Applied Energy 193 (2017) 96–111

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

The behaviour of multiple reaction fronts during iron (III) oxide reduction in a non-steady state packed bed for chemical looping water splitting

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HIGHLIGHTS

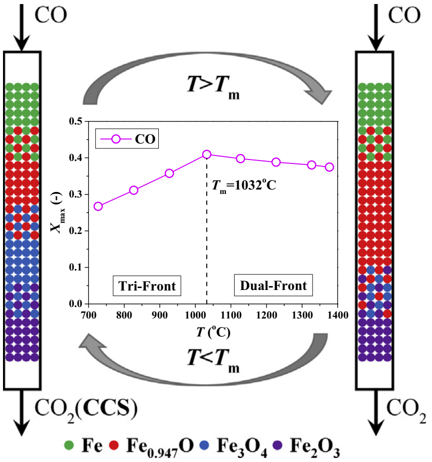
- Simultaneous movement of multiple reaction fronts in the packed bed is observed.
- The merging temperature (T_m) is a vital parameter for the reduction behaviour.
- When the reduction temperature is above T_m, three reaction fronts turn into two.
- A raised physical model is demonstrated by thermodynamically controlled reduction.
- The maximum solid conversion can reach 0.409 for CO case, and 0.554 for H_2 case.

ARTICLE INFO

Article history:
Received 17 July 2016
Received in revised form 8 January 2017
Accepted 14 January 2017

Keywords:
Chemical looping water splitting
Multiple reaction fronts
Merging temperature
Maximum solid conversion
Reduction step
Iron-based oxygen carrier

GRAPHICAL ABSTRACT



ABSTRACT

Owing to the unclear temporal and spatial variations of axial solid conversion in a packed bed using iron (III) oxide as an oxygen carrier, we directly observe these variations by means of a sub-layer approach. The results indicate that the behaviour of the multiple reaction fronts during iron (III) oxide reduction by CO or H_2 within a packed bed for chemical looping water splitting (CLWS) is strongly dependent on the reaction temperature. When the reaction temperature is lower than the merging temperature, three reaction fronts, i.e., Fe_2O_3-Fe_3O_4, Fe_3O_4-$Fe_{0.947}O$ and $Fe_{0.947}O$-Fe, and three product zones, i.e., Fe_3O_4, $Fe_{0.947}O$ and Fe, will appear in the packed bed. In contrast, when the reaction temperature is higher than the merging temperature, the Fe_2O_3-Fe_3O_4 and Fe_3O_4-$Fe_{0.947}O$ fronts merge, leading to the disappearance of the Fe_3O_4 zone. As a result, only the Fe_2O_3-$Fe_{0.947}O$ and $Fe_{0.947}O$-Fe fronts, as well as $Fe_{0.947}O$ and Fe zones will appear in the packed bed. These reduction behaviours are verified by two breakthrough curves, one for $T < T_m$ and one for $T > T_m$, from the thermodynamically controlled reduction of iron (III) oxide in the packed bed. The reaction front movement model, which is proposed based on the reduction behaviour, can be used to determine the maximum solid conversion of the reduction step, i.e., the thermodynamic limitation of the reduction step, in the packed bed CLWS. The maximum solid conversion can reach 0.409 for the CO case and 0.554 for the H_2 case. The first discovery of both the behaviours of the reaction

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http://dx.doi.org/10.1016/j.apenergy.2017.01.036

Nomenclature

Abbreviations

CLC	chemical looping combustion
CLWS	chemical looping water splitting
GC	gas chromatograph
Lk	sub-layer Lk (k = 1, 2, . . . , 10)
XRD	X-ray diffraction

Symbols

l	length (m)
$M_{Fe_2O_3}$	molar mass of iron (III) oxide (kg/mol)
P	partial pressure (kPa)
Q_m	molar flow (mol/s)
S	cross-sectional area of the packed bed (m^2)
T	reduction temperature (°C)
T_m	merging temperature (°C)
X	solid conversion (–)
y	molar composition (–)
γ	reaction conversion coefficient (–)
δ	solid consumption coefficient (–)
ρ_b	bulk density (kg/m^3)
φ	solid conversion coefficient (–)
ω	reaction front velocity, i.e., rate of the reaction front movement (m/s)

Superscripts

eq	equilibrium state

Subscripts

Fe_aO_b-Fe_iO_j	reaction front
Fe_iO_j	product zone
in	inlet gas of the packed bed
max	maximum solid conversion of the reduction step

fronts movement and the thermodynamic limitations of the reduction step standardizes the criteria for both the oxygen carrier evaluation and the optimization of the operating conditions and provides theoretical support for scaling up the packed bed and developing new technology for packed bed CLWS.

1. Introduction

Fossil fuel is widely used in both stationary and mobile energy systems [1] and has caused serious regional and global environment problems, such as the production of haze [2] and climate change [3]. Commonly, hydrogen is regarded as a clean energy source without a carbon footprint because it can be used as fuel in internal combustion engines and fuel cells with water as the only product [4]. However, approximately 96% of hydrogen is currently produced from fossil energy, and the CO_2 produced during this process has not been effectively captured [5]. Thus, fossil-based hydrogen cannot be considered to be a low-carbon energy source. Although low-carbon hydrogen production technologies, including biomass conversion and solar photolysis, have greatly progressed in recent years, hydrogen production from fossil energy with carbon capture will still share the main market for the foreseeable future due to its efficiency and commercialization issues [6,7].

Chemical looping water splitting (CLWS) has been developed from the steam-iron scheme [8–10], in which high purity hydrogen is produced through water splitting on reduced iron oxides (Fig. S1, supplementary material). By adding an air combustion step, the Fe_3O_4-$Fe_{0.947}O$/Fe redox cycle in the steam-iron scheme can be extended to Fe_2O_3-$Fe_{0.947}O$/Fe. Through assistance by iron (III) oxide with prior thermodynamic properties (Fig. 1), the fossil fuel is completely combusted, resulting in the direct production of pure hydrogen with inherent CO_2 separation [11–13]. This process includes reduction, water splitting and combustion steps, which are also referred to as chemical looping gasification [14] or chemical looping hydrogen generation [15]. Owing to the use of lattice oxygen in the oxygen carrier for combustion [16,17], less NO_x and dioxins are produced [18–21] so that cleaner hydrogen can be achieved in this process.

There are different reactor types for CLWS, such as a fluidized bed, a moving bed or a packed bed reactor. The fluidized bed is commonly used for the chemical looping combustion (CLC) of gaseous fuels and solid fuels [22–24]. A combustion efficiency of 96.33% has been achieved during the CLC of bituminous coal in a 5 kW_{th} fluidized bed using hematite as the oxygen carrier [25]. With the assistance of fluidized bed CLC, the efficiency penalty for a power plant to achieve 98% of CO_2 capture has been reduced to 3.9%, and the additional cost of the fluidized bed CLC relative to the fluidized bed technology was 20 €/tonne CO_2 [26]. Considering this, a fluidized bed has also been used for CLWS [27,28]. Rydén [27] conducted continuous operation of CLWS in a circulating fluidized-bed reactor with particles of Fe_2O_3 (60 wt%)/$MgAl_2O_4$ as oxygen carriers. Hydrogen with an average purity of 74.6% (N_2 free basis) was obtained when the 67.0% of CO was converted. In addition, a moving bed or a packed bed is another configuration for

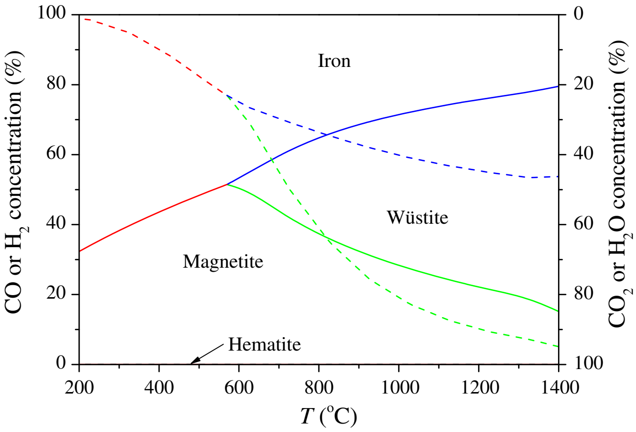

Fig. 1. Thermodynamic equilibrium phase diagrams of the iron-carbon-system (solid line) and iron-hydrogen-system (dash line). The black line near the temperature axis, red line, green line, and blue line represent Fe_2O_3-Fe_3O_4, Fe_3O_4-Fe, Fe_3O_4-$Fe_{0.947}O$, and $Fe_{0.947}O$-Fe, respectively. The original data are from Barin [49]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)