Fuel reactor modelling for chemical looping combustion: From micro-scale to macro-scale

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A B S T R A C T

Chemical looping combustion (CLC) is a promising technology able to convert energy whilst managing CO2 emissions. The CLC system is composed of two fluidised bed reactors working in different hydrodynamic regimes. Transition metal particles circulate between the two reactors to carry out the oxidation and reduction reactions with air and fuel, respectively. This technology, which might be embedded into a fuel power plant for electricity generation, would lead to higher thermal plant efficiency than other technologies for carbon capture. The main concern about the technology is related to the total solid inventory needed to achieve full gas conversion which is believed to count for most of the cost of a CLC power plant. Thus, noteworthy attention is given to the modelling of the reactors to optimise the solid inventory and thus the plant’s cost. In this work, a 2D computational fluid dynamics (CFD) analysis of the fuel reactor is carried out. The results, in terms of the effect of the different kinetic and hydrodynamic conditions on the outlet gas conversion, are compared with the results using a macro-scale model implemented in Aspen Plus. Based on the micro scale (CFD) outcomes, the macro scale model is enhanced to capture the main physics influencing the performance of the fuel reactor. The latter is considered more suited as power plant simulator for thermal efficiency and cost estimations.

1. Introduction

CO2 capture from fuel power plants is a commitment involving industry and academia to reduce the CO2 emissions in atmosphere and thus mitigate the global temperature rising. Chemical looping combustion (CLC) is a promising technology, initially patented by Lewis and Gilliland [1], to capture pure CO2 streams with low energy penalties [2–4]. The CLC process is based on metal oxide solid particles that circulate between two reactors to carry out the fuel combustion. Air reacts with metal solid particles in the air reactor (riser) to produce metal oxide particles that are conveyed from the air reactor to the fuel reactor where a reaction with the fuel occurs (Fig. 1). The outlet stream from the fuel reactor is composed by CO2 and H2O easily separable by condensation; the outlet stream from the riser is mostly nitrogen and un-reacted oxygen at high temperature. A well-studied design of the CLC system assumes a riser working in fast fluidisation regime to convey the solid particles from the oxidiser to the reducer and a fuel reactor working in bubbling bed regime [5–7]. The overall reaction system is merely a fuel combustion reaction with the following main features: air is never mixed with the fuel (thus reducing consistently NOx emissions), energy penalties for CO2 capture are much lower compared to other technologies [3,4,8,9].

Nickel, iron and copper metal oxides with different inert supports are the most tested materials when reacting with gaseous fuel such as methane, hydrogen and carbon monoxide [10–14]: they should be cheap and environmentally sustainable. The enhancement of durability, mechanical strength and long term high reactivity of these materials represents the key to make the CLC technology viable. Kinetic and hydrodynamic phenomena occurring in both reactors affect largely the CLC system, specifically in terms of reaction volumes, total solid inventory into the fluidised beds and consequently the make-up of the solid oxygen carrier. Those phenomena have to be investigated carefully since the main issue influencing the competitiveness of the CLC technology is related to the cost of the solid particles [15].

In this scenario, a reactor model that helps to predict optimal operating conditions of the CLC system plays a crucial role in reducing the capital and operating cost of the whole fuel power plant.

Aspen Plus software is largely used by industries to simulate a variety of chemical and petrochemical processes. The software provides operational blocks to implement most of the units
characterising engineering processes. A whole plant made of blocks connected by mass and energy streams can be implemented: mass and heat macro balances are solved across the blocks. Thermal efficiency estimation and cost analysis can be readily undertaken for the whole process. The disadvantage of this macro level approach is that some unit operations, such as fluidised bed reactors, cannot be simulated with a good degree of reality. For this reason, several efforts were carried out in the past [16–19] to mimic the real behaviour of fluidised bed reactors.

Computational fluid dynamics (CFD) simulations for chemical looping combustion purposes [20–27] have been employed to understand at the particle level how the kinetics and the hydrodynamics influence the motion of the solid particles into a fluidised bed, the gas–solid contact efficiency and therefore the outlet fuel

| Symbol | Description |
|--------|-------------|
| A      | fuel reactor superficial area (m²) |
| C_b    | gas bubble concentration (kmol/m³) |
| C_e    | emulsion gas concentration (kmol/m³) |
| C_i    | gas concentration of the i component (kmol/m³) |
| D      | fuel reactor diameter (m) |
| d_b    | bubble diameter (m) |
| D_p    | diffusion coefficient of the n gas species (kg m⁻¹ s⁻¹) |
| D_sp   | particle size (m) |
| D_sn   | diffusion coefficient of the n solid species (kg m⁻¹ s⁻¹) |
| e      | restitution coefficient (–) |
| E_a    | activation energy (kJ/kmol) |
| e_w    | wall restitution coefficient (–) |
| F_NO_in| inlet metal oxide flow-rate (kmol/s) |
| F_NO_out| outlet metal oxide flow-rate (kmol/s) |
| F_s    | solid circulating mass flow-rate (kg/s) |
| g      | gravity acceleration (m/s²) |
| g_o    | radial distribution function (–) |
| h      | generic fuel reactor height (m) |
| H      | height of fuel reactor (m) |
| H_i    | height of the i stage (m) |
| K_be   | mass transfer coefficient between bubble and cloud (s⁻¹) |
| K_ce   | mass transfer coefficient between bubble and emulsion (s⁻¹) |
| k_i    | kinetic constant (mol¹⁻ⁿ x m³ⁿ⁻³ s⁻¹) |
| k_o    | kinetic constant (mol¹⁻ⁿ x m³ⁿ⁻² s⁻¹) |
| L_f    | height of a fluidised bed (m) |
| L_m    | height of a fixed bed (m) |
| n      | order of reaction (–) |
| p      | pressure (Pa) |
| P_fuel | fuel power (MW) |
| P_g    | gas pressure (Pa) |
| P_s    | solid pressure (Pa) |
| r_c    | core radius (m) |
| R_e    | Reynolds number of the solid phase (–) |
| r_g    | grain radius (m) |
| r_n    | reaction rate of the n gas specie (kg m⁻³ s⁻¹) |
| r_n_Aspen | Aspen Plus reaction rate (kmol s⁻¹ m⁻³) |
| r_n_CFD | CFD reaction rate (kmol s⁻¹ m⁻³) |
| r_p    | particle radius (m) |
| r_sn   | reaction rate of the n solid specie (kg m⁻³ s⁻¹) |
| T      | temperature (°C) |
| U_b    | gas bubbles velocity (m/s) |
| U_e    | gas emulsion velocity (m/s) |
| Umf    | minimum fluidisation gas velocity (m/s) |
| u_p    | inlet superficial gas velocity (m/s) |
| V      | whole fluidised bed volume (m³) |
| V_b    | bubble phase volume (m³) |
| V_CSTR | CSTR volume (m³) |
| V_emulsion | emulsion volume (m³) |
| W_f    | solid inventory in the fuel reactor (kg) |
| X      | radial direction (–) |
| X_g    | gas conversion (–) |
| X_s    | solid conversion in the fuel reactor (–) |
| X_MO   | metal oxide conversion at the riser exit (–) |
| Y      | axial direction (–) |
| Y_n    | mass fraction of the n gas specie (–) |
| Y_Mi   | metal mass fraction (–) |
| Y_MO   | metal oxide mass fraction (–) |
| Y_sn   | mass fraction of the n solid specie (–) |
| Z_MO   | metal oxide volumetric fraction (–) |
| δ      | coefficient for the interphase force between gas and solid (kg m⁻³ s⁻¹) |
| ε_b    | gas volume fraction in the bubble phase (–) |
| ε_g    | gas volume fraction in the emulsion phase (–) |
| ε_f    | gas volume fraction in bubbling conditions (–) |
| ε_v    | gas volume fraction in a fluidised bed (–) |
| ε_m    | gas volume fraction in a fixed bed (–) |
| ε_gv   | gas void at minimum fluidisation conditions (–) |
| ε_d    | solid volume fraction in a fluidised bed (–) |
| η_p    | gas phase expansion factor (–) |
| ρ_Mi   | metal density (kg/m³) |
| ρ_MO   | metal oxide density (kg/m³) |
| ρ_s    | solid density (kg/m³) |
| s       | volumetric fraction of the bubble phase (–) |
| τ_g    | gas stress tensor (Pa) |
| τ_s    | solid stress tensor (Pa) |
| ϕ      | angle of internal friction (–) |
| Θ      | granular temperature (m² s⁻²) |
| Y      | energy dissipation rate (kg m⁻¹ s⁻³) |
| U_g    | velocity of the gas phase (m/s) |
| U_s    | velocity of the solid phase (m/s) |
| μ_s    | frictional viscosity (kg m⁻¹ s⁻¹) |
| μ_g    | solid shear viscosity (kg m⁻¹ s⁻¹) |
| μ_b    | solid bulk viscosity (kg m⁻¹ s⁻¹) |
| μ_v    | gas viscosity (kg m⁻¹ s⁻¹) |

Fig. 1. Chemical looping combustion system.
conversion. The disadvantages of this micro level approach are related to the computational cost, the long runs of simulation and in particular the small domain that can be processed (few or most commonly just one unit processed).

The present work aims to model the fuel reactor of the CLC system using a CFD approach to achieve a better understanding of the kinetic and hydrodynamic phenomena involved. The results from the micro scale approach are analysed and compared with those obtained from a macro scale approach using Aspen Plus model. The latter results are improved to increase the accuracy of the macro scale model making it useful for future thermal efficiency and economic evaluations of a fully integrated CLC power plant.

2. Description of the parameters for modelling comparison

The metal oxide reduction rate is lower than its oxidation rate under the same temperature conditions [5,10,11,13]; consequently, a higher solid inventory into the fuel reactor than into the air reactor is expected to get full gas conversion. The present work focuses on a better understanding of the bubbling fuel reactor behaviour at the macro and micro scale to get useful information about the minimum/optimal solid inventory needed into the reducer (the fuel reactor).

2.1. Fuel reactor in Aspen Plus

The system under investigation is a fuel reactor sized for 10 MW of fuel power working at 950 °C under atmospheric pressure. The reduction reaction involves pure methane that reacts with nickel oxide to produce CO₂, H₂O and nickel to be regenerated in the air reactor. The kinetic data for the NiO reduction and the physical properties of the solid particles come from Abad et al. [15] as summarised in Table 1.

From the CLC theory, it is known that the metal oxide conversion at the riser exit X_{MO exit} and the solid circulating flow-rate F_s between the air and fuel reactor affect greatly the total solid inventory [5,13,15]. High values of X_{MO exit} mean high amount of nickel converted to NiO in the air reactor; thus, more nickel oxide is available to react with methane in the reducer keeping high the reduction rate in the fuel reactor and so reducing its solid inventory [5,15]. Solid circulating flow-rates, F_s, higher than the stoichiometric ratio of oxygen carrier to fuel lead to higher values of the reduction rate and thus lower solid inventory in the bed. Furthermore, high solid circulating flow-rate conveys more heat from the air reactor to the fuel reactor reducing the drop in temperature between the two fluidised beds and sustaining the endothermic reaction at the riser exit X_{MO exit} equal to 0.9 and F_s about 8 times higher than the stoichiometric ratio of oxygen carrier to fuel are considered optimal operating conditions and thus, they are chosen as operating conditions of our macro scale model (Table 2). A parallel study on the air reactor [17] showed that at atmospheric conditions typical fast fluidisation regimes are reached keeping an air reactor area that allows for applying high solid circulating flow-rate. Indeed, reasonable values of solid circulating flow-rate per area unit close to 50 kg/(m²s) [5], were found.

Table 2

| Fuel reactor operating conditions in Aspen Plus model. |
|-----------------|-----------------|
| \( P_{fuel} \)  | 10              |
| \( W_{fr} \)    | 3000 kg         |
| \( T \)         | 950 °C          |
| \( X_{MO exit} \) | 0.9             |
| \( L_m \)       | 0.45 m          |

The kinetic rate \( r_i \) Aspen implemented in Aspen Plus is expressed as follows [17]:

\[
r_i^{\text{Aspen}} = \frac{k_i \cdot e^{-\frac{Ea}{Rg}}}{r_g} (1)
\]

and

\[
k_i = 3 \cdot k_g \cdot e^{-\frac{Ea}{r_g}} \quad (2)
\]

Eq. (1) is derived from the shrinking core model applied to spherical grain geometry in a form suitable to be implemented in Aspen Plus. The reduction rate is a function of the solid fraction, \( e_g \), the gas concentration, \( C_g \), and the metal oxide conversion inside the bed, \( X_j \). The kinetic expression is divided by the gas void \( e_g \) because the reference volume of reaction is the volume occupied by the gas phase.

Different ways to explicit the solid conversion are reported in the literature [5,22,24,25]; the most suitable way to carry out a steady state simulation in Aspen Plus is to relate the solid conversion to the molar metal oxide flow-rate, \( F_{NiO} \), as expressed in Eq. (3):

\[
X_j = 1 - \frac{F_{NiO \text{ out}}}{F_{NiO \text{ in}}} \quad (3)
\]

Even if the heterogeneous gas–solid reaction proceeds via three steps, i.e. external mass transfer, internal diffusion and chemical reaction [28], the reduction of NiO with methane is assumed to be controlled by the chemical reaction step [10,12,15] (Eq. (2)).

2.2. Fuel reactor in MFIX

Computational fluid dynamics (CFD) is carried out using an open source code called MFIX (Multiphase Flow with Interphase eXchange [29]).

A 2D reactor is filled up with solid particles in a packed bed manner at time equal zero. At the beginning of the simulation, nitrogen flows uniformly from the bottom to the top of the bed fluidising the solid particles. After 2 s of simulation, the feed is switched from nitrogen to methane and the simulation runs until approximately constant values of flue gas concentrations are achieved (pseudo stationary condition). Nitrogen is used at time equal zero (with no reaction occurring) to help the convergence at the beginning of the simulation. The initial conditions are shown in Table 3. More details of the CFD model employed are given in Section 3.

The size of the reactor must be decreased compared to the system implemented in Aspen Plus to reduce the computational costs. The hydrodynamic conditions simulated in Aspen Plus are kept to guarantee a right comparison between micro and macro model. The reactor is scaled to a fuel power of 10 kW just reducing the area to 34.8 cm² that means 300 g/kW of solid inventory in the bed at the same height of fixed bed \( L_m \) modelled in Aspen Plus.

Table 1

| Kinetic parameters and physical properties of solid particles [15]. |
|---------------------------------------------------------------|
| Oxygen carrier | NiO           |
| Inert support  | Al₂O₃         |
| Total NiO content | 60%       |
| Active NiO content | 40%       |
| Particle size \( d_p \) | 2.00E–04 m   |
| Grain radius size \( r_g \) | 6.90E–07 m   |
| Particle density \( \rho_s \) | 3446 kg/m³  |
| Kinetic coefficient \( k_o \) | 0.71 mol⁻¹m⁻³s⁻¹ |
| Activation energy \( E_a \) | 78,000 kJ/kmol |
| Order of reaction \( n \) | 0.8         |
As reported by Mahalatkar et al. [25], the fuel reactor can be simulated over the time by decoupling it from the air reactor for the following reasons:

- The amount of solid material inside the bed is high compared to the reacting gas flow-rate, implying that the metal oxide conversion does not appreciably change during the simulation time (of the order of few seconds).
- Few seconds of simulation are enough to reach pseudo stationary conditions at approximately constant metal oxide conversion; consequently, such the solid flow-rate is not needed to be simulated for replacing the converted metal oxide particles.

In MFIX environment, the initial NiO mass fraction (i.e. 36%) is chosen equal to the NiO mass fraction in the inlet solid flow-rate simulated in Aspen Plus (X_{\text{NiO,ex}} is assumed to be 0.9). This assumption does not influence greatly the comparisons between the micro model (CFD) and the macro model (Aspen Plus) since in either CFD or Aspen simulations this value is almost constant, so its influence on the kinetic rate is the same. Indeed, in CFD the metal oxide conversion does not appreciably change during the simulation time due to few seconds of simulation; in Aspen, the metal oxide conversion changes slightly, regardless the degree of gas conversion, since the solid flow-rate applied for models comparison is 8 times higher than the stoichiometric one (F_{\text{g}} = 75 kg/s).

The kinetic rate, in the form of Eq. (1), must be modified in its solid conversion term because no solid flow-rate circulates across the fuel reactor. Different expressions are reported in the literature to define the average solid conversion term as the volumetric fraction of reacted metal oxide into the solid particles:

\[
(1 - X_j) = \frac{r_j}{r_p} = Z_{\text{NiO}} = \frac{Y_{\text{NiO}}}{Y_{\text{NiO}} + \frac{F_{\text{g}}}{F_{\text{p}}}} Y_{\text{Ni}}
\]

where Z_{\text{NiO}} is the volumetric fraction of NiO and Y_{\text{NiO}} and Y_{\text{Ni}} are the mass fraction of NiO and Ni, respectively. The kinetic rate is finally expressed as:

\[
r_{\text{CFD}} = k_i \cdot \epsilon_v \cdot C_v^4 \cdot \left( \frac{Y_{\text{NiO}}}{Y_{\text{NiO}} + \frac{F_{\text{g}}}{F_{\text{p}}}} Y_{\text{Ni}} \right)^{\frac{1}{4}}
\]

Compared to Eq. (1), the kinetic rate does not include the gas void fraction because the reference reaction volume is the total volume of the computational cell.

The comparison between the steady state case implemented in Aspen Plus and the pseudo stationary case implemented in MFIX under the same operating conditions is run for two different case studies called “high” and “low” kinetics. High kinetics refers to the value of k_i obtained from the data reported by Abad et al. [15] and shown in Table 1, whereas low kinetics refers to a fictitious low value of k_i equal to 0.1. The different kinetics (with two orders of magnitude difference) affect largely the hydrodynamics of the system allowing for a better understanding and comparison between the macro scale model (Aspen Plus) and the micro scale model (CFD).

### 3. CFD model

#### 3.1. Governing equations

The 2D model implemented in MFIX code is based on the Eulerian–Eulerian approach. Gas and solid phases are considered as continuum phases in the domain under investigation. The solid phase is characterised by uniform spherical particles of constant mean density and diameter. Continuity and momentum equations in two directions (x and y) are solved for both phases and the exchange of mass and momentum between them is taken into account. No energy equations are solved because the reduction reaction is slightly endothermic and the drop in temperature under few seconds of simulation is negligible. All the equations come from the well known theory embedded in the MFIX code [29] and they are listed in the Appendix A.

#### 3.2. Initial and boundary conditions

No-slip boundary condition for the gas phase and the free-slip condition for the solid phase are applied at the wall. At the inlet section of the bed the Dirichlet boundary condition is applied (with constant inlet mass flux) whereas at the outlet section of the bed the Neumann boundary condition is assumed (with constant outlet pressure).

The domain is divided into 7000 cells (see Table 3) and for each cell the continuity and momentum equations of each phase are solved simultaneously with linear solvers (finite volume method). The algorithm applied to solve the set of partial differential equations (PDE) is an extension of SIMPLE algorithm [30] introduced for the solution of pressure–velocity coupled PDE.

The scalar variables are positioned at the cell centre whereas the vector variables at the cell faces (staggered grid arrangement). The convection terms of PDE are discretised using a second upwind order called Superbee to improve the numerical accuracy and the bubble shape resolution [29]. Finally, MFIX code uses a variable time step and the range selected is between 10^{-4} and 10^{-8} s.

#### 3.3. CFD results

As mentioned, all the CFD simulations run in a computational domain divided in 7000 cells. A grid independence test was carried out increasing the number of cells up to 28,000. No appreciable effects on the flow behaviour and main variables were found. Low and high kinetics (see Section 2) are implemented to study their effect on the hydrodynamics and the outlet gas concentrations. High kinetic simulations run for 10 s whereas low kinetic
simulations run for 15 s since longer times are needed to achieve pseudo stationary condition in terms of gas outlet concentrations (Fig. 2).

A pure nitrogen flow-rate is fed at 36 cm/s up to $t = 2$ s. For $t > 2$ s, the feed flow-rate is switched from pure nitrogen to methane (Figs. 2 and 3) and the heterogeneous reaction with NiO occurs.

The delay in the methane mass fraction detection after $t > 2$ s is due to the time that the methane feed flow-rate needs to cross the whole fluidised bed. Further delay in CO$_2$ and H$_2$O mass fraction detections is related to the very low kinetics of reaction. Indeed, this effect is not noticeable at the high kinetics (Fig. 3).

Fig. 4 shows the void fraction in the dense phase versus $X$ axis averaged over $Y$ axis between 12.95 and 16.45 cm. The low kinetics case is averaged over time between 13 and 15 s whereas the high kinetics case is averaged over time between 8 and 10 s.

The reaction of methane with NiO is characterised by an increase of the number of moles in the gas phase (with an expansion factor $\xi$ equal to 2). Thus, high kinetics, which lead to high methane conversion, produce an increase in the gas volume fraction. Inversely, the solid volume fraction shows higher values in the low kinetics case (Fig. 5).

Bubbles formation occurs at the bottom of the fluidised bed and they rise and coalesce along the bed height mostly far from the walls. Thus, higher solid volume fractions are expected to be found close to the walls (Fig. 5).

Fig. 6 shows the axial component of the gas velocity $V_g$ for the two cases under investigation. Two main features can be noticed: the applied no-slip condition for the gas phase (with $V_g$ equal to zero at the walls) and higher values of $V_g$ in the centre of the bed due to the bubble tendency to rise mostly towards the centre. The rising of the bubbles creates recirculation of the solid phase in the so called “emulsion phase” that leads to negative value of $V_g$ close to the walls. As previously explained, high methane conversion produces a considerable increase in the gas volumetric flow-rate and thus in the axial gas velocity.
Fig. 7 shows the axial component of the solid velocity, $V_s$, for both high and low kinetics cases. The solid free slip condition is verified (with $V_s \neq 0$) at the walls. The bubbles' rising pushes the solid particles upward in the centre of the bed and subsequently they fall down following the recirculation motions.

Fig. 8 shows the change in axial gas velocity, $V_g$, versus $Y$ axis averaged over time and $X$ axis. The double effect of the heterogeneous reaction and the reduction of the void space ($\varepsilon_g < 1$) produces an abrupt increase in $V_g$ in the dense phase, which is particularly pronounced for high kinetics. The value of $V_g$ at the bed exit follows the increase in the number of moles due to the methane conversion.

The outlet value of $V_g$ verifies Eq. (6):

$$V_{g\text{ outlet}} = V_{g\text{ inter}} * (1 + \zeta * X_g)$$  \hspace{1cm} (6)

where $\zeta$ is the expansion factor for the gas species and $X_g$ is the methane conversion.

Figs. 9 and 10 show the gas volume fraction and the mass fraction of the gas species along the bed for low and high kinetics, respectively.

The main features characterising the bubbling regime can be observed: the bubbles' formation takes place few centimetres above the gas inlet; bubbles rise mostly at the centre of the bed increasing in volume and coalescing along the bed height. At high kinetics, bubbles are larger and their motion approaches the turbulent regime (Fig. 10) due to the high methane conversion that leads to high increase in number of moles in the gas phase. This phenomenon can be ideally explained with the transfer of the gas exceeding the minimum fluidisation velocity $U_{mf}$ from the emulsion phase at high solid content to the bubble phase at high gas content [31]. Due to larger and faster bubbles and their burst at the interface dense phase-freeboard, at high kinetic conditions higher bed expansion is detected. At low kinetics (Fig. 9), high values of un-reacted methane mass fraction are observed, mainly in the centre of the bed where most of the bubble phase takes place. The reaction occurs mainly in the bottom section of the bed characterised by an average high solid volume fraction, high methane mass fraction and no well defined bubble phase; far from the bottom region, bubble phase formation determines gas by-pass along the bed that is subtracted from the high reacting regions (Fig. 11); thus poor gas conversion is expected to occur. At high kinetics, the reaction occurs mainly in the bottom phase and gas by-pass apparently has no effect in lowering the gas conversion. This outcome is affected by the assumed condition of inlet uniform gas flow-rate. Modelling the gas distributor (preferably in a 3D simulation) is expected to show bubble formation after few millimetres above the distributor reinforcing the negative effect of gas by-pass on the gas conversion.

Being aware that the gas distributor (not modelled in our work) can affect the development of the bubbles in terms of location and percentage of occupied volume and thus the gas conversion, the simulations carried out at two different kinetics conditions show that high reacting solid materials are important to achieve full gas conversion in a fluidised bed operating under bubbling regime.

No freeboard effect in the kinetic reaction is detected [20,22,32]. The influence of the freeboard region, characterised by low solid content on the gas conversion, was experimentally demonstrated [31,33,34]. As reported by Wang et al. [32], the zero solid–gas contact efficiency in the freeboard might be related to the failure of the Eulerian–Eulerian approach to describe the gas/solid mechanisms in regions at very low solid particles concentrations. An Eulerian–Lagrangian approach might help to estimate the reduction of the reaction in the freeboard region.

4. Aspen Plus model

At the macroscopic scale, a bubbling bed can be ideally thought as made of two phases: a so called "emulsion phase", characterised by good mixing of gas and solid particles, and a so called "bubble phase" at low content of solid acting as gas by-pass along the bed. This representation comes from the Davidson and Harrison theory [35] that states how the excess of gas to keep the minimum fluidisation condition in the emulsion phase is transferred to the bubble phase. Several authors [16–18,36] modelled the bubble phase as a plug flow reactor (PFR) and the emulsion phase as a perfect mixing reactor (CSTR). The bed is axially divided into stages; each stage is composed by two sub-reactors: PFR to mimic the bubble phase and CSTR to mimic the emulsion phase (Fig. 12). Gas mass transfer occurs between the exit streams of the two sub-reactors at the end of each stage. Isothermal conditions within the bed are assumed and the radial mass solid gradient is neglected.

In this work, the hydrodynamics (see Table 4) is implemented using subroutines written in Excel which are linked to the Aspen Plus environment through the so called "calculator blocks". In the "Feed Calculator" block (Fig. 12), a split of the inlet volumetric flow-rate to enter the two phases, bubble and emulsion, has to be accomplished. The difference $U_{b} - U_{e}$ is the term driving the split. The approach proposed by Johnson et al. [37] and applied also by Adanez et al. [38] is taken into account. Johnson et al. [37] reported an expression of the volumetric bubble fraction independent of the height of the bed. Combining the two phase theory with the dependence of the bubble velocity, $U_{b}$, from the bubble diameter and...
applying the Darton correlation for the bubble size [39]. Johnson et al. [37] first defined a function \( f_2 \) and, after some manipulations, they expressed the volumetric fraction of the bubble phase, \( \sigma \), as a function of \( f_2 \) and the difference \( U_0 - U_{imp} \) (see Table 4). \( \sigma \) is the volumetric fraction of the bubble phase in the whole bed and its value is independent of the height in the bed. Given \( \sigma \), the rise bubble velocity, \( U_b \), is calculated from the gas mass balance. Thus, the inlet volumetric gas flow-rate can be split into two streams entering the first PFR and CSTR reactors to run the bubbling bed model. At the end of each stage the superficial gas velocity, \( U_0 \), the bubble gas velocity, \( U_b \), the bubble volume fraction, \( \sigma \), the bubble diameter, \( d_b \), and the volumes of the two sub-reactors, are updated to be used in the next stage. The variables aforementioned need to be updated at the beginning of each stage for the following reasons: the increase in number of moles, which is produced as a consequence of the gas conversion, determines an increase in the superficial gas velocity and thus in \( U_b \) and \( \sigma \); the bubble growth along the bed height leads to an increase in the bubble diameter \( d_b \). All these variables influence the mass transfer term between the two phases and thus the updated inlet gas concentrations \( (C_{CH_4}, C_{CO_2} \text{ and } C_{H_2O}) \) to the next stages (Eqs. (7) and (8)):}

\[
C_{b(i+1)} = C_{bi} - K_{be} \cdot (C_{bi} - C_{ei}) \cdot \frac{H_i}{U_b} \quad (7)
\]

\[
C_{e(i+1)} = C_{ei} + K_{be} \cdot (C_{bi} - C_{ei}) \cdot \frac{H_i}{U_e} \cdot \left( \frac{\sigma}{1 - \sigma} \right) \quad (8)
\]

where \( H_i \) is the height of the \( i \) stage. The overall mass transfer coefficient \( K_{be} \) between bubbles and emulsion is calculated applying the equations proposed by Kunii and Levenspiel [31] (see Table 4).

The kinetic expression (Eq. (1)) is introduced in each sub-reactor through subroutines written in FORTRAN language.

Porrazzo et al. [17] reported how the suitable number of stages to model the fluidised bed depends on kinetic and hydrodynamic considerations. It was found that 5 stages provide outcomes of reasonable accuracy in terms of gas conversion at the bed exit under different operating conditions [17].

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**Fig. 9.** Gas volume fraction and mass fractions of gas species at \( t = 15 \text{s} \) for low kinetics.

**Fig. 10.** Gas volume fraction and mass fractions of gas species at \( t = 10 \text{s} \) for high kinetics.

**Fig. 11.** Gas volume fraction and reaction rate (\([\text{mol/(cm}^3 \text{s})]\)) at \( t = 15 \text{s} \) and low kinetics.
Implemented equations to mimic the hydrodynamics of the bubbling bed.

| Implemented equations to mimic the hydrodynamics of the bubbling bed. |
|---------------------------------------------------------------|
| Superficial gas velocity in the emulsion phase             |
| \[ U_{s} = \frac{U_{o}}{d_{b}^{0.4} (h + 4/\sqrt{A_{e}})^{0.8} g^{-0.2}} \] |
| Bubble diameter \[ d_{b} \]                                   |
| \[ f_{b} = \frac{(2.25 - 0.7 \rho_{s} U_{o})}{(15 - U_{o}/U_{mf})} \] |
| Volumetric fraction of bubble phase \[ \sigma \]              |
| \[ \sigma = \frac{1 - (1 - \rho_{s} U_{o})}{2} \]           |
| Rise bubbles velocity at \[ U_{b} \neq U_{mf} \]             |
| \[ U_{b} = \frac{U_{o} - (1 - \rho_{s} U_{o})}{\rho_{s} U_{o}} \] |
| Fluidised bed void \[ \epsilon_{f} \]                       |
| \[ \epsilon_{f} = \sigma \phi_{b} + (1 - \sigma) \phi_{e} \] |
| Height of a fixed bed \[ L_{n} \]                           |
| \[ L_{n} = \frac{U_{o}^{1.3}}{U_{o}^{1.3} - U_{mf}^{1.3}} \] |
| Height of fluidised bed \[ L_{f} \]                          |
| \[ L_{f} = \frac{U_{o}^{1.3}}{U_{o}^{1.3} - U_{mf}^{1.3}} \] |
| Mass transfer coefficient cloud/bubble \[ K_{bc} \]         |
| \[ K_{bc} = 4.5 \times \left( \frac{U_{o}}{d_{b}} \right)^{0.8} \times \left( \frac{\rho_{s} \rho_{e} \phi_{b} \phi_{e}}{\sigma} \right) \] |
| Mass transfer coefficient cloud/emulsion \[ K_{ce} \]       |
| \[ K_{ce} = 6.77 \times \left( \frac{\rho_{s} \rho_{e} \phi_{b} \phi_{e}}{\sigma} \right)^{0.8} \] |
| Overall mass transfer coefficient bubble/emulsion \[ K_{o} \] |
| \[ K_{o} = \frac{1}{\frac{1}{K_{bc}} + \frac{1}{K_{ce}}} \]     |
| Bubble phase volume \[ V_{b} \]                             |
| \[ V_{b} = V \times \sigma \]                               |
| Emulsion phase volume \[ V_{e} \]                           |
| \[ V_{e} = V \times (1 - \sigma) \]                         |
| PRF volume \[ V_{PRF} \]                                   |
| \[ V_{PRF} = V_{b} + \phi_{b} \]                           |
| CSTR volume \[ V_{CSTR} \]                                 |
| \[ V_{CSTR} = V_{e} + \phi_{e} \]                          |

### 4.1. A new concept of stages

A number of authors applied the concept of dividing axially the bubbling bed in stages and considering a number of stages of the same length [16–18,36]. Previous CFD simulations showed how most of the heterogeneous reaction occurs at the bottom of the fluidised bed since the reacting gas concentration is higher and the bubbles’ diameter at the bottom of the bed is at its minimum. Furthermore, the incoming gas, which encounters the solid particles, creates turbulent motions that enhance the gas–solid contact efficiency promoting an increase in the gas conversion.

The mass transfer between the bubble and the emulsion phase decreases significantly along the bed due to the increase in the bubble diameter that reduces the mass transfer coefficient \( K_{bc} \). Moreover, the increase in the bubble volumetric fraction, \( \sigma \), along the bed, due to the gas expansion, reduces the emulsion volume fraction and thus the portion of the bed where most of the reaction takes place. Consequently, a new concept of stages is introduced. Porrazzo et al. [17] reported a multi stage model where the whole bed was divided into 5 stages of the same length. The new concept of stages refers to a different split of the bed length according to the following strategy: 4 stages are used to model the bottom of the bed whereas the last (fifth) stage is used to model the rest of the fluidised bed length.

Based on the increment in the bubble diameter per unit bed height (Fig. 13), as an indicator of the mass transfer effectiveness between the two phases, 4 stages are employed to model the first 10 cm of the bed above the inlet and the last stage is employed to model the rest of the bed length. The trend of the mass transfer coefficient \( K_{bc} \) follows the same trend of the incremental bubble diameter per height unit. In this way, we assure a good utilisation of the limited number of stages employed since we mainly focus on the modelling of the bed zone where most of the phenomena of interest occur.

### 4.2. Comparative results CFD – Aspen Plus

The two fuel reactor models (MFIX and Aspen Plus) were tested under different operating conditions: various superficial gas velocity, solid inventory and kinetics of reaction.

Fig. 14 shows the variation of the methane mass fraction along the bed height for different superficial gas velocities at constant solid inventory and low kinetics.

The values of the \( CH_{4} \) mass fraction in the Aspen Plus model are detected at the end of each reaction stage. The \( CH_{4} \) mass fraction in the CFD model is averaged over \( X \) axis and over time between 13 and 15 s.

In both models, the reduction in the superficial gas velocity \( U_{o} \) determines a decrease in the methane mass fraction and thus an increase in the gas conversion; indeed, values of \( U_{o} \) closer to the minimum fluidisation velocity lead to a reduction of the gas bypass through the bubble phase promoting the reaction in the emulsion phase. The increase in methane conversion is amplified from the fact that keeping constant the area of the reactor, a decrease in \( U_{o} \) leads to a decrease in the fuel power and thus the same amount of solid inventory reacts with less methane flow-rate driving the gas conversion to higher values. As mentioned previously, most of the reaction occurs in the bottom of the bed where gas

![Figure 12. Composition of the stages in Aspen Plus.](image12)

![Figure 13. Incremental bubble diameter per height unit versus bed length.](image13)
and solid show high contact efficiency. The Aspen Plus model assumes an initial split of the superficial gas flow-rate between the two phases based on the amount of gas exceeding the minimum fluidisation conditions [17]; thus, part of the gas flow-rate is initially subtracted to react with the solid particles leading to lower values of gas conversion compared to the CFD model. In the CFD model, we assume uniform inlet gas flow-rate and the modelling of the gas distributor is not taken into account. The gas distributor plays a role in affecting the bubble phase in terms of bubble diameter and distance of initial formation from the bottom of the bed [31,40]. For this reason, it is believed that the modelling of a gas distributor in a 3D CFD simulation could give a better match between the macro-scale and micro-scale models.

The mass transfer term plays a negligible role far from the inlet, determining almost flat profiles of methane mass fraction above 10 cm from the inlet. This aspect justifies the implementation of just one stage to model the rest of the bed height in Aspen Plus.

Fig. 15 shows the methane conversion at the bed exit for the two models at different initial superficial gas velocities. As mentioned, the Aspen model provides lower results of the methane conversion compared to the CFD model due to the initial split of the gas flow-rate at the bed inlet. The CFD trend is slightly affected by fluctuations in the axial velocity component (pseudo stationary condition). The difference in the outlet gas conversion between the two models ranges from 1% to 6%.

Fig. 16 shows the variation of the methane mass fraction along the bed for different solid inventories at initial superficial gas velocity equal to 36 cm/s and low kinetics. The reduction in the solid inventory, expressed as height of fixed bed $L_m$, determines lower gas residence time into the bed leading to lower gas conversion. The Aspen model captures this feature in the last stage of reaction that is smaller in terms of volume of reaction at lower solid inventories. Explanation of the effect of the change in the solid inventory on the gas conversion with the change in the gas residence time fails by looking at the CFD trends. In this case, the change in solid inventory affects the solid volume fraction distribution in the bottom of the bed and thus the kinetic rates: higher solid inventories lead to higher average solid volume
fraction in the bottom zone given that statistically more solid particles participate to the recirculation motions into the bed; consequently, higher solid volume fraction lead to higher kinetic rates and thus lower methane mass fractions.

The comparison in gas conversion at the bed exit between the two models is good (Fig. 17). The difference in the outlet gas conversion between the two models is below 3%.

The same analysis on the methane mass fraction under different superficial gas velocities and solid loading is carried out for the case at high kinetics. Fig. 18 shows the change in gas mass fraction along the bed for different superficial gas velocities. The effect of the reaction kinetics, in reducing steeply the methane mass fraction at the bottom of the bed is more evident for high kinetics. The effect of changing the superficial gas velocity on the gas conversion is much more appreciable from the Aspen model calculations. Also, in this case, lower values of \( U_o \) determine higher gas conversion. From Fig. 19 it is noticeable how the difference in the gas conversion between the two models decreases at lower \( U_o \).

At lower \( U_o \) values, less gas flow-rate goes to the bubble phase and the effect of the initial gas splitting in the Aspen model is reduced: decreasing \( U_o \), the gas conversion values from the two models tend to converge. The difference in the outlet gas conversion between the two models ranges from 0.05% to 15%.

At high kinetics, a change in solid inventory in a range 20–45 cm of height of fixed bed does not influence appreciably the methane gas conversion in both models.

5. Conclusions

The work compared two models for CLC bubbling bed, one at macro-scale (Aspen Plus) and one at micro-scale level (CFD). The two models were compared under different operating conditions. Based on CFD simulations, a new division of the number of stages in Aspen Plus was introduced to capture the phenomena occurring at the bottom of the bed. The methane mass fraction trends along the bed and outlet gas conversions were evaluated at different kinetic rates, inlet superficial gas velocities and solid inventories. Despite the construction of the multi-stage macro-scale model is based on idealised hydrodynamic and kinetic phenomena, the trends and the overall results from the two models are comparable. The multi-stage model implemented in Aspen Plus can capture the influence of the kinetics, superficial gas velocity and solid inventory on the gas conversion. A new division of the stages that models better the bottom of the fuel reactor reduces the gap between the macro-scale and micro-scale model. It is believed that a 3D modelling of a gas distributor at micro-scale level might enhance the match between the two models since bubbles’ formation and diameter are affected by the distributor design. The difference in the outlet gas conversion between the two models can be evaluated with good confidence for engineering purposes. Consequently, the macro-scale model of the fuel reactor, embedded into a fuel power plant simulation, can lead to a reasonable estimation of the effect of the reaction operating conditions on the overall thermal efficiency, capital and operating cost of a fuel power plant based on the CLC technology.
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Appendix A

The MFIX governing equations applied are listed below [29]:

Continuity and species transport equations

$$\frac{\partial}{\partial t} (\rho \mathbf{U}) + \nabla \cdot (\rho \mathbf{U} \mathbf{U}) = \sum_{n=1}^{N_{eq}} I_{eq} + \sum_{n=1}^{N_{eq}} I_{g} + \sum_{n=1}^{N_{eq}} I_{s}$$

Momentum equations

$$\frac{\partial}{\partial t} (\rho \mathbf{U}) + \nabla \cdot (\rho \mathbf{U} \mathbf{U}) = -\nabla P + \nabla \cdot \tau + \sum_{n=1}^{N_{eq}} I_{eq} + \sum_{n=1}^{N_{eq}} I_{g} + \sum_{n=1}^{N_{eq}} I_{s}$$

Conservation of granular energy

$$\rho \mathbf{U} - \nabla = 0$$

$$\mathbf{u} - \nabla = \begin{pmatrix} -K_{e} \frac{\partial \phi (\mathbf{D}_{\mathbf{u}})}{\partial \mathbf{U}_{g}} + \sqrt{K_{e}^{2} \frac{\partial \phi (\mathbf{D}_{\mathbf{u}})}{\partial \mathbf{U}_{g}} + 4K_{e}^{2} \frac{\partial \phi (\mathbf{D}_{\mathbf{u}})}}{2} + 2K_{e} \frac{\partial \phi (\mathbf{D}_{\mathbf{u}})}}{2} \end{pmatrix}$$

$$K_{e} \frac{2(1-e^{2})}{d} \mathbf{U}_{g}$$

Drag force model

$$\beta = \frac{3M}{4V_{in} d_{p}^{2}} \frac{d_{p}}{4}$$

$$V_{in} = \frac{0.5 (A - 0.06Rc + \sqrt{(0.036Rc^{2}) + 0.12Rc(2B - A) + A^{2}})}{2}$$

$$A = \frac{e_{g}^{14}}{28} \leq \frac{8.5}{28}$$

$$B = \frac{\varepsilon_{g}}{28} \geq \frac{0.85}{28}$$

$$R_{c} = \frac{\rho \mathbf{U}_{g} - \mathbf{U}_{l}}{\mu_{g}}$$

References

[1] Lewis WK, Gilliland ER. Production of pure carbon dioxide. Int Pat USA: 1954.

[2] Naqvi R, Bolland O, Brandvold Oy, Heile K. Chemical looping combustion—analysis of natural gas fired power cycles with inherent CO2 capture. ASME turbo expo 2004: power for land, sea, and air. Am Soc Mech Eng 2004;301–9.

[3] Wolf J, Anheden M, Yon J. Performance analysis of combined cycles with chemical looping combustion for CO2 capture. In: Proceedings of 18th Pittsburg coal conference; 2001. p. 3–7.

[4] Wolf J, Anheden M, Yon J. Comparison of nickel-and iron-based oxygen carriers in chemical looping combustion for CO2 capture in power generation. Fuel 2005;84:993–1006.

[5] Lyngfelt A, Leckner B, Mattisson T. A fluidized-bed combustion process with inherent CO2 separation; application of chemical-looping combustion. Chem Eng Sci 2001;56:3101–13.

[6] Mattisson T, Jernstad L, Linderholm C, Lyngfelt A. Reactivity of a spray-dried NiO/NiAl2O4 oxygen carrier for chemical-looping combustion. Chem Eng Sci 2011;66:4636–44.

[7] Ryu HJ, Jin GT, Yi CK. Demonstration of inherent CO2 separation and NOx emission in a 50 kW chemical-looping combustor: continuous reduction and oxidation experiment. In: Proceedings of the 7th international conference on greenhouse gas control technologies; 2004. p. 5–9.

[8] Audus H. Leading options for the capture of CO2 at power stations. In: Proceedings of the fifth international conference on greenhouse gas control technologies; 2000. p. 13–16.

[9] Göttlicher G, Pruschke R. Comparison of CO2 removal systems for fossil-fuelled power plant processes. Energy Convers Manage 1997;38:5173–8.

[10] García-Labiano F, de Diego LF, Adánez J, Abad A, Gayán P. Temperature variations in the oxygen carrier particles during their reduction and oxidation in a chemical-looping combustion system. Chem Eng Sci 2005;60:851–62.

[11] García-Labiano F, Adánez J, de Diego LF, Gayán P, Abad A. Effect of pressure on the behavior of copper-, iron-, and nickel-based oxygen carriers for chemical-looping combustion. Energy Fuels 2006;20:26–33.

[12] Hussain MM, de Lasa HI. Chemical-looping combustion (CLC) for inherent CO2 separations—a review. Chem Eng Sci 2008;63:4433–51.

[13] Mattisson T, Lyngfelt A, Cho P. The use of iron oxide as an oxygen carrier in chemical-looping combustion of methane with inherent separation of CO2. Fuel 2001;80:1953–62.

[14] Ryu H-J, Bae D-H, Han K-H, Lee S-Y, Jin G-T, Choi J-H. Oxidation and reduction characteristics of oxygen carrier particles and reaction kinetics by unreacted core model. Korean J Chem Eng 2001;18:833–7.

[15] Abad A, Adánez J, García-Labiano F, de Diego LF, Gayán P, Celaya J. Mapping the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion. Chem Eng Sci 2007;62:533–49.

[16] Jafari R, Sotudeh-Gharebagh R, Mostoufi N. Modular simulation of fluidized bed reactors. Chem Eng Technol 2004;27:123–9.

[17] Porrazzo R, White G, Ocone R. Aspen Plus simulations of fluidised beds for chemical looping combustion. Fuel 2014;136:46–56.

[18] Sarvar-Ammari A, Sotudeh-Gharebagh R, Bashiri H, Mostoufi N, Hajghatalab A. Sequential simulation of a fluidized bed membrane reactor for the steam methane reforming using ASPE PLUS. Energy Fuels 2007;21:3593–8.

[19] Sotudeh-Gharebagh R,Legros R, Chauki J, Paris J. Simulation of circulating fluidized bed reactors using Aspen Plus. Fuel 1998;77:327–37.
Deng Z, Xiao R, Jin B, Song Q, Huang H. Multiphase CFD modeling for a chemical looping combustion process (fuel reactor). Chem Eng Technol 2008;31:1754–66.

Deng Z, Xiao R, Jin B, Song Q. Numerical simulation of chemical looping combustion process with CaSO4 oxygen carrier. Int J Greenhouse Gas Control 2009;3:368–75.

Jung J, Gamwo IK. Multiphase CFD-based models for chemical looping combustion process: fuel reactor modeling. Powder Technol 2008;183:401–9.

Kruggel-Emden H, Rickelt S, Stepanek F, Munjiza A. Development and testing of an interconnected multiphase CFD-model for chemical looping combustion. Chem Eng Sci 2010;65:4732–45.

Kruggel-Emden H, Stepanek F, Munjiza A. A study on the role of reaction modeling in multi-phase CFD-based simulations of chemical looping combustion. Oil Gas Sci Technol – Rev IFP Energies nouvelles 2011;66:313–31.

Mahalatkar K, Kuhlman J, Huckaby ED, O’Brien T. Computational fluid dynamic simulations of chemical looping fuel reactors utilizing gaseous fuels. Chem Eng Sci 2011;66:469–79.

Wang S, Liu G, Lu H, Chen J, He Y, Wang J. Fluid dynamic simulation in a chemical looping combustion with two interconnected fluidized beds. Fuel Process Technol 2011;92:385–93.

Wang S, Yang Y, Lu H, Wang J, Xu P, Liu G. Hydrodynamic simulation of fuel-reactor in chemical looping combustion process. Chem Eng Res Des 2011;89:1501–10.

Levenspiel O. Chemical reaction engineering. New York: Wiley; 1972.

Syamlal M, Rogers W, O’Brien TJ. MFIX documentation: theory guide. technical note, DOE/METC-94/1004, NTIS/DE94000087. Springfield, VA: National Technical Information Service; 1993.

Patankar S. Numerical heat transfer and fluid flow. CRC Press; 1980.

Kunii D, Levenspiel O. Fluidized reactor models. 1. For bubbling beds of fine, intermediate, and large particles. 2. For the lean phase: freeboard and fast fluidization. AIChE 1970;16:1226–34.

Wang X, Jin B, Zhang Y, Zhong W, Yin S. Multiphase computational fluid dynamics (CFD) modeling of chemical looping combustion using a CuO/Al2O3 oxygen carrier: effect of operating conditions on coal gas combustion. Energy Fuels 2011;25:3815–24.

De Lasa HI, Grace JR. The influence of the freeboard region in a fluidized bed catalytic cracking regenerator. AIChE J 1979;25:984–91.

Furusalo S, Kikuchi T, Miyaschi T. Axial distribution of reactivity inside a fluid-bed reactor. AIChE J 1976;22:354–61.

Davidson J, Harrison D, Jackson R. Fluidized particles. Cambridge University Press; 1983.

Hashemi Sohi A, Eslami A, Shiekhi A, Sotudeh-Gharebagh R. Sequential-based process modeling of natural gas combustion in a fluidized bed reactor. Energy Fuels 2012;26:2058–67.

Johnson F, Andersson S, Leckner B. Expansion of a freely bubbling fluidised bed. Powder Technol 1991;68:117–23.

Adánez J, García-Labiano F, de Diego LF, Plata A, Celaya J, Gayán P, et al. Optimizing the fuel reactor for chemical looping combustion. In: 17th international conference on fluidized bed combustion. American Society of Mechanical Engineers; 2003. p. 173–82.

Darton RC, La Nauze RD, Davidson FF, Harrison D. Bubble growth due to coalescence in fluidised beds. Trans IChemE 1977;55:274.

Geldart D, Bayens J. The design of distributors for gas-fluidized beds. Powder Technol 1985;42:67–78.