Energy Conversion and Management 160 (2018) 289–301

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Process simulation and thermodynamic evaluation for chemical looping air separation using fluidized bed reactors

Zhikai Deng, Bo Jin*, Yunlei Zhao, Hongxia Gao, Yangqiang Huang, Xiao Luo, Zhiwu Liang*

Joint International Center for CO_2 Capture and Storage (iCCS), Provincial Hunan Key Laboratory for Cost-effective Utilization of Fossil Fuel Aimed at Reducing Carbon-dioxide Emissions, College of Chemistry and Chemical Engineering, Hunan University, Lushannan Road 1, Changsha 410082, China

ARTICLE INFO

Keywords:
Chemical looping air separation
Process simulation
Thermodynamic analysis
Multi-variable optimization
Fluidized bed

ABSTRACT

Chemical looping air separation (CLAS) is considered as a promising method for providing an efficient and economic oxygen supply for integration into oxy-fuel combustion power plants. This study is the first to develop a process model, identify the process characteristics, and optimize the thermodynamic behavior for CLAS processes using fluidized bed reactors. In the process developed model, a fast fluidized bed model and a bubbling fluidized bed model are used to respectively represent the oxidation reactor and the reduction reactor, while fluidized bed hydrodynamics and oxygen carrier redox reaction kinetics are considered to grasp the unique characteristics of CLAS process. The effects of operating parameters on CLAS operation are identified and observed that high reduction temperature and high fluidizing gas flow rate can enhance oxygen carrier conversion and reduce energy penalty in the reduction reactor. Multi-variable optimization to minimize specified energy consumption illustrates that, 38.1% energy savings can be achieved and the optimal oxidation operating temperature, reduction operating temperature, air flow rate, and fluidizing gas flow rate are determined as 830 °C, 950 °C, 1133.7 L/h, and 58.4 L/h, respectively. These results are valuable for use by engineers to optimize the process design and achieve energy-efficient operation for CLAS processes.

1. Introduction

The severe impact on the global climate caused by enormous greenhouse gas emissions has raised wide spread public concern. CO_2 from the combustion of fossil fuels makes up more than half of the greenhouse gases emitted into the atmosphere. CO_2 capture and storage (CCS) has been proposed as one of the key technologies to reduce global CO_2 emissions [1]. Among the CCS methods, oxy-fuel combustion has been recognized as a promising technology to allow the capture of CO_2 emitted from power plants. It uses a mixture of oxygen and recycled flue gas instead of air to combust with fuel, and the flue gas is processed in the CO_2 compression and purification unit to obtain CO_2 products for other industrial applications. To satisfy the oxygen demand, a large scale oxygen production method must be used. Typically, conventional oxygen production methods include adsorption, membrane separation, and cryogenic distillation [2]. Although the cryogenic process is considered as the only commercially available method for this application [3,4], its high energy penalty and high economic cost are severe liabilities. Thus, it is essential that an energy-efficient and cost-effective oxygen production method be developed for the promotion and realization of oxy-fuel combustion technology.

Due to its low energy footprint, simple operation and low capital cost, chemical looping air separation (CLAS) [5] has been proposed as an alternative option for oxygen supply in oxy-fuel combustion power plants [6]. As shown in Fig. 1, continuous oxygen production from CLAS can be achieved by the redox reactions of an oxygen carrier (OC) to absorb and release oxygen in two separate reactors. Two forms of reactors can be used: fixed bed and fluidized bed. In the fixed bed arrangement, the OC is placed in the bed with a certain solid load or inventory, and redox reactions take place by switching between different carrying gases. Oxygen is released during OC reduction using CO_2/steam, whereas oxygen is absorbed when OC is oxidized in an air atmosphere. In the fluidized bed arrangement, the OC circulates between the two separate reactors in interconnected fluidized beds. Theoretically, CLAS can achieve energy-efficient or even auto-thermal operation, since exothermic oxidation and endothermic reductions are combined in a single process. Only 0.08 kWh/m^3 average specific power consumption or just 26% of that for advanced cryogenic air separation system is needed [5].

$$Me_xO_{y-2} + O_2 \rightarrow Me_xO_y \tag{1}$$

$$Me_xO_y \rightarrow Me_xO_{y-2} + O_2 \tag{2}$$

---

* Corresponding authors.
E-mail addresses: kingjinbo1988@hnu.edu.cn (B. Jin), zwliang@hnu.edu.cn (Z. Liang).

https://doi.org/10.1016/j.enconman.2018.01.039
Received 29 October 2017; Received in revised form 8 January 2018; Accepted 17 January 2018

Nomenclature

a	decay factor
A_2	Avrami-Erofe'ev random nucleation and subsequence growth model
A_i	pre-exponential factors, $(m^3/mol)^{0.5}$ min^{-1} or min^{-1}
A_{OR}	cross-sectional area of the oxidation reactor, m^2
A_{RR}	cross-sectional area of the reduction reactor, m^2
Ar	Archimedes number
A_t	cross-sectional area of bed diameter, m^2
C_{O_2}	oxygen concentration, $kmol/m^3$
c_{oxi} or c_{red}	oxygen concentration at oxidation or reduction reactor outlet
D_{OR}	oxidation reactor diameter, cm
dp	average diameter of particles, m
D_B	diameter of the bubble, cm
D_{BM}	maximum diameter of the bubble, cm
D_{B0}	initial diameter of the bubble, cm
D_{RR}	reduction reactor diameter, cm
E_i	activated energy, kJ/mol
$f_{g,b}$	the fraction of fluidized bed volume occupied by gas in the bubble
$f_{g,e}$	the fraction of fluidized bed volume occupied by gas in the emulsion
g	gravitational acceleration, $9.8\,m/s^2$
G_s^*	saturated mass flux of solids, $kg/m^2/s$
G_s	solid recirculation rate, kg/h
h	height above the distributor plate, m
H_{bed}	the bed height at minimum fluidization conditions, m
H_{mf}	the expanded bed height at fluidization conditions, m
H_d	height of the dense zone, m
H_l	height of the lean zone, m
H_{riser}	height of the riser, m
H_R	height of the reduction, m
k_i	kinetic constants
m_{OC}	mass of the oxygen carrier during reactions
M_{CuO}	molecular weight of CuO, kg/m^3
M_{Cu_2O}	molecular weight of Cu_2O, kg/m^3
n_d	number of orifice openings in the distributor
n_{o_2}	the flow rate of oxygen produced, kmol/h
$P_{O_2,eq}$	oxygen equilibrium partial pressure, kPa
P_{ambi}	operation pressure of reactor, kPa
Q_{total}	total heat supplied to the process from outside, kW
$-r_i$	reaction rate of the CuO or Cu_2O, kgmole/s
R_2	phase boundary reaction mechanism model
Re	Reynolds number
Re_p	Reynolds number of particles
R_g	constant of ideal gases, 8.314 J/mol/k
T	temperature of the reaction, °C
u_{mf}	minimum fluidization velocity, m/s
u_b	velocity of bubble, m/s
u_0 or u_g	superficial gas velocity, m/s
u_t	terminal velocity of a falling particle, m/s
V_{O_2}	the standard molar volume of the gas, $22.4\,m^3/kmol$
W_{inv}	the total mass inventory of solids in the fluidization bed, kg
$X_{OC,i}$	conversion ratio of the oxygen carrier during the reduction or the oxidation
Y_{CuO}	volume fraction of CuO in solids
Y_{Cu_2O}	volume fraction of Cu_2O in solids
z	distance above the surface of the bed, m

Greek symbols

α	ratio of wake volume to bubble volume
δ_b	volumetric fraction of bubbles in the bottom bed
ε_b	volumetric fraction of bed occupied by bubbles
ε_f	average voidage of bed
ε_{fb}	average voidage of freeboard
ε_{mf}	voidage at minimum fluidization condition
ε_s	volume fraction of solids
ε_s^*	maximum volume fraction of solids that can be pneumatically transported
ε_{sd}	volume fraction of solids in the lower dense region of a fluidized bed
ε_{se}	volume fraction of solids at the reactor exit
μ_g	viscosity of gas, kg/m/s
ρ_g or ρ_s	density of gases or solids, kg/m^{-3}
φ_s	particle sphericity
ΔG	Gibbs free energy change, kJ/mol
ΔP	pressure drop, kPa

Acronyms

BFB	bubbling fluidized bed
CCS	carbon capture and storage
CLAS	chemical looping air separation
CSTR	continuous stirred tank reactor
ME	metal
MEO	metallic oxide
OC	oxygen carrier
OR	oxidation reactor
RR	reduction reactor
SEC	specific energy consumption
SQP	sequential quadratic programming
TGA	thermogravimetric analysis
THD	transport disengagement height

In order to implement the CLAS process, it is essential to obtain suitable OCs. Screening from the available metal oxides employed in chemical looping processes [7–11], Mn-based (Mn_3O_4/Mn_2O_3), Co-based (CoO/Co_3O_4) and Cu-based (Cu_2O/CuO) OCs are found to be thermodynamically favorable candidates [5,12,13]. Cu-based OC has been widely studied and considered to be the most desirable choice because of its high oxygen transport capacity, high reactivity and low solid inventory [14–17]. However, its applicability might be limited because of its tendency to agglomerate and its low mechanical strength at high operating temperatures. To overcome these limitations, a binder material (such as ZrO_2, SiO_2, Al_2O_3 or $MgAl_2O_4$) is added into the OC to improve its ability to resist sintering and attrition [14,16,18]. Several studies have investigated these inert supports and reported their reactivities. Song et al. [15] analyzed the reactivity and stability of potential OCs, and showed that SiO_2 supported CuO displayed the maximum oxygen transport capacity as well as the highest oxygen transport rate for oxygen release and uptake. These researchers identified gas-solid reaction mechanisms of CuO/SiO_2 that fit well with varied Cu content under redox reactions, developed a $CuO\text{-}MgO\text{-}SiO_2$ based OC to improve the long-term operating stability [19], and designed and tested an experimental facility using interconnected fluidized beds [20]. Similarly, Wang et al. [21] experimented and compared the reduction reaction kinetics of Cu-based OC supported with SiO_2, TiO_2, and ZrO_2. The nucleation and nuclei growth was determined to be the most likely reaction mechanism. These researchers also measured the reactivity of Cu-based OCs using SiO_2, TiO_2, ZrO_2 and $MgAl_2O_4$ as binders in a fixed bed apparatus [17] and tested the capability and reactivity of CuO/ZrO_2 in a TGA [14]. As well, Young