Model-assisted analysis of fluidized bed chemical-looping reactors

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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.

Keywords: *chemical-looping, CO₂ capture, bubbling bed fluidization, reactor design, simulation.*

1. Introduction

Chemical-looping combustion (CLC) has emerged as a promising process for fuel combustion with low-cost CO₂ 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).

In the context of modeling and simulation of CLC Reducers, approaches such as computational fluid dynamics (CFD) and hydrodynamic models have been proposed (Adanez 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 and coworkers (2011; 2013, 2012) 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. (2011; 2014) considered the impact of solid in the bubble phase and successfully simulated the experimental results of their 10kW_{th} 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, Brahim 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-Nordenkamp et al., 2009; P. Kolbitsch et al., 2009; Philipp Kolbitsch et al., 2009; 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 Figure 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 identify reactor configurations that operate within the bubbling bed fluidization regime. Accordingly, the data used in this work include the studies by Jerndal et. al. (2010), Chandel et al. (2009), Iliuta et al. (2010) and Yazdanpanah et al. (2014), as summarized in Table 1. As shown in Figure S.2, the oxygen carriers used in the studies of Table 1 belong to the Geldart type B classification.

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 ₂ O ₄	60% NiO/NiAl ₂ O ₄	15% NiO/Al ₂ O ₃	60% NiO/NiAl ₂ O 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 *	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	17374

Note: * 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.

The validity of the bubbling fluidization regime, lack of slugging, and negligible elutriation, were assessed for all the experimental data listed in Table 1. The regimes of fluidization for

Geldart type A and B particles are shown in Figure 1, in terms of the dimensionless particle size, $d_p^* = Ar^{1/3}$, and velocity, $U^* = Re/Ar^{1/3}$. This analysis is based on the work of Bi and Grace (1995), updated to account for the more general correlation of Haider and Levenspiel (1989) for the particle terminal velocity, U_t^* . The shaded areas in Figure 1 illustrate ranges of stable operation in the corresponding hydrodynamic regime (Bubbling Fluidization, Fast Fluidization, Conveying (Jin et al., 2003), and Spouting in conical reactors (Olazar et al., 2004)). Bubbles appear at the minimum fluidization velocity for Geldart B particles and are distinct up to the onset of turbulent fluidization (Re_c in Figure 1), while entrainment of particles becomes significant at Re_{se} .

Figure 1: Regimes of gas – solid fluidization (Bi and Grace, 1995) and the corresponding fluidization regime for the data published by Chandel et al. (2009), Iliuta et al. (2010), Yazdanpanah et al. (2014) and Jerndal et al. (2010).

Depending on the bed location and reaction time (affecting temperature and gas composition), the ranges of d_p^* and U^* for the units considered in this study were estimated as shown in Figure 1. These ranges correspond to loose enclosures of the conditions studied here and are in no way exclusive or deterministic. Since reaction molar change, temperature and pressure variations affect the gas velocity, the space-averaged transient velocity is shown here. In conclusion, the operating conditions of all the reactors considered in this study correspond to regimes well-below the critical velocity of elutriation, $Re_{se} = 1.53 Ar^{0.5}$ (Marmo et al., 1999). In

particular, the fluidization regimes of the reactors designed by Chandel et al. (2009), Jerndal et al. (2010), and Yazdanpanah et al. (2014) fall right into the bubbling bed regime. The operating flow regime employed by Iliuta et al. (2010) is shown to be somewhat below the bubbling bed regime, but higher than the minimum fluidization velocity. For all the units studied, slugging is not likely to occur (explored with the Yagi and Muchi criterion (Rhodes, 2008), not shown here).

2.1 Reaction kinetics network

The mean particle diameter of all the oxygen carriers used in the fluidized bed reactors considered in this study is below 205 μm . Thus, intraparticle diffusion was neglected (García-Labiano et al., 2005; Han et al., 2014, 2013). The developed model utilizes the kinetic model reported in Zhou et al. (2013), which was developed on the basis of a large list of literature data on the reduction of NiO by CH_4 in fixed bed reactors. The relevant reactions include NiO reduction reactions (with CH_4 , H_2 and CO), Ni-catalyzed reforming reactions (steam reforming, dry reforming, and water-gas shift), and Ni-catalyzed carbon formation and elimination reactions (CH_4 decomposition and carbon gasification by H_2O and CO_2). Partial oxidation products, H_2 and CO , are produced by oxygen carrier reduction reactions and Ni-catalyzed reactions, but are further converted to CO_2 and H_2O *via* NiO reduction and catalytic reactions. The kinetic expressions, kinetic parameters, thermodynamic equilibrium constants, and adsorption coefficients were shown and discussed in detail in Zhou et al. (2013). The analysis therein was based on fixed bed data and, thus, amongst the objectives of this work is to explore the validity and generality of this reactions scheme, its kinetics and parameter values, as applied to fluidized bed reactors.

2.2 Model description

A dynamic three-phase (bubble, emulsion and wake) model was used to simulate the dense bed hydrodynamics (Kunii and Levenspiel, 1968a, 1968b). The model considers gas bubbles flowing through a dense emulsion phase at a relative velocity given by the minimum fluidization velocity (u_{mf}), with gas percolating through the bed of solids. The diameter of bubbles increases with bed height and is assumed uniform over the radial bed coordinate. The main mechanism for the circulation of solids in the bed is the rising bubbles, which carry a wake of solids (Figure S.1). A small fraction of the solids reaching the dense bed top is entrained to the freeboard, whereas the remaining solids flow downwards due to gravity, forming countercurrent flow. Therefore, a good mixing between gas and solids is established in the dense bed. Gas-solid mass exchange between the bubble/wake and emulsion phases is taken into account *via* diffusive and convective mass transfer. Two energy balances (bubble/wake and emulsion, respectively) are applied for the dense phase, under the assumption that the gas and solids are at the same temperature in each phase (bubble and emulsion). The temperature gradient between the two phases is determined by the interphase heat transfer plus the heat of reaction. Entrainment of the particles from the dense phase into the freeboard is considered, while elutriation of carry-over solids out of the freeboard is neglected. The freeboard region is modeled as a 1-D two-phase (gas and solid) transient plug flow reactor with axial dispersion. The composition and temperature variations in the lateral direction are neglected in the model. While some lateral variations may occur, due to imperfect mixing and other effects of the reactor walls, for a well-mixed fluidized bed system with good distribution of solid and gas, it is expected that the lateral variations are minimal and thus, a 1-D modeling approach is sufficient. The mass, energy and momentum balances of the 3-phase model are presented in Appendix A. All the correlations used for the

estimation of the hydrodynamic variables and the properties of the gas and solids in the reactors studied are provided in the Supporting Information.

The mass and energy balances were integrated in Matlab 2013 (The Mathworks Inc., 2013). The partial differential equations (PDEs) were discretized in the axial direction using backward finite differences. The implicit DAE system was integrated over time using the open source Sundials IDA solver (Lawrence Livermore National Laboratory, 2012), which integrates the algebraic equations (gas velocity, dense phase bed height, and pressure balance equations) using a variable-order (from 1 to 5) backward differentiation method. The algebraic equations were solved using direct, dense Jacobians. The model was also developed in and validated with the equation-oriented environment of gPROMS (Process Systems Enterprise, 2012).

3. Model validation

The model described in Section 2 and detailed in the Appendix was applied to experimental data from the literature, presented in Table 1. It should be noted that the results discussed herein do not entail any parameter or model fitting; instead, they are pure predictions using the hydrodynamic model described in Section 2 and the kinetic model developed previously (Zhou et al., 2013). The focus of this section is to demonstrate the capability of the model to represent the literature data without further fitting, with the objective to use this model and the same reactor configurations for illustrating the impact of assumptions and model parameters on possible conclusions in terms of CLC effectiveness (CO_2 capture efficiency, CH_4 conversion, oxygen carrier agglomeration or attrition, etc.). Therefore, all the data analyzed here use CH_4 as the fuel and a NiO oxygen carrier. We acknowledge that small variations can occur because of the differences in the oxygen carriers used in each experimental study, but the objective of this

analysis is to demonstrate the overall ability of the model to capture the literature data and not perfect data predictions.

Jerndal et al. (2010) performed fluidized bed CLC experiments with a spray-dried NiO/NiAl₂O₄ oxygen carrier. In Figure 2, application of the model to the experimental data of Jerndal et al. at 950 °C is shown. The reactivity of the oxygen carrier appears low initially, with some CH₄ slip observed, which is well captured by the model. Typically, the reduction of NiO is initiated by nuclei formation (Sedor et al., 2008; Zhou et al., 2014b) or the production of metallic Ni that catalyzes CH₄ steam reforming reactions (Cabello et al., 2014) and further promote the reduction reactions. After the initial low reactivity period, the gas product at the exit of the reactor contains mostly CO₂, due to the relative excess of NiO. The overall CO₂ selectivity is maintained at high levels for the entire reduction time, which is one of the benefits of performing CLC in a fluidized bed compared to a fixed-bed reactor (Zhou et al., 2014a).

Figure 2: Chemical-looping reduction selectivity using Ni/NiO and CH₄ in the fluidized bed reactor of Jerndal et al. (2010) at 950 °C.

Chandel et al. (2009) studied the reactivity of Ni- and Cu/Fe-based oxygen carriers in a semi-batch fluidized bed reactor by varying the number of redox cycles, reactor temperature (800 – 900 °C), bed inventory (2.5 – 6 kg) and fuel flow, with the conclusion that 97% CO₂ capture

efficiency was achievable in their setup. Figure 3 shows the prediction of the experimental data of the pilot-scale bubbling bed reactor of Chandel et al. with NiO/NiAl₂O₄ at 800 °C. Again a CH₄ slip was measured (and is predicted by the model), due to the low initial oxygen carrier reactivity. A detailed sensitivity analysis in terms of the CH₄ slip is presented in Section 4. As shown in Figure 3, higher concentrations of partial oxidation products, CO and H₂, are detected in the experimental data of Chandel et al. and are predicted by the model. The presence of CO and H₂ is mainly attributed to the limited amount of oxygen carrier in the bubble phase and the thermodynamic limitations of NiO to completely convert CH₄ to CO₂ and H₂O.

Figure 3: Chemical-looping reduction selectivity using Ni/NiO and CH₄ in the fluidized bed reactor of Chandel et al. (2009) at 800 °C.

Reduction of a Ni-based oxygen carrier by CH₄, was also investigated in a semi-batch fluidized bed by Iliuta et al. (2010) at 600 – 810 °C. Small H₂ (1 mol%) and zero CO emissions were detected and almost complete CH₄ conversion was achieved with the outlet gas being mainly composed of CO₂ and H₂O. Figure 4 shows the comparison of experimental data with model predictions for the gas product selectivity and solid conversion from Iliuta et al. at 623 °C. The exit gas composition is well-predicted by the model. The experimentally measured, space-averaged NiO conversion (36 mol% NiO) is also well-predicted by the model, as shown in

Figure 4(b). The initial over-prediction of H_2O could possibly be attributed to the uncertainty of the hydrodynamic regime for this system, which as discussed operates below the bubbling bed regime. A detailed analysis of the effect of bubble size on the CH_4 slip in CLC is discussed in Section 4.

Figure 4: Chemical-looping reduction selectivity using Ni/NiO and CH_4 in the fluidized bed reactor of Iliuta et al. (2010) at 623 °C. The NiO conversion after 2 min of reduction was measured at 36 mol%, while the respective model prediction was 34 mol%.

Yazdanpanah et al. (2014) performed CLC experiments with pure CH_4 and $\text{NiO/NiAl}_2\text{O}_4$ in a 10kW_{th} pilot plant at various fuel flow rates and oxygen carrier loadings. They observed that approximately 1 – 3 mol% CH_4 escaped the reactor unreacted, depending on the fuel flow and dense bed height. In their modeling effort, a better fit of the experimental data was obtained when solid in the bubble was considered in the model. Figure 5 presents the comparison of the experimental data with the predictions of this study for the exit gas product selectivity of Yazdanpanah et al. (2014). The 2.5 – 3 min delay time in the experimental data was due to the large volume of the fluidized bed reactor and downstream system components, which was modeled in this case using the detailed reactor and downstream components geometry provided in Yazdanpanah et al. (2011). Almost complete CH_4 conversion (>95%) was achieved with negligible CO and H_2 produced (Figure 5). Overall, the predictions of CO_2 and CH_4 for all the

cases studied were satisfactory, while the H_2 and CO were not that well captured by the model. The latter can possibly be attributed to the uncertainty in the kinetics of methane decomposition reaction (Zhou et al., 2013) and the fact that the support in the work by Yazdanpanah et al. was a $NiAl_2O_4$ spinel which can catalyze some of the reforming reactions.

Figure 5: Chemical-looping reduction selectivity using Ni/NiO and CH_4 in the fluidized bed reactor of Yazdanpanah et al. (2014) at 800 °C.

In summary, the developed process model and the kinetics developed previously were shown to be of satisfactory agreement with experimental data from the literature, without further fitting or tuning. Thus, the reactor model can be used for design purposes, as it is predictive of the most significant CLC phenomena. On the basis of the accuracy and generality of the developed model, sensitivity analyses with respect to crucial hydrodynamic parameters and correlations, such as the bubble size, mass transfer and reactions in the freeboard region are shown in Section 4. Moreover, the effects of attrition-related particle size change and jet-induced attrition rate on the Reducer efficiency are studied.

4. Sensitivity of the model to its assumptions and parameters

Fluidized bed models rely heavily on the use of semi-empirical and empirical correlations for the calculation of key model parameters, such as the minimum fluidization velocity, bubble volume fraction, bubble size, interphase mass and heat transfer coefficients. A brief survey of

some commonly used correlations employed to calculate parameters for the three-phase model is presented in Tables B.1 and B.2 in the Appendix. The objective of this Section is to analyze the sensitivity and accuracy of the model, with respect to the correlations commonly used for the prediction of bubbling bed hydrodynamics, focusing on their applicability to CLC modeling.

4.1 Bubble/wake correlations

The variation of the bubble diameter with bed height is typically expressed with empirical linear, exponential, and fractional relationships, as shown in Table B.1. The corresponding effect of bed height to the predicted bubble size is plotted in Figure B.1, for bed geometry and operating conditions shown therein. The deviation of the calculated bubble diameter for longer reactors is significant and needs to be analyzed beforehand (given that these correlations are empirical). As discussed previously, the accuracy of the model prediction for the data by Iliuta et al. (2010) is not high. At the same time, it should be reminded that the operating regime of this reactor falls outside the regime for stable bubbling fluidization (Figure 1). Therefore, it is of interest to evaluate the effect of bubble size on the performance of the model, at different (constant) bubble sizes. Figure 6 illustrates the effect of bubble size on the temperature difference between the bubble and emulsion phases. The indicated small and large bubbles are calculated by Eq. (S.3) and (S.4), respectively, while the medium bubble is estimated as their average. Heat transfer is enhanced for smaller bubbles due to the larger interphase area, which results in narrow temperature differences between the bubble and the emulsion phase (Figure 6). This is consistent with the results by Hatzantonis et al. (2000) and is a direct result of the heat transfer equation. The corresponding gas product distributions at the exit of the reactor are shown in Figure 6(c). Compared with the prediction of the bubble-growth model (Figure 4(a)), more unreacted CH_4 is predicted by the constant bubble size model with large bubbles. Assuming

only small bubbles, no CH₄ slip is observed, as shown in Figure 6(c). Jung and Gamwo (2008) concluded that low fuel CLC conversions can be attributed to the large and fast bubbles passing through the reactor, which agrees with Figure 6(c). It is also evident that for the specific experimental configuration, the sensitivity of complete combustion products with respect to bubble size is minor. This is due to the fast kinetics of the reduction of NiO by H₂ and CO.

Figure 6: Effect of bubble size on the temperature difference between the bubble and emulsion phases predicted by the constant-bubble size model: (a) transient profile at reactor height of 0.22m (near the dense bed top); (b) spatial profile at experiment time of 2 min (end of reduction step); (c) chemical-looping reduction selectivity. Data (points) and reactor configuration correspond to the fluidized bed reactor of Iliuta et al. (2010) at 623 °C with a constant-bubble size model using large bubble (solid lines) and small bubbles (dashed lines).

Yazdanpanah et al. (2011; 2014) considered a small fraction of solids in the bubble and obtained a better prediction of their experimental data, compared to model predictions with solid-free bubbles. In order to assess the significance of the solids in the bubble wake, a comparison of the model predictions with and without consideration of the wake phase was carried out, using the reactor configuration and data by Yazdanpanah et al. Figure 7 presents the comparison of the experimental data reported by Yazdanpanah et al. and model predictions, with the assumptions of solid-containing or solid-free bubbles. Better predictions are obtained by considering the wake phase, while the model assuming solid-free bubbles predicts lower fuel conversion and CO₂ selectivity. It becomes clear that consideration of the solid fraction in the bubble wake is a very

important model parameter, especially when the reactivity and selectivity of the CLC Reducer is of interest (as is always the case in CLC).

Figure 7: Effect of solid in the bubble/wake on the prediction of chemical-looping reduction selectivity using Ni/NiO and CH₄ in fluidized bed reactor of Yazdanpanah et al. (2014) at 750 °C (dashed-lines: no solid in the wake; solid-lines: with solid in the wake).

4.2 Mass transfer correlations

Unreacted CH₄ severely impacts the greenhouse gas mitigation efficiency of CLC. In a bubbling fluidized bed reactor, unconverted CH₄ is commonly seen at the initial stages of the reduction step and has been successfully simulated (Iliuta et al., 2010; Jung and Gamwo, 2008; Wang et al., 2012; Yazdanpanah et al., 2014; Zhou et al., 2013). This CH₄ slip is attributed to the slow initial reduction (or reforming) kinetics of the oxygen carrier. A relatively long reaction time is required to initiate the fuel conversion by forming the NiO nuclei or producing sufficient amount of metallic Ni to catalyze CH₄ reforming reactions. Thus, short contact times between the gas and solid in the bubble/wake result in unreacted CH₄ slipping through fast bubbles, without reacting during the initial stage of the reduction step. As shown in Figure 3, the CH₄ slip at the onset of the reduction in the reactor by Chandel et al. (2009) is relatively large. To explore the CH₄ slip phenomenon in the experimental data reported by Chandel et al., the effect of the mass transfer between the bubble and emulsion is investigated. Mass transfer affects the amount

of oxygen carrier and gas in the bubble and wake phases, and thus alters the initial reaction rates and the unconverted CH_4 escaping the reactor. Two commonly used mass transfer correlations reported by Sit & Grace (1981) and Kunii & Levenspiel (1969) (Table B.2) were implemented in the model. Figure 8(a) presents the responses of the model, in terms of concentration differences between the bubble and emulsion, using the mass transfer correlation of Table B.2. The correlation by Kunii and Levenspiel (1969) predicts a more disparate gas composition.

Figure 8: (a): Effect of different mass transfer correlations (Sit & Grace (1981) - SG) and Kunii and Levenspiel (1969) - KL) on the gas composition difference between the bubble and emulsion phases. (b-c): Predicted dense phase gas composition under the assumptions of (b) no mass transfer; and (c) rapid mass transfer between the two phases. The model predictions for the bubble and the emulsion phase in Figure (c) are almost indistinguishable from each other because of the rapid mass transfer. The experimental configuration of the reactor of Chandel et al. (2009) at 800 °C was used.

For the same data pseudo conditions (rapid transfer and no transfer) were applied, to explore the effect of mass exchange in bubbling bed CLC reducers. As shown in Figure 8(b), in the absence of mass transfer between bubbles and emulsion, a large amount of CH_4 bypasses the oxygen carrier-poor bubble phase, resulting in partial oxidation products. CH_4 is completely oxidized in the emulsion phase due to abundant NiO. On the contrary, with rapid mass exchange between the two phases (Figure 8(c)), the overall reaction rate is faster and generally similar gas

distributions are observed in both phases. Therefore, good gas distributor designs are required to reduce the bubble size and thus enhance mass transfer and mitigate CH₄ slip in CLC systems.

4.3 Entrainment and reaction in freeboard region

In this Section we showcase the significance of considering entrainment of the solids in the freeboard region of the CLC fluidized bed and the corresponding reactions. Figure 9 presents the axial profiles of gas composition in the Reducer (reactor configuration and oxygen carrier properties are from Iliuta et al. (2010)) with and without consideration of the reactions in the freeboard region. The axial profiles shown correspond to the experiment time instance of 0.75 min, when some CO, H₂ and CH₄ are present at the exit of the reactor, to demonstrate the contribution of the freeboard to CH₄ reactivity and CO₂ selectivity. The axial gas profile of Figure 9 is shown for the dense and freeboard regions for the two cases studied. The reactions in the freeboard further convert the unreacted CH₄ and improve the CO₂ selectivity upon exiting the dense bed. Similar results were obtained by Abad et al. (2010), who noted that the reaction in the freeboard is significant in obtaining high combustion efficiency. Also, Pröll et al. (2009) observed that the presence of solids in the freeboard region contributes to increased fuel power for their 120 kW_{th} bench-scale plant.

Figure 9: Axial profiles of gas composition in the chemical-looping bubbling bed Reducer of Iliuta et al. (2010) at 623 °C and experiment time $t = 0.75\text{min}$.

4.4 Mean particle size

The particle size distribution and mean particle size strongly affect the fluidization regime of a CLC Reducer. For instance, attrition is known to fragment and abrade the particles, especially after extended continuous operation. De Diego et al. (2007) reported that the average particle size of the oxygen carrier in the Reducer decreased from 222 μm to 207 μm after 100 hours of operation as a consequence of the attrition/fragmentation of larger particles, and also due to the shrinking of the particles by internal phase changes. On the contrary, Rydén et al. (2009) observed that the size of their NiO/Mg-ZrO₂ oxygen carrier increased from 135 μm to 145 μm after 40 hours of testing in a fluidized bed reactor and they related that to an increase in particle porosity. Lyngfelt and Thunman (2005) and Johansson et al. (2006) tested a Ni-based oxygen carrier in a 10 kW chemical-looping combustor for 12 days and found that the mean particle size increased from 60 μm to 114 μm . It is clear that attrition and particle fragmentation will have a negative impact on the CLC process economics, whereas agglomeration and oxygen carrier microstructural changes may affect the reactivity and intraparticle diffusion limitations. However, it is unclear to what degree these changes affect the reactivity in the Reducer due to changes in its hydrodynamic regime.

To investigate the effect of mean particle size on CLC performance in a bubbling bed reactor, the change in mean particle size after 4 hours and 300 hours of operation in the 10 kW chemical-looping plant of Lyngfelt and Thunman (2005) is modeled. For this demonstration we neglect the possible changes in the oxygen carrier microstructure, and focus on the mere effect of mean particle size on bed hydrodynamics. Figure 10 presents the gas outflow from the two phases (bubble and emulsion) and the transient solid conversion profiles with particle sizes as measured

after 4 and 300 hours of operation ($d_p=60\mu\text{m}$ and $140\mu\text{m}$, respectively) by Lyngfelt and Thunman (2005). Overall, the molar flows decrease in the bubble and increase in the emulsion as the particle size increases. Larger particles produce larger minimum fluidization velocity, smaller bubble rise velocity, and smaller fraction of bubbles in the dense phase. Slightly higher solid conversion efficiency is predicted for the system operated with larger particles (after 300 h operation), as shown in Figure 10(c). This indicates that better contact is achievable between the two phases for the larger particles, which can be explained by the lower fraction of gas passing through the bubbles for larger particles, when the reaction rate is essentially particle size – independent (Abad et al., 2010; Adanez et al., 2012). Therefore, in addition to the effects of agglomeration (or fragmentation) of the oxygen carrier on reaction kinetics, one needs to consider the corresponding effect on hydrodynamics, which is a CLC-specific phenomenon.

Figure 10: Predicted transient profile of (a, b) gas molar flow and (c) NiO conversion in the bubble and emulsion phases after (a) 4h and (b) 300h of operation. The reactor data of Chandel et al. (2009) are used for the simulation with particle sizes as reported by Lyngfelt and Thunman (2005).

4.5 Reducer Gas Distributor

Perforated (Kronberger et al., 2005; Riffart et al., 2011; Ryu et al., 2004) and porous (Dennis and Scott, 2010; Jerndal et al., 2009b; Rydén, 2008; Rydén et al., 2008; Wang et al., 2010) plates are two commonly used distributors in bubbling fluidized units. From the modeling

perspective, different correlations exist for the initial bubble size of the various types of distributors, as shown in Table B.1. One of the benefits of using porous plates or perforated plates with many small orifices is their superior contacting patterns. Therefore, a CLC system with a porous plate distributor is expected to generate more complete oxidation products rather than partial products. Drawbacks of porous plate distributors include their high-pressure drop, low construction strength, low resistivity against thermal stresses and possible gradual clogging by fine particles, which hinder their use in industrial operations (Kunii and Levenspiel, 1969). Perforated plate distributors are more common in industry due to their low cost and simplicity for fabrication. Reportedly, a porous gas distributor was used in the reactor of Jerndal et al. (2010). With an outlook on CLC scale-up, the attrition rate of the CLC unit of Jerndal et al. (2009a) with an industrially practical perforated plate gas distributor is studied here, focusing only on the gird jet induced attrition (Kramp et al., 2011; Werther and Reppenhagen, 1999). For this analysis, a perforated plate was considered that matches the experimental results of Jerndal et al. (2010) at 950 °C. Since synthetic oxygen carriers are typically dispersed on a support of high mechanical strength, it was assumed that the particles will be abraded rather than broken (Werther and Reppenhagen, 2003, 1999). In abrasion mode, the fines are immediately lost after their production due to the rather small size of the abrasion-produced fines (1 – 3 µm). This loss is very significant in CLC, because of the cost of synthetic oxygen carriers (and in particular Ni). For a multi-orifice perforated plate, the loss of oxygen carrier due to fines generated by jet-induced attrition was estimated by (Werther and Reppenhagen, 1999; Werther and Xi, 1993):

$$m_{loss,jet} = \frac{C_{jet} d_p \rho_g D^6}{d_{ori}^4 n_{ori}^2} u^3 ,$$

where C_{jet} is a particle-size independent, material-specific constant and usually measured experimentally. Here, a value of $52.6\text{E-}6 \text{ s}^2/\text{m}^2$ (Werther and Reppenhagen, 1999) was used, which corresponds to jet-induced attrition of a typical FCC catalyst. For the CLC experiment carried out by Jerndal et al. (2010), the estimated jet grid-induced attrition rate of the Reducer is about $1.82\text{E-}07 \text{ kg/s}$. Due to repeated redox cycles in a semi-batch fluidized bed the total amount of oxygen carrier decreases with time.

Figure 11 shows the CO_2 selectivity in the semi-batch reactor of Jerndal et al. (2010), with a perforated plate distributor, which causes the oxygen carrier to be abraded for up to 9 hours. The CO_2 selectivity in Figure 11 was calculated as $X_{\text{CO}_2} = \frac{F_{\text{CO}_2, \text{out}}}{F_{\text{CH}_4, \text{in}}}$. The minimum of selectivity at approximately 0.06 min of experiment time was due to the CH_4 slip at the initial stage of reduction. This initial CH_4 slip is attributed to the slow initial reaction kinetics to form NiO nuclei reaction sites or to produce metallic Ni to catalyze CH_4 reforming reactions. As a result of the short residence time of the gas/solid in the bubble/wake, some CH_4 in the fast bubbles passes through the reactor without reacting in the initial stage of the reduction step. As shown in Figure 11, the CO_2 selectivity generated by reducing the 15 g of *fresh* oxygen carrier can be maintained at high level ($> 90\text{mol}\%$) for over 1 min. The overall CO_2 selectivity drops as the oxygen carrier is fluidized for extended time. The CO_2 selectivity decreases to $85\text{mol}\%$ after oxygen carrier utilization for 9 hours in repeated reduction cycles. Therefore, in order to continuously generate CO_2 of high purity in the reduction cycle for the reactor of Jerndal et al., at least 2.0 g oxygen carrier need to be added to the system every 3 hours. Also, note that this analysis does not consider the oxygen loss due to attrition in the Oxidizer, cyclones, loop seals and transfer lines of an integrated CLC plant, which are likely even more severe.

Figure 11: CO₂ selectivity in a semi-batch reactor with the oxygen carrier being abraded along the multiple repeated cycles up to 9 hours. Simulations refer to the CLC reducer of Jerndal et al. (2010).

5. Conclusions

A hydrodynamic model was developed with consideration of mass, energy and momentum balances, gas molar expansion, and reactions in the dense bed and the freeboard to predict the dynamic behavior of a bubbling fluidized bed reactor for chemical-looping reduction. The process and kinetic models were shown to agree well with literature experimental data, for various nickel-based oxygen carriers, and a wide range of operating conditions and reactor geometries. Sensitivity analyses were performed on the basis of the validated process model. It was found that smaller bubbles are desirable for their rapid heat transfer and enhanced fuel combustion efficiency. The entrainment and reactivity in the freeboard region was shown to significantly improve the overall solid conversion and fuel combustion efficiency. The effect of the mass transfer between the bubble and emulsion phases on the dynamic behavior of the reactor was quantified and is a significant measure of the fuel conversion in the bubble phase. Furthermore, the impact of extended continuous fluidization on the average particle size and the reactor dynamics was explored. The effect of the jet-induced attrition rate on CO₂ selectivity was estimated to be significant. Overall, this process model can be used as a predictive simulation and design tool for chemical-looping reduction in a bubbling fluidized bed. Further application of this process model on Cu-based chemical-looping processes, implementation in system-level CLC process design studies and scale-up of the fluidized bed reactor are underway (Nordness et al., 2014; Zhou et al., 2015, 2014c).

Acknowledgments

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NOMENCLATURE

A_{lk}	binary interaction parameter
A_R	cross-sectional area of the reactor tube [m ²]
C_{dis}	discharge coefficient
$C_{j,b}$	bulk concentration of gaseous reactant [kmol/m ³]
$C_{j,b}$	solid concentration in the upper limit of the dense phase
$C_{s,f}$	solid concentration in the freeboard
$C_{g,b}$	total gas concentration in the bubble phase [kmol/m ³]
$C_{g,e}$	total gas concentration in the emulsion phase [kmol/m ³]
Cp_b	heat capacity of the gas mixture of the bubble phase [J/mol K]
Cp_e	heat capacity of the gas mixture of the emulsion phase [J/mol K]
Cp_f	heat capacity of the gas mixture of the freeboard region [J/mol K]
$C_{i,w}$	concentration of solid species i in wake phase
$C_{i,e}$	concentration of solid species i in emulsion phase
$C_{i,f}$	concentration of solid species i in emulsion phase
$Cp_{i,w}$	heat capacity of the solid species i in the wake phase
$Cp_{i,e}$	heat capacity of the solid species i in the emulsion phase
$Cp_{i,f}$	heat capacity of the solid species i in the freeboard region
d_b	bubble diameter [m]
d_{be}	equilibrium bubble diameter [m]
d_{b0}	initial bubble diameter [m]
d_{bm}	maximum bubble diameter [m]
d_p	particle diameter [m]
d_{ori}	orifice diameter [m]
D	reactor diameter [m]
$D_{ax,jf}$	axial dispersion coefficient of species j in the freeboard region [m ² /s]
D_{ij}	binary gas phase diffusivities [cm ² /s]
D_j	diffusion coefficient of component j in the mixture [m ² /s]
f_s	solids-wall friction coefficient
G_s	mass flux of solid [kg/m ² s]
G	mass flux of gas [kg/m ² s]

h	length element
h_{pc}	particle convective component of U [$\text{J}/\text{m}^2 \text{K s}$]
h_{gc}	gas convective component of U [$\text{J}/\text{m}^2 \text{K s}$]
h_r	radiative heat transfer component of U [$\text{J}/\text{m}^2 \text{K s}$]
H	reactor height [m]
H_d	dense phase height [m]
H_f	freeboard region height [m]
H_{mf}	dense phase height at minimum fluidization [m]
$H_{be,j}$	heat exchange coefficient between bubble-emulsion [$\text{J}/\text{s m}^3 \text{K}$]
$H_{bc,j}$	heat exchange coefficient between bubble-cloud [$\text{J}/\text{s m}^3 \text{K}$]
$H_{ce,j}$	heat exchange coefficient between cloud-emulsion [$\text{J}/\text{s m}^2 \text{K}$]
$K_{be,j}$	gas exchange coefficient between bubble-emulsion [s^{-1}]
$K_{eb,j}$	gas exchange coefficient between emulsion-bubble [s^{-1}]
$K_{bc,j}$	gas exchange coefficient between bubble-cloud [s^{-1}]
$K_{ce,j}$	gas exchange coefficient between cloud-emulsion [s^{-1}]
$K_{ew,i}$	coefficient of solid exchange between emulsion and wake per unit of solid volume in emulsion [s^{-1}]
$K_{we,i}$	coefficient of solid exchange between wake and emulsion per unit of solid volume in wake [s^{-1}]
$k_{g,b}$	thermal conductivity of the gas mixture in the bubble phase [$\text{W}/\text{m K}$]
$k_{g,e}$	thermal conductivity of the gas mixture in the emulsion phase [$\text{W}/\text{m K}$]
M_i	molecular mass of solid component i , [kg/kmol]
$m_{loss,jet}$	jet-induced attrition rate, [kg/s]
n_{ori}	number of orifice openings in the distributor
n	total number of gas species
P	pressure [bar]
P_c	critical pressure [bar]
p_{fs}	solids-wall frictional pressure [bar]
$R_{q,b}$	rate for reaction q per unit mass of the oxygen carrier in bubble phase [$\text{kmol}/\text{kg}_{\text{carrier}} \text{s}$]
$R_{q,e}$	rate for reaction q per unit mass of the oxygen carrier in emulsion phase [$\text{kmol}/\text{kg}_{\text{carrier}} \text{s}$]
$R_{q,f}$	rate for reaction q per unit mass of the oxygen carrier in freeboard region [$\text{kmol}/\text{kg}_{\text{carrier}} \text{s}$]

t	time [s]
T_{bed}	bed temperature [K]
T_b	temperature of the bubble phase [K]
T_c	critical temperature [K]
T_r	reduced temperature
T_e	temperature of the emulsion phase [K]
T_{wall}	temperature at the wall [K]
T_f	temperature of the freeboard region [K]
T_0	initial temperature [K]
u_{mf}	minimum fluidization velocity [m/s]
u_b	bubble velocity [m/s]
u_e	emulsion velocity [m/s]
u_s	downward solid velocity in emulsion [m/s]
$u_{s,f}$	solid velocity in freeboard [m/s]
$u_{g,f}$	gas velocity in freeboard [m/s]
u_{sg}	superficial gas velocity [m/s]
u_t	single particle terminal velocity [m/s]
W_{OC}	oxygen carrier load [kg]
X	NiO conversion
y_j	gas fraction of species j
z	reactor coordinate [m]
U	overall heat transfer coefficient [$\text{J/m}^2 \text{K s}$]

Greek letters

Γ	reduced inverse thermal conductivity
α	fraction of wake in bubbles
ε	numerical constant, near unity
κ_{bed}	emissivity of the bed surface, 0.5 – 0.9
κ_{wall}	emissivity of heat transfer surface, 0.02 – 0.2 (light surface), 0.8 – 0.85 (dark surface)
κ_{b-w}	generalized emissivity
ε_{bed}	dense bed porosity

ε_{mf}	minimum fluidization porosity
ε_f	freeboard porosity
μ_m	viscosity of the gas mixture [N-s/m ²]
σ	Stefan-Boltzmann constant, 5.67E-8 [W/m ² /K ⁴]
δ	fraction of bubbles in bed
ρ_p	solid density [kg/m ³]
ρ_g	gas density [kg/m ³]
ξ_{gs}	gas-solid contact efficiency in the freeboard region
ϕ	particle sphericity
λ_{ax}	axial heat dispersion coefficient [W/m K]
λ_j	thermal conductivity of the species j [W/m K]
λ_s	thermal conductivity of the oxygen carrier [W/m K]
$\lambda_{tr,j}$	translational thermal conductivity for species j
$\Delta H_{q,b}$	heat of reaction q in the bubble phase[J/mol]
$\Delta H_{q,e}$	heat of reaction q in the emulsion phase[J/mol]
$\Delta H_{q,f}$	heat of reaction q in the freeboard region [J/mol]
Δp_{dis}	pressure drop across the distributor [Pa]
Δp_{bed}	pressure drop across the bed [Pa]

Subscripts

ax	axial
b	bubble
d	dense phase
e	emulsion
f	freeboard
mf	condition at minimum fluidization
ori	condition at orifice
P	particle
q	reaction
i	solid phase species (Ni, NiO, C, inert support)
j	gas phase species (CH ₄ , H ₂ , H ₂ O, CO, CO ₂ , Ar, N ₂)

APPENDIX A: Model equations

The mass, energy and momentum equations of the model presented are provided in the following. All the hydrodynamic parameters and gas and solids properties are provided in the Supporting Information with Notation and References reported herein.

Mass balance

The following partial differential equations describe mass transfer by convection, exchange between phases, cross-flow and the reaction terms. The cross-flow between phases is caused by variation in bubble and emulsion properties with height, with λ determining the direction of cross-flow (Sane et al., 1996).

Gas in the bubble phase:

$$\begin{aligned} (\delta + \alpha\delta\epsilon_{mf}) \frac{\partial C_{j,b}}{\partial t} + \frac{\partial(u_b(\delta + \alpha\delta\epsilon_{mf})C_{j,b})}{\partial z} = \\ K_{j,be}(C_{j,e} - C_{j,b})(\delta + \alpha\delta\epsilon_{mf}) + (\lambda_1 C_{j,b} + \lambda_2 C_{j,e}) \frac{\partial(u_b(\delta + \alpha\delta\epsilon_{mf}))}{\partial z} + R_{j,b}(C_{j,b})\rho_P\alpha\delta(1 - \epsilon_{mf}) \end{aligned} \quad (A.1)$$

Gas in the emulsion phase:

$$\begin{aligned} (1 - \delta - \alpha\delta)\epsilon_{mf} \frac{\partial C_{j,e}}{\partial t} + \frac{\partial(u_e(1 - \delta - \alpha\delta)\epsilon_{mf}C_{j,e})}{\partial z} = \\ K_{j,eb}(C_{j,b} - C_{j,e})(1 - \delta - \alpha\delta)\epsilon_{mf} - (\lambda_1 C_{j,b} + \lambda_2 C_{j,e}) \frac{\partial(u_b(\delta + \alpha\delta\epsilon_{mf}))}{\partial z} + R_{j,e}(C_{j,e})\rho_P(1 - \delta - \alpha\delta)(1 - \epsilon_{mf}) \end{aligned} \quad (A.2)$$

Solid in the wake phase:

$$\begin{aligned} \alpha\delta(1 - \epsilon_{mf})\rho_P \frac{\partial C_{i,w}}{\partial t} + \frac{\partial(u_b\alpha\delta(1 - \epsilon_{mf})\rho_P C_{i,w})}{\partial z} = \\ K_{i,we}(C_{i,e} - C_{i,w})\rho_P\alpha\delta(1 - \epsilon_{mf}) + (\lambda_1 C_{i,w} + \lambda_2 C_{i,e}) \frac{\partial(u_b\alpha\delta(1 - \epsilon_{mf})\rho_P)}{\partial z} + \\ R_{i,w}M_i\rho_P\alpha\delta(1 - \epsilon_{mf}) \end{aligned} \quad (A.3)$$

Solid in the emulsion phase:

$$\begin{aligned}
& (1-\delta-\alpha\delta)(1-\varepsilon_{mf})\rho_p \frac{\partial C_{i,e}}{\partial t} + \frac{\partial(u_s(1-\delta-\alpha\delta)(1-\varepsilon_{mf})\rho_p C_{i,e})}{\partial z} = \\
& K_{i,ew}(C_{i,w}-C_{i,e})(1-\delta-\alpha\delta)(1-\varepsilon_{mf})\rho_p - (\lambda_1 C_{i,w} + \lambda_2 C_{i,e}) \frac{\partial(u_b\alpha\delta(1-\varepsilon_{mf})\rho_p)}{\partial z} + \\
& R_{i,w}M_i\rho_p(1-\delta-\alpha\delta)(1-\varepsilon_{mf})
\end{aligned} \tag{A.4}$$

Gas in the freeboard:

$$\varepsilon_f \frac{\partial C_{j,f}}{\partial t} + u_{g,f} \frac{\partial C_{j,f}}{\partial z} = \varepsilon_f \frac{\partial}{\partial z} (D_{ax,j,f} \frac{\partial C_{j,f}}{\partial z}) + (1-\varepsilon_f) R_{j,f} \rho_p \tag{A.5}$$

Solid in the freeboard:

$$\frac{\partial C_{i,f}}{\partial t} + u_{s,f} \frac{\partial C_{i,f}}{\partial z} = R_{i,f} M_i \tag{A.6}$$

Energy balance

The energy balance considers separate temperature profiles for the bubble and emulsion phases in the model. A detailed discussion and the temperature profile inside the emulsion and bubble phases of the fluidized bed designed by Chandel et al. (2009) was shown previously. (Zhou et al., 2014a) It should be noted that the temperature fluctuations for all the reactors considered in this study are relatively small ($\Delta T < 80$ °C). Therefore, the energy balance can be neglected if one needs to reduce the complexity of the proposed model. However, the energy balance has to be included when significant temperature fluctuations might occur; in particular in scale-up bubbling fluidized bed analyses. The energy balance follows in accordance with the three-phase theory.

Bubble phase:

$$\begin{aligned}
& \left((\delta + \alpha \delta \varepsilon_{mf}) C_{p,b} C_{g,b} + \alpha \delta (1 - \varepsilon_{mf}) \rho_P \sum C_{p,i,w} C_{i,w} / M_i \right) \frac{\partial T_b}{\partial t} + \\
& \left((\delta + \alpha \delta \varepsilon_{mf}) C_{g,b} C_{p,b} u_b + \alpha \delta (1 - \varepsilon_{mf}) u_b \rho_P \sum C_{p,i,w} C_{i,w} / M_i \right) \frac{\partial T_b}{\partial z} = \\
& (\delta + \alpha \delta \varepsilon_{mf}) \sum y_j H_{be} (T_e - T_b) + \alpha \delta (1 - \varepsilon_{mf}) \sum (-\Delta H_{q,b}) (-R_{q,b}) \rho_P + \\
& (\lambda_1 T_b C_{p,b} C_{g,b} + \lambda_2 T_e C_{p,e} C_{g,e}) \frac{\partial}{\partial z} (u_b (\delta + \alpha \delta \varepsilon_{mf})) \\
& + \sum (\lambda_1 T_b C_{p,i,w} C_{i,w} / M_i + \lambda_2 T_e C_{p,i,e} C_{i,e} / M_i) \frac{\partial}{\partial z} (u_b \alpha \delta (1 - \varepsilon_{mf}) \rho_P)
\end{aligned} \tag{A.7}$$

Emulsion phase:

$$\begin{aligned}
& \left((1 - \delta - \alpha \delta) \varepsilon_{mf} C_{p,e} C_{g,e} + \frac{\rho_P (1 - \delta - \alpha \delta) (1 - \varepsilon_{mf}) \sum C_{i,e} C_{p,i,e}}{M_i} \right) \frac{\partial T_e}{\partial t} + \\
& \left((1 - \delta - \alpha \delta) \varepsilon_{mf} C_{g,e} C_{p,e} u_e + \frac{\rho_P (1 - \delta - \alpha \delta) (1 - \varepsilon_{mf}) u_s \sum C_{i,e} C_{p,i,e}}{M_i} \right) \frac{\partial T_e}{\partial z} \\
& = (1 - \delta - \alpha \delta) \varepsilon_{mf} \sum y_j H_{j,eb} (T_b - T_e) + (1 - \delta - \alpha \delta) (1 - \varepsilon_{mf}) \sum (-\Delta H_{q,e}) (-R_{q,e}) \rho_P \\
& - (\lambda_1 T_b C_{p,b} C_{g,b} + \lambda_2 T_e C_{p,e} C_{g,e}) \frac{\partial}{\partial z} (u_b (\delta + \alpha \delta \varepsilon_{mf})) - \\
& \sum \left(\lambda_1 T_b C_{p,i,w} \frac{C_{i,w}}{M_i} + \frac{\lambda_2 T_e C_{p,i,e} C_{i,e}}{M_i} \right) \frac{\partial}{\partial z} (u_b \alpha \delta (1 - \varepsilon_{mf}) \rho_P) + \frac{U (T_{wall} - T_e)}{H_d}
\end{aligned} \tag{A.8}$$

Freeboard region:

$$\begin{aligned}
& (\varepsilon_f C_{p,f} C_{g,f} + (1 - \varepsilon_f) \rho_P \sum C_{p,i,f} C_{i,f} / M_i) \frac{\partial T_f}{\partial t} + \\
& (\varepsilon_f C_{p,f} C_{g,f} u_{g,f} + (1 - \varepsilon_f) \rho_P \sum C_{p,f,s,i} C_{f,s,i} u_{s,f} / M_i) \frac{\partial T_f}{\partial z} = \\
& \varepsilon_f \frac{\partial}{\partial z} (\lambda_{ax} \frac{\partial T_f}{\partial z}) + (1 - \varepsilon_f) \rho_P \sum (-\Delta H_{q,f}) (-R_{q,f}) - 4U (T_f - T_{wall}) / D
\end{aligned} \tag{A.9}$$

Momentum balance

A pressure gradient analysis (Bollas et al., 2002) is used in this study. The static head of solids is the dominant contribution, while the pressure drop caused by solids-wall friction

(Kqnnno and Saito, 1969) and static head of gas are also considered. Gas-wall frictional pressure is insignificant (Bollas et al., 2002) and thus neglected in this study.

$$-\frac{dp}{dz} = \frac{dp_{fs}}{dz} + (1 - \varepsilon_{bed})\rho_P g + \varepsilon_{bed}\rho_g g, \quad (A.10)$$

$$\frac{dp_{fs}}{dz} = \frac{2f_s G_s^2}{D\rho_P(1 - \varepsilon_{bed})}, \quad (A.11)$$

with the friction coefficient for the solids phase estimated by

$$f_s = \frac{0.0285\sqrt{gD}}{\left[\frac{G_s}{\rho_P(1 - \varepsilon_{bed})} \right]}. \quad (A.12)$$

Boundary and initial conditions

The boundary and initial conditions are as follows:

$$\begin{aligned} t = 0 \quad & C_{inert} = C_{inert}(t=0), \quad C_j = 0 \quad j = \text{CH}_4, \text{H}_2, \text{CO}, \text{CO}_2, \text{H}_2\text{O}, \quad C_{NiO} = C_{NiO}(t=0), \quad C_{Ni} = 0, \quad C_C = 0, \\ & T_b = T_e = T_f = T_0 \\ z = 0 \quad & C_{CH_4} = C_{CH_4, in}, \quad C_{inert} = C_{inert, in}, \quad C_j = 0, \quad j = \text{H}_2, \text{CO}, \text{CO}_2, \text{H}_2\text{O}, \quad C_{i, w} = C_{i, e}, \quad T_b = T_e = T_{inlet} \\ z = H_d \quad & C_{i, e} = C_{i, w}, \quad P|_{z=H_d} = P_{out} \end{aligned}$$

APPENDIX B: Model correlations examined in this study

The hydrodynamic correlations and property methods used in this work are provided in the Supporting Information. Here we provide a summary of the available correlations for the estimation of the bubble size in bubbling fluidized beds (Table B.1) and for the estimation of the mass transfer between the bubble and the emulsion phases. The sensitivity of the CLC Reducer model with respect to these correlations is discussed in detail in Section 4.

Table B.1: Bubble size correlations applicable to Geldart B particles

Ref.	Correlation	Initial value	Applicable conditions
(Werther, 1976)	$d_b = d_{b0} \left(1 + 27.2(u - u_{mf})\right)^{\frac{1}{3}} (1 + 6.84h)^{1.21}$	$d_{b0} = 0.00835$	$D > 0.2$ m, $d_p = 100 - 350$
(Darton, 1977)	$d_b = 0.54(u - u_{mf})^{0.4} (h + 4\sqrt{A_0})^{0.8} g^{-0.2}$	-	$A_0 = 0.000056$ m ² (porous plate) $D = 0.1 - 1.2$ m, $d_p = 75 - 470$, $u_{mf} = 0.01 - 0.3$ m/s, $u - u_{mf} = 0.036 - 0.7$ m/s
(Rowe, 1976)	$d_b = (u - u_{mf})^{0.5} (h + h_0)^{0.75} g^{-0.25}$	-	$D = 0.3 - 1.3$ m, $d_p = 39 - 320$ $u_{mf} = 0.0034 - 0.098$ m/s $u - u_{mf} = 0.011 - 0.154$ m/s $h_0 = 0.772 + 0.006h$ (perforated plate); $h_0 = 0$ (porous plate)
(Mori and Wen, 1975)	$d_b = d_{bm} - (d_{bm} - d_{b0}) \exp\left(-\frac{0.3h}{D}\right)$	$d_{b0} = \frac{3.77(u - u_{mf})^2}{g}$	
(Horio and Nonaka, 1987)	$\left(\frac{\sqrt{d_b} - \sqrt{d_{be}}}{\sqrt{d_{b0}} - \sqrt{d_{be}}}\right)^{1 - \frac{\gamma_m}{\eta}} \left(\frac{\sqrt{d_b} - \sqrt{g}}{\sqrt{d_{b0}} - \sqrt{g}}\right)^{1 + \frac{\gamma_m}{\eta}}$ $= \exp\left(-\frac{0.3h}{D}\right)$	(porous plate) $d_{b0} = 0.347 \left(\frac{Ar(u - u_{mf})}{n_{ori}}\right)^{0.4}$ (perforated plate)	$D = 0.3 - 1.3$ m, $d_p = 60 - 450$; $u_{mf} = 0.005 - 0.2$; $u - u_{mf} = 0.008 - 0.48$

The impact of the various correlations presented in Table B.1 on the reactor length-dependent bubble diameter is shown in Figure B.1. For this analysis a hypothetical reactor was used, consistent with the dimensions and velocities of the reactors studied (Table 1). The objective of Figure B.1 is to illustrate the variance of bubble diameter with respect to the correlation used.

Figure B.1: Bubble diameter as estimated by different correlations for Geldart type B particles fluidization ($D = 0.5$ m, $H = 0.5$ m, $u_{mf} = 0.03$ m/s, $u_{sg} = 0.15$ m/s).

Table B.2: Commonly used mass transfer correlations for the 3-phase bubbling bed model

Reference	Mass transfer correlations
(Kunii and Levenspiel, 1968a)	$K_{bc,j} = 4.5 \left(\frac{u_{mf}}{d_b} \right) + 5.85 \left(\frac{D_j^{0.5} g^{0.25}}{d_b^{\frac{5}{4}}} \right), K_{ce,j} = 6.78 \left(\frac{\varepsilon_{mf} D_j u_b}{d_b^3} \right)^{\frac{1}{2}}$
(Sit and Grace, 1981)	$K_{be,j} = 0.4 \left(\frac{u_{mf}}{d_b} \right) + 5.85 \left(\frac{D_j^{0.5} g^{0.25}}{d_b^{\frac{5}{4}}} \right)$

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