Chemical Engineering Science 134 (2015) 619–631

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Model-assisted analysis of fluidized bed chemical-looping reactors

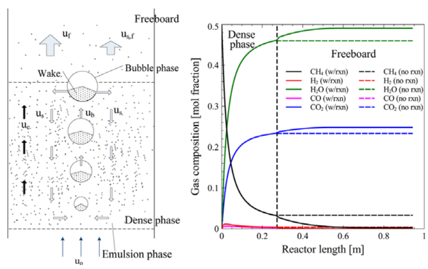
Zhiquan Zhou, Lu Han, George M. Bollas *

Department of Chemical & Biomolecular Engineering, University of Connecticut, Storrs, 191 Auditorium Road, Unit 3222, Storrs, CT 06269, USA

HIGHLIGHTS

- Three-phase model for chemical-looping reduction of NiO with CH_4.
- Model is predictive of the exit gas composition of the literature data.
- Analysis of the sensitivity of model predictions to hydrodynamic parameters.
- The effect of reactor hydrodynamics on CLC performance is explored.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 February 2015
Received in revised form
26 April 2015
Accepted 18 May 2015
Available online 3 June 2015

Keywords:
Chemical-looping
CO_2 capture
Bubbling bed fluidization
Reactor design
Simulation

ABSTRACT

A three-phase hydrodynamic model is employed for the analysis of experimental data of chemical-looping reduction with nickel-based oxygen carriers and methane as the fuel. The model rigorously accounts for the mass, energy, and pressure balances, and the effect of oxygen carrier entrainment in the freeboard region. Model predictions are in good agreement with the relevant experimental data. The capability of the model to be used in the scale-up of fixed-bed kinetic studies of oxygen carriers to fluidized bed pilot-scale reactors is illustrated. The generality and validity of the model are analyzed, so that it can be used for further reactor design studies. In particular, sensitivity analyses, in terms of the crucial hydrodynamic parameters and correlations are carried out and the effects of important parameters, such as bubble size, mass transfer, oxygen carrier entrainment and reactions in the freeboard, on the performance of the chemical-looping reducer are investigated.

1. Introduction

Chemical-looping combustion (CLC) has emerged as a promising process for fuel combustion with low-cost CO_2 separation and NO_x pollution control. CLC takes advantage of the redox behavior of certain metal oxides (oxygen carriers, OC) to seize oxygen in an Oxidizer reactor, which is used thereafter to oxidize a fuel in a separate reactor, the Reducer. Solids circulation between the two reactors is typically accomplished with interconnected fluidized bed configurations, including riser and bubbling fluidized beds (Lyngfelt et al., 2001), two bubbling fluidized beds (Adánez et al., 2006) and dual circulating fluidized bed reactors (Pröll et al., 2009). Alternative reactor concepts for CLC include alternating flow fixed-bed reactors (Noorman et al., 2010), moving bed reactors (Fan et al., 2008), and rotating fixed-bed reactors (Håkonsen and Blom, 2011; Zhao et al., 2013). Compared with fixed-bed reactors, fluidized bed reactors are more suitable to process large inventories of solids with small pressure drop and uniform temperature profiles (Zhou et al., 2014a). Bubbling fluidized bed reactors are the most common implementation of lab- and pilot- scale CLC Reducers (Chandel et al., 2009; Gayán et al., 2009; Hoteit et al., 2009; Iliuta et al., 2010; Mattisson et al., 2008; Ryu et al., 2008, 2009). Therefore, most experimental and theoretical work has focused on CLC Reducers operating in the bubbling bed regime, for which pilot-scale experience suggests a smooth transition to the commercial scale, on the basis of well-established scaling-up procedures (Rüdisüli et al., 2012).

* Corresponding author. Tel.: +1 860 486 4602.
E-mail address: george.bollas@uconn.edu (G.M. Bollas).

http://dx.doi.org/10.1016/j.ces.2015.05.037
0009-2509/

In the context of modeling and simulation of CLC Reducers, approaches such as computational fluid dynamics (CFD) and hydrodynamic models have been proposed (Adánez et al., 2012). CFD is capable of representing the detailed hydrodynamic characteristics of the reactor, but it is computationally intensive and has limited applications to process design and sensitivity analysis. Mahalatkar et al. (2011, 2010), Jung and Gamwo (2008), Deng et al. (2009) and Wang et al. (2012, 2013) developed CFD models to simulate the performance of CLC Reducers in bubbling or circulating fluidized beds. Summarizing their results and conclusions, it was observed that fuel conversion can be hindered by large and fast bubbles passing through the reactor and agreement with experimental data depends on the accuracy of the bubble phase modeling.

On the contrary, hydrodynamic modeling approaches (Davidson and Harrison, 1963; Kunii and Levenspiel, 1968a, 1968b; Shiau and Lin, 1993; Tabis and Essekkat, 1992) are more suitable for reactor design and process sensitivity analyses. In the context of simulation of chemical-looping reactors, hydrodynamic models have been often used to provide insights to process efficiency and selectivity. Brown et al. (2010) used the two-phase model by Davidson and Harrison (1963) with the assumptions of bed isothermality and negligible solid carry-over in the bubbles to simulate CLC in a bubbling bed reactor and validated the model against their experimental data. Yazdanpanah et al. (2014) and Yazdanpanah (2011) considered the impact of solid in the bubble phase and successfully simulated the experimental results of their 10 kW pilot plant. Iliuta et al. (2010) utilized the Kunii and Levenspiel three phase model (Kunii and Levenspiel, 1968a, 1968b) and successfully predicted their semi-batch CLC reduction reactor data. Their model assumes an isothermal bed and negligible solids entrainment to the freeboard. A similar simulation approach was used by Sahir et al. (2013) for the fuel reactor modeling of chemical-looping with oxygen uncoupling (CLOU). The interconnected fluidized bed reactor model proposed by Xu et al. (2007) considered a particle population balance with a two-phase hydrodynamic model for the Reducer, assuming perfect solid mixing in the emulsion phase. Similarly, Brahimi and coworkers (Brahimi et al., 2012; Choi et al., 2012) developed a mathematical model with particle population balance to study the optimal operating range for a continuous bubbling bed CLC process. In the analysis by Hofbauer and coworkers (Bolhàr-Nordenkampf et al., 2009; Kolbitsch et al., 2009a, 2009b; Kronberger et al., 2003) the presence of a freeboard region was shown to significantly improve fuel conversion (Pröll et al., 2009). Similar findings were presented by Abad et al. (2010), for a steady state CuO-based CLC system. Recently, Peltola et al. (2013a, 2013b) presented a one-dimensional dynamic model of CLC in a dual fluidized bed reactor system focusing the scale-up considerations for CLC.

In this work, a transient hydrodynamic model is developed with the objective to predict and analyze the behavior of CLC bubbling bed Reducers operating with CH_4 and supported NiO. The Kunii and Levenspiel (1969, 1968b) three-phase model is used for the simulation of batch CLC reduction experiments. Reaction kinetics, developed previously (Zhou et al., 2014b, 2013) for fixed-bed reactor kinetics analyses, is used for the prediction of bubbling bed Reducers performance, without further fitting. This kinetics model is inclusive of the heterogeneous and catalytic reactions of CH_4 and its partial oxidation products, CO and H_2 and thus it allows for an overall analysis of gaseous CLC with Ni oxygen carriers. The reactor energy balance, pressure balance, gas volume change due to reactions and pressure variations, and the effect of oxygen carrier entrainment in the freeboard region are all considered in the model. The process and kinetic models are validated against experimental data from the literature and then used for sensitivity analyses with respect to crucial hydrodynamic parameters, correlations and assumptions. The effects of mean particle size change, grid design and its related jet-induced attrition rate on the Reducer efficiency and CH_4 oxidation selectivity are studied. Therefore, this work presents a comprehensive analysis (void of parameter fitting) of the modeling framework suitable for the simulation of the reduction step in CLC. Emphasis is placed on the sensitivity of the model to its assumptions, parameters and process particularities, in an effort to provide an accurate and realistic framework for the design of optimal CLC Reducers.

2. Literature survey of bubbling bed experimental data and corresponding model

The operation of CLC fluidized bed Reducers was approximated by a bubbling regime, shown schematically in Fig. S.1 of the Supporting information. In bubbling fluidized bed reactors, a distinct upper surface of the dense phase has been experimentally observed and simulated (Kunii and Levenspiel, 1997, 1990, 1969, 1968a, 1968b; Mahalatkar et al., 2011; Shuai et al., 2011), which is not the case for dense circulating fluidized beds. Thus, a preliminary screening of the available experimental data was performed, with the objective to

Table 1
Experimental conditions and oxygen carrier properties of the bubbling bed CLC Reducers studied.

Properties	Jerndal et al. (2010)	Chandel et al. (2009)	Iliuta et al. (2010)	Yazdanpanah et al. (2014)
Furnace temp (°C)	950	800	623, 645, 810	750
P (atm)	1	1	1	1
NiO/support	40% $NiO/NiAl_2O_4$	60% $NiO/NiAl_2O_4$	15% NiO/Al_2O_3	60% $NiO/NiAl_2O_4$
Oxygen carrier load (kg)	0.015	2.5	0.3	6.3, 10
Particle size (μm)	125–180	171	140	201
Geldart powder group	B	B	B	B
Specific surface area (m^2/s)	0.91	7	102	2
Bulk density (kg/m^3)	2400	2200	1100	2050
Sphericity[a]	0.99	0.98	0.95	0.95
Fuel composition	100% CH_4	100% CH_4	10%, 50% CH_4 in Ar	100% CH_4
Gas flow rate (m^3/s)	7.50E−06	2.00E−04	2.00E−05	1.39E−04, 2.08E−04
I.D. (mm)	22	96	46	130
Bed height (m)	0.03	0.21	0.23	0.33, 0.55
Reactor height (m)	0.5	1	0.94	1
Space time (s $gNiO^0$/g Fuel)	1254	9747	5297	17,374

Note: [a] Particle sphericity depends on the shape of the OCs, ranging from 0.75 to 0.99, roughly estimated by supporting experimental techniques, such as scanning electron microscopy.