed reactor. The reactor was self-designed, developed, and fabricated by our research group, as shown in Fig. 2. The reactor was a quartz glass tube with an inner diameter of 35 mm and a length of 380 mm. A porous plate was placed at the bottom as the gas distributor for a uniform gas distribution in the reactor. A cuboid with a length of 390 mm, width of 260 mm, and height of 140 mm was in conjunction to the reactor to prevent gas leakage. An analytical-grade scale with a detectable range from 0 to 200 g (± 0.0001 g) was placed inside it. An electric furnace was surrounded the reactor to maintain a relatively uniform temperature during the experiment. The flowrates of the feeding gas were controlled by the mass flowrate controllers (MFC). The outlet gas was introduced to a trap consisting, an ice-water cooler, silica gel desiccant, and a cotton filter, successively. The clean-up train was connected to remove tar, steam and fly ash from the exhaust gas before being fed into a multi-component gas analyzer. The gas analyzer had five different channels. The CO, CO₂, and CH₄ channels were equipped with Non-Dispersive Infra-Red (NDIR) detectors. The O₂ channel used an electrochemical oxygen detector. The H₂ channel was a Thermal Conductivity Detector (TCD). The detectable range of each gas (CO, CO₂, CH₄, and H₂) was from 0 to 100% ($\pm 2\%$) except O₂ (from 0 to 21%, $\pm 0.2\%$). The control system managed different gas flowrates and temperature changing programs. The uncertainty of this apparatus was shown in Supplementary Material (Table S1).

Download English Version:

<https://daneshyari.com/en/article/6679654>

Download Persian Version:

<https://daneshyari.com/article/6679654>

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