Modelling of the Chemical-Looping Combustion of Methane using a Cu-based Oxygen-Carrier

Alberto Abad*, Juan Adánez, Francisco García-Labiano, Luis F. de Diego, Pilar Gayán

Instituto de Carboquímica (CSIC), Department of Energy and Environment

Miguel Luesma Castán 4, 50018 Zaragoza, Spain

Abstract

A mathematical model for a bubbling fluidized bed has been developed to simulate the performance of the fuel-reactor in chemical looping combustion (CLC) systems. This model considers both the fluid dynamic of the fluidized bed and freeboard and the kinetics of reduction of the oxygen-carrier, here CuO impregnated on alumina. The main outputs of the model are the conversion of the carrier and the gas composition at the reactor exit, the axial profiles of gas concentrations and the fluid dynamical structure of the reactor. The model was validated using measurements when burning CH₄ in a 10 kWth prototype using a Cu-based oxygen-carrier. The influence of the circulation rate of solids, the load of fuel gas, the reactor temperature and size of the oxygen-carrier particles were analyzed. Combustion efficiencies predicted by the model showed a good agreement with measurements. Having validated the model, the implications for designing and optimizing a fuel-reactor were as flows. The inventory of solids for a high conversion of the fuel was sensitive to the reactor’s temperature, the solids’ circulation rate and the extent to which the solids entering to the reactor had been regenerated. The optimal ratio of

* Corresponding author. Tel.: +34 976 73 39 77; fax: +34 976 73 33 18.

E-mail address: abad@icb.csic.es.
oxygen-carrier to fuel was found to be 1.7 to 4 for the Cu-based oxygen-carrier used here. In this range, the inventory of solids to obtain a combustion efficiency of 99.9% at 1073 K was less than 130 kg/MWth. In addition, the model’s results were very sensitive to the resistance to gas diffusing between the emulsion and bubble phases in the bed, to the decay of solids’ concentration in the freeboard and to the efficiency contact between gas and solids in the freeboard. Thus, a simplified model, ignoring any restriction to gas and solids contacting each other, will under-predict the inventory of solids by a factor of 2 to 10.

**Keywords:** Chemical-looping combustion; methane; natural gas; copper oxide; fluidization; modelling
Nomenclature

\( a \) decay factor for the solids concentration in the freeboard

\( A_0 \) area of the gas-distributor per nozzle, \( \text{m}^2 \) per nozzle

\( A_r \) cross section area of the reactor, \( \text{m}^2 \)

\( Ar \) Archimedes number

\( b \) stoichiometric factor in the reduction reaction, \( \text{mol of solids reacting (mol of gas)}^{-1} \)

\( c \) stoichiometric factor in the reduction reaction, \( \text{mol of solids reacting (mol of gas)}^{-1} \)

\( C_g \) concentration of gas, \( \text{mol m}^{-3} \)

\( C_s \) concentration of solids, \( \text{kg m}^{-3} \)

\( d \) stoichiometric factor in the combustion of fuel with oxygen, \( \text{molO}_2 \) per mol of fuel

\( d_b \) diameter of bubble, \( \text{m} \)

\( d_p \) diameter of particle, \( \text{m} \)

\( \bar{d}_p \) mean diameter of particle, \( \text{m} \)

\( D_g \) diffusivity of gas, \( \text{m}^2 \text{s}^{-1} \)

\( D_r \) diameter of reactor, \( \text{m} \)

\( E \) activation energy, \( \text{J mol}^{-1} \)

\( E(t) \) function of the distribution of residence time

\( f_b \) empirical function given by Eq. (13)
\( F_i \) \quad \text{molar flow of i compound, mol s}^{-1}

\( F_{in} \) \quad \text{inlet molar flow to the reactor, mol s}^{-1}

\( F_{out} \) \quad \text{outlet molar flow from the reactor, mol s}^{-1}

\( g \) \quad \text{acceleration due to gravity, m}^2 \text{s}^{-1}

\( \Delta H_c^0 \) \quad \text{standard heat of combustion of the gas fuel, kJ mol}^{-1}

\( k \) \quad \text{rate constant of the reaction, mol}^{1-n} \text{ m}^{3n-2} \text{ s}^{-1}

\( k_0 \) \quad \text{preexponential factor of the rate constant, mol}^{1-n} \text{ m}^{3n-2} \text{ s}^{-1}

\( k_{be} \) \quad \text{coefficient for gas exchange between bubble and emulsion, s}^{-1}

\( k_g \) \quad \text{coefficient of mass transfer around the particle, m s}^{-1}

\( m \) \quad \text{instantaneous mass of the oxygen-carrier, kg}

\( m_{ox} \) \quad \text{mass of the oxygen-carrier in the oxidized form of the metal oxide, kg}

\( m_{red} \) \quad \text{mass of the oxygen-carrier in the reduced form of the metal oxide, kg}

\( m_{OC,FR} \) \quad \text{inventory of solids in the fuel-reactor, kg MW}^{-1}

\( \dot{m}_c \) \quad \text{characteristic circulation rate, kg s}^{-1} \text{ MW}^{-1}

\( M_O \) \quad \text{molecular weight of oxygen, 16 g mol}^{-1}

\( n \) \quad \text{order of reaction}

\( r_g \) \quad \text{radius of a grain, m}

\( S_{Cu} \) \quad \text{specific surface area of metallic copper, m}^2 \text{ g}^{-1}
Sc  Schmidt number

Sh  Sherwood number

\(-\overline{r}_g\)  average reaction rate of gas, mol m\(^3\)s\(^{-1}\)

\(-\overline{r}_s\)  average reaction rate of oxygen-carrier, mol m\(^3\)s\(^{-1}\)

\(-\overline{r}_s^{*}\)  average reaction rate of oxygen-carrier following the scheme of reactions 20-22, mol m\(^3\)s\(^{-1}\)

\(-r_s'\)  average reaction rate of the oxygen-carrier for an individual particle, mol s\(^{-1}\)

\(-r_s^{*}\)  average reaction rate of the oxygen-carrier for an individual particle following the scheme of reactions 20-22, mol s\(^{-1}\)

\(-r_g''\)  reaction rate of gas, s\(^{-1}\)

\(-r_s''\)  reaction rate of the oxygen-carrier, s\(^{-1}\)

\(-r_s^{*''}\)  reaction rate of the oxygen-carrier following the scheme of reactions 20-22, s\(^{-1}\)

\(R_g\)  constant for the ideal gases, J mol\(^{-1}\)K\(^{-1}\)

\(R_{OC}\)  oxygen transport capacity, kg of oxygen per kg of oxygen-carrier

\(Re_{p,mf}\)  Reynolds number at minimum fluidization conditions

\(t\)  time, s

\(t_{mr}\)  mean residence time, s
\( t_r \) reaction time from conversion of the carrier \( X_s = 0 \) until the maximum variation in the conversion, s

\( T \) temperature, K

\( u_0 \) velocity of the total gas flow, m s\(^{-1}\)

\( u_{bc} \) velocity of a single bubble, m s\(^{-1}\)

\( u_{gf} \) velocity of the gas throughflow, m s\(^{-1}\)

\( u_{mf} \) velocity of minimum fluidization, m s\(^{-1}\)

\( u_{vis} \) visible velocity of a bubble, m s\(^{-1}\)

\( V \) volume, m\(^3\)

\( V_M \) molar volume, m\(^3\) mol\(^{-1}\)

\( x_i \) mass fraction of the compound i

\( X_g \) conversion of gas

\( X_s \) conversion of the oxygen-carrier for the reduction reaction

\( \bar{X}_{o,AR} \) mean conversion of particles for oxidation reaction reached in the air-reactor

\( \bar{X}_s \) mean conversion of particles for reduction reaction

\( y_i \) mole fraction of gas i

\( z \) height or vertical position in the reactor, m
Greek symbols

$\delta_b$  fraction of bubble in the dense bed

$\varepsilon_b$  porosity at the dense bed

$\varepsilon_g$  coefficient of expansion of the gas mixture

$\varepsilon_z$  porosity at the height $z$ above distributor

$\varepsilon_{mf}$  porosity at minimum fluidization

$\phi$  ratio of oxygen-carrier to fuel

$\Phi_{FR}$  characteristic reactivity defined by Eq. (46)

$\mu_g$  viscosity of fluidizing gas, kg m$^{-1}$ s$^{-1}$

$\eta_c$  efficiency of combustion

$\rho_g$  density of gas, kg m$^{-3}$

$\rho_m$  molar density, mol m$^{-3}$

$\rho_{m,O}$  molar density of oxygen in carrier, at-g oxygen m$^{-3}$ particle

$\rho_s$  density of solid, kg m$^{-3}$

$\tau$  time for complete conversion of the carrier, s

$\tau_m$  mean time for complete reaction of the carrier, s

$\xi_{gs}$  efficiency of contact between gas and solids in the freeboard
Ψ  ratio of the visible bubble flow to the total flow through the bubbles

Subscripts

b  bubble phase

c  combustion

e  emulsion phase

ex  particle’s exterior

exc  excess over the minimum fluidization velocity

f  freeboard region

in  inlet

out  outlet

p  particle

s  solid carrier

WGS  water-gas shift
1. Introduction

Chemical Looping Combustion (CLC) is nowadays an attractive option to decrease the greenhouse gas emissions affecting global warming, because it is a combustion process with inherent separation of CO₂ and, therefore, without energy losses [1]. The CLC concept is based on the transfer of oxygen from the combustion air to fuel by means of an oxygen-carrier in the form of a metal oxide, which takes place in two separate reactors. Solid particles based on Fe, Ni and Cu have been extensively investigated as feasible oxygen-carriers to be used in CLC systems. A review of the oxygen-carriers developed by several researchers can be found elsewhere [2].

In CLC systems, the conventional combustion reaction is replaced by two successive reactions forming a chemical loop. The solids circulate between two interconnected reactors, the fuel-reactor and the air-reactor. In the fuel-reactor, the metal oxide reacts with the gaseous fuel to produce CO₂ and H₂O. Pure CO₂, ready to compression and storage, will be readily recovered by condensing the steam. The oxygen-carrier is regenerated with air in the air-reactor, and it is ready to start a new cycle. The heat involved in the global process is the same as for normal fuel gas combustion.

The most common design of a CLC plant includes a high-velocity riser for the air-reactor and a low-velocity fluidized bed for the fuel-reactor, with the oxygen-carrier in the form of metal oxide particles circulating between them [3]. A fundamental part of the reliability of a CLC system is based on the behaviour of the fuel-reactor. This will determine the gas losses obtained at the exit of the reactor and maybe the necessity to take additional actions, as to recirculate the unburned gases, e.g. CO, H₂ or CH₄, after removing H₂O and CO₂ from the flue gas, or to add a final gas polishing step with pure oxygen. The modelling of the reactor would be helpful for the design, optimization, and scale-up of the process, in order to obtain high combustion efficiencies in a CLC system. Few works have been presented in the literature for the modelling of the reactors involved
in a CLC system. Adánez et al. [4] and García-Labiano et al. [5] modeled the fuel-reactor using empirical correlations for the fluid dynamic of a fluidized bed based on the two-phase theory [6]. Kolbitsch et al. [7] modeled the methane combustion using a Ni-based oxygen-carrier in a 120 kW chemical looping combustor using a simplified fluid dynamics for the air- and fuel-reactors and an efficiency factor to define the gas-solids contact. Jung and Gamwo [8] developed a multiphase CFD-based model to predict the first 10 s of the reduction with methane of a Ni-based oxygen-carrier in a batch fluidized bed reactor. Deng et al. [9] developed also a CFD-based model to predict the first 6 s of H2 conversion using CaSO4 as oxygen-carrier. They concluded that bed temperature was the most important operating parameter affecting the performance of a CLC. However, no models have been validated until now against experimental data.

The objective of this work is to develop and validate a model describing the fuel-reactor in a CLC system, which could be later used to obtain basic design parameters of the fuel-reactor and optimize its operation. The model has been developed considering both the fluid dynamics of a bubbling fluidized bed, composed of a dense bed and freeboard, and the rate of the oxygen-carrier reduction by the gaseous fuel. The fuel-reactor model has been validated against the experimental data obtained during CH4 combustion using a CuO-based oxygen-carrier –here denoted as Cu14Al-I– in the 10 kWth prototype existing at the “Instituto de Carboquímica” (ICB-CSIC, Spain). Although the work has been focused on the combustion of CH4 by means of a CuO-based oxygen-carrier, the model could be easily modified for the use of any other oxygen-carriers (CuO, NiO, Fe2O3, etc.) or fuel gas (natural gas, syngas, etc.). Moreover, the kinetics of reduction of the Cu14Al-I oxygen-carrier with CH4, CO and H2 have been determined for use in the model.

2. Experimental

To validate the fuel-reactor model, experimental data obtained during 200 h of continuous operation in a 10 kW CLC prototype was used. Methane was used as fuel gas and the oxygen-
carrier was a CuO-based material prepared by the incipient wet impregnation method. The more relevant results of this work can be found elsewhere [10,11].

2.1. Oxygen-carrier

The Cu14Al-I oxygen-carrier prepared by impregnation was selected based on results of a previous work [12], where it was identified as a promising oxygen-carrier among different CuO/Al2O3 materials tested. The oxygen-carrier particles were prepared by dry impregnation of copper nitrate solution (5.0 M) on particles of γ-alumina (Puralox NWa-155, Sasol Germany GmbH). Two different particle sizes were used: 0.1-0.3 and 0.2-0.5 mm. A detailed description of the preparation method can be found elsewhere [10]. Table 1 shows the main properties of the fresh oxygen-carrier, as well as the obtained after 100 h of continuous operation in pilot plant tests. The oxygen transport capacity, \( R_{OC} \), was defined as the mass fraction of oxygen that can be used in the oxygen transfer process, and was calculated as \( R_{OC} = (m_{ox} - m_{red})/m_{ox} \), where \( m_{ox} \) and \( m_{red} \) are the masses of the oxidized and reduced form of the metal oxide, respectively. Some loss in the oxygen transport capacity up to 50 h of operation was evidenced because of the decrease on the CuO content of the carrier, as shown in Table 1. After that, the oxygen transport capacity was maintained roughly constant up to 100 h of operation. The actual value for the CuO fraction in each experimental test was used for the model simulations, which ranged from 14% to 9.5%.

2.1.1. Determination of kinetic parameters

A main input to the model is the rate constant for the reaction between the oxygen-carrier and the fuel gas. The kinetic of reaction determines the reaction rate of the particles of oxygen-carrier at the concentration of fuel gas surrounding the particles, which is given by the model. The kinetic of the reduction reactions with CH4, H2 and CO of the CuO-based oxygen-carrier have been carried out in a CI Electronics Ltd. thermogravimetric analyzer (TGA), described previously [13]. The particle size used for the determination of the kinetic parameters was 0.1-0.3 mm. Although CH4
was the fuel gas used in the CLC plant [10], also the kinetics of reduction with CO and H₂ were determined because it is believed that these gases are intermediate products in the CH₄ conversion scheme, as it is discussed below.

Reactivity of fresh and used particles in the 10 kW prototype after 10, 25, 50 and 100 h were determined. The reduction reactivity of the oxygen-carrier particles was not affected by the operation time in the combustor [11], and the conversion vs. time data of unreacted fresh particles were used for the determination of the kinetic parameters. The composition of the gas used to characterise the kinetics of reduction was varied to cover the great majority of the gas concentrations present in the fluidized-bed fuel-reactor of a CLC system (fuel, 5-70 vol %; H₂O, 0-48 vol %; CO₂, 0-40 vol %). The temperature was varied from 873 to 1073 K. In previous tests, it was checked that the H₂O or CO₂ content does not affect to the observed reaction rate.

For the determination of the kinetic parameters, a similar procedure to that showed in reference [13] was used in this work. Initially, to establish whether external film mass transfer and/or interparticle diffusion were affecting the reaction rate, the gas flow rate and the sample weight were varied in the range 6-14 cm³ s⁻¹ STP and from 20 to 80 mg, respectively. It was observed that the reaction rate was not affected by the amount of sample used or the flow rate, indicating that external and interparticle diffusion was not of importance. Moreover, several experiments showed that particle sizes in the range 90-500 μm did not affect the reaction rates, indicating the resistance to gas diffusing inside the particles was not important. The experimental results agreed with previous calculations where we find the low relevance of the mass or heat transfer inside of similar particles [14], and the reaction is likely chemical reaction determining.

Thus, a uniform conversion and temperature inside the particle was assumed [14]. The particle was assumed to be composed by spherical grains of CuO, which reacts following a shrinking core model (SCM) with control by the chemical reaction in the grain surface. As it was showed in a
previous work using a similar CuO-based oxygen carrier [13], it was assumed that the reduction of CuO proceeds towards Cu in one step, i.e., the partial reduction to Cu₂O was not considered.

The conversion used in this work is referred to the reduction reaction, and it is defined as \( X_s = \frac{(m - m_{red})}{(m_{ox} - m_{red})} \), \( m \) being the instantaneous mass of the oxygen-carrier. The equations that describe this model under chemical reaction control in the grain are the following [13]

\[
\frac{t}{\tau_i} = X_s \\
\tau_i = \frac{r_{g,CuO}}{b_1 V_{M,CuO} k_i C_i^n}
\]

where the rate constant follows an Arrhenius type dependence with temperature

\[
k_i = k_{0,i} e^{\frac{E_i}{RT}}
\]

The reaction rate of the oxygen-carrier, defined as \( dX_s/dt \), was obtained by

\[
(-r_{x,i})' = \frac{dX_s}{dt} = \frac{1}{\tau_i}
\]

The mean radius of the grains of metallic copper in the product of reaction, \( r_{g,Cu} \), was 1.2*10⁻⁶ m, calculated from the surface area of Cu obtained by H₂ chemisorption in a Micromeritics AutoChem 2920 apparatus (\( S_{Cu} = 0.034 \) m²/g):

\[
r_{g,Cu} = \frac{3x_{Cu}}{S_{Cu} \rho_{Cu}}
\]

The mean radius of the grains of copper oxide \( r_{g,CuO} \) was 1.4*10⁻⁶ m. This value was obtained considering the ratio of the molar volume of CuO \( (V_{M,CuO} = 12.4 \) cm³/mol) to the molar volume of Cu \( (V_{M,Cu} = 7.1 \) cm³/mol).

As an example of the determination of the kinetic parameters, Fig. 1 shows the conversion vs. time curves for the reduction of the oxygen-carrier with CH₄ at different fuel gas concentrations.
and temperatures. Experimental data are represented by symbols, and model predictions are represented as continuous lines. The conversion of the carrier was complete in all of the cases, and the reaction rate increased with increasing the fuel gas concentration or temperature. The reaction rates for the carrier, \((-r_s)\), followed the order CH$_4$>H$_2$>CO. However, the reaction rate for the gas, \((-r_{g,i})\), calculated as

\[
(-r_{g,i})' = \frac{(-r_{s,i})'}{b_i}
\]

followed the order H$_2$>CO>CH$_4$, because of the specific value of the stoichiometric coefficient $b_i$ for every fuel gas, see Table 2.

Considering the reaction controlled by the chemical reaction, and isothermal conditions in the particles [14], the values of the time for complete conversion, $\tau$, were obtained from the slope of the plot of $X_s$ versus $t$; see Eq. (1). The kinetic parameters for the reduction of the oxygen-carriers with CH$_4$, H$_2$ and CO, shown in Table 2, were obtained from an analysis of $\tau$ values obtained for different gas concentrations and temperatures, similarly to García-Labiano et al. [13]. The activation energies determined for H$_2$ and CO (20 and 11 kJ/mol, respectively) were lower than for CH$_4$ (106 kJ/mol). Also, the reaction order depended on the reacting gas, and values from 0.5 to 0.8 were found. The reaction order obtained for these gases agree to those obtained for a similar CuO-based oxygen carrier [13], but the values for the activation energy are some lower. In other work, Chuang et al. [15] found similar values ($E = 28\pm12$ kJ/mol) for the direct reduction of CuO to Cu using CO as reacting gas. Chuang et al. concluded that, at the interval of temperatures used in this work, the reduction of CuO proceeds via Cu$_2$O as intermediate compound, and the activation energy estimated for this reaction was at least $E = 80$ kJ/mol [15]. However, from the conversion vs time curves showed in Fig. 1 it is observed that the reaction for the oxygen carrier
Cu14Al-I proceeds in one step, and the assumption made that the direct reduction of CuO to Cu seems to be valid, which agrees to the low activation energy obtained.

2.2. 10 kWth CLC prototype

A schematic diagram of the 10 kWth chemical-looping combustor used is shown in Fig. 2. The plant was designed to facilitate the introduction of changes in the circulation rate of solids keeping the ratio of oxygen to fuel constant. In this way, the study of the effect of the circulation rate of solids on the combustion efficiency is straightforward. Both the fuel-reactor (1) and air-reactor (2) consisted in bubbling fluidized-bed reactors. In the fuel-reactor the fuel gas—pure methane—reacts with the oxygen-carrier to give CO₂ and H₂O. The furnace surrounding the fuel-reactor (10) was used for necessary heating during the start-up period and eventual counterbalancing of heat losses allowing accurate control of the operating temperature. The solids previously reduced in the fuel-reactor were then transported to the air-reactor through a loop seal fluidized bed reactor (3a). The regeneration of the oxygen-carrier took place in the air-reactor allowing residence times high enough for achieving the complete oxidation of the reduced carrier. The fully oxidized carrier was taken up by a pneumatic system (4), recovered by a high-efficiency cyclone (5), and sent to a solids reservoir (6) setting the solids ready to start a new cycle. The loop seal (3a) and the solids reservoir (6) prevent the gas mixing between air- and fuel-reactors flows. The solids valve (7) controlled the flow rate of solids entering the fuel-reactor. A diverting solids valve (8) allowed the measurement of the solids flow rates at any time. A detailed description of the prototype can be found elsewhere [10,11]. In this work, the fuel-reactor behavior was modeled using the parameters showed in Table 3.

From an analysis of the results obtained in the 10 kW prototype, it can be extracted some relevant conclusions for the model development [10,11]. During methane combustion using the Cu14Al-I oxygen-carrier, the major unconverted gas was CH₄, indicating that CH₄ reforming by the reaction
products, i.e. H2O and CO2, is not much relevant in the fuel-reactor. However, relatively high amounts of H2 and CO were found when the reactor operated under-stoichiometric conditions. Likely, H2 and CO can appear as intermediate products from the direct reaction of methane with the oxygen-carrier or considering the decomposition of methane to H2 and C, which must reacts quickly to CO because not carbon deposition was found on particles. In both cases, the reaction rate is controlled by the methane conversion, supporting the assumption that H2 and CO act as intermediate products. Moreover, the concentrations of CO, CO2, H2 and H2O at the reactor exit were close to the WGS equilibrium. So, it was assumed that WGS equilibrium is fulfilled in the whole fuel reactor.

The behaviour of the CLC was evaluated calculating the combustion efficiency, $\eta_c$, defined as the ratio of the flow of oxygen taken up by the fuel gas leaving the fuel-reactor to the flow of oxygen needed for the complete conversion of fuel gas to CO2 and H2O

$$\eta_c = \frac{(2y_{CO} + y_{CO} + y_{H2O})_{out} F_{out}}{(4y_{CH4})_{in} F_{in}}$$

where $F_{in}$ and $F_{out}$ are the molar flows at the inlet and outlet of the fuel-reactor, respectively, and $y_i$ is the mole fraction of gas i. The ratio of oxygen-carrier to fuel ($\phi$) was defined by Eq. (7), where $F_{CuO}$ and $F_{CH4}$ are the molar flow rates of the CuO and CH4 in the fuel-reactor, respectively. A value of $\phi = 1$ corresponds to the stoichiometric CuO amount needed for a full conversion of the CH4 to CO2 and H2O.

$$\phi = \frac{F_{CuO}}{4 F_{CH4}}$$
3. Fuel-Reactor Modeling

The fuel-reactor model describes the behavior of a bubbling fluidized bed (BFB) to process a fuel gas with continuous circulation of an oxygen-carrier. The mathematical model has been developed to simulate the performance of the fuel-reactor using any type of oxygen-carrier (CuO, NiO, Fe₂O₃, etc.) or fuel gas (CH₄, syngas, etc.) in chemical looping combustion systems. However, in this work the development of the model has been focused on methane combustion using a CuO-based oxygen-carrier because these were the fuel gas and material used to validate the model.

The fuel-reactor model includes both dense bed and freeboard regions of a typical BFB. The hypotheses considered for the model were: steady state, isothermal bed at macroscopic level, perfect mixing of the solids in the dense bed and freeboard, no existence of particle fragmentation or attrition, and no elutriation. The model is one-dimensional and it considers lateral exchange of gas between bubbles and emulsion in the dense bed. The fuel-reactor model was composed by two modules, corresponding to fluid dynamics and mass balances. Because of the gas expansion produced as methane is converted, the gas velocity in the fuel-reactor varies with the methane conversion. This affects to the fluid dynamics of the fluidized bed and depends on the reaction rate of fuel gas with the oxygen-carrier. Therefore, fluid dynamics and mass balances in the reactor must be solved simultaneously.

3.1. Fluid dynamics of the reactor

The reactor was divided into two regions with respect to solids concentration: 1) a dense bed with a high and roughly constant solids concentration; and 2) a freeboard or dilute region above the dense bed, where there is a pronounced decay in solids concentration with height. Nevertheless, the solids in the entire reactor were considered to be perfectly mixed, i.e., the average conversion of solids was the same anywhere in the fuel-reactor.
3.1.1. Fluid dynamics in the dense bed

The dense bed is defined as the zone located at the bottom of the bed characterized by a roughly constant solids concentration. The gas flow in the dense bed is considered by a modified two phase flow as proposed by Johnsson et al. [16]. The total gas flow is divided in three parts: 1) the flow in the particulate or emulsion phase at the minimum fluidization velocity, $u_{mf}$; 2) the visible bubble flow, $u_{vis}$, related to the gas in the bubbles at the rising velocity of the bubbles; and 3) the gas throughflow, $u_{tf}$, corresponding to an excess of inlet gas over the gas in the emulsion and bubbles, which pass through the bubbles. Thus, the total gas flow, $u_0$, is divided following the equation:

$$u_0 = (1 - \delta_b)u_{mf} + u_{vis} + u_{tf}$$  \hspace{1cm} (8)

At this point, it is worth noting that the mean gas velocity, $u_0$, varies inside the bed with height above the distributor because of the gas expansion during methane conversion. The gas flow was considered as plug flow in all zones of the reactor. A gas exchange between bubbles ($u_{vis}$ and $u_{tf}$) and emulsion ($u_{mf}$) is considered allowing the exchange of products and reactants between these phases. The model assumes that the emulsion phase remains under minimum fluidization conditions. Several equations can be found in the literature to calculate the Reynolds number at minimum fluidization conditions. In this work, a widely used correlation proposed by Wen and Yu was used [17]:

$$Re_{p,mf} = \frac{u_{mf} \rho_g \bar{d}_p}{\mu_g} = \sqrt{C_1^2 + C_2 Ar} - C_i$$  \hspace{1cm} (9)

The values for $C_1 = 27.2$ and $C_2 = 0.0408$ suggested by Grace [18] were used. The visible bubble flow and the throughflow are calculated as

$$u_{vis} = \psi(u_0 - u_{mf} (1 - \delta_b))$$  \hspace{1cm} (10)
\[ u_g = (1 - \psi)(u_0 - u_{mf}(1 - \delta_b)) \] (11)

where \( \psi \) is the ratio of the visible bubble flow, \( u_{vis} \), to the total flow through the bubbles, \( u_{vis} + u_{th} \), and it is calculated as

\[ \psi = f_b \left( h + 4\sqrt{A_0} \right)^{0.4} \] (12)

The parameter \( A_0 \) is the gas-distributor area per nozzle. The function \( f_b \) was calculated from the following equation:

\[ f_b = \frac{0.26 + 0.70e^{-3300d_p}}{0.15 + u_0 - u_{mf}}^{1/3} \] (13)

The bubble fraction in the dense bed is

\[ \delta_b = \frac{u_{vis}}{u_{vis} + u_{bx}} \] (14)

With the assumption of the minimum fluidization porosity in the emulsion phase, the single bubble velocity, \( u_{bx} \), is

\[ u_{bx} = 0.71\sqrt{g d_b} \] (15)

\( d_b \) being the bubble diameter.

Once obtained the fraction of bubbles in the bed, \( \delta_b \), the average bed porosity at a fixed position in the dense bed can be obtained as

\[ \epsilon_b = (1 - \delta_b)\epsilon_{mf} + \delta_b \] (16)
The porosity at the minimum fluidization conditions, \( \varepsilon_{mf} \), was obtained using the equation proposed by Grace [18]

\[
\varepsilon_{mf} = 0.586 \Delta r^{0.029} \left( \frac{\rho_e}{\rho_s} \right)^{0.021}
\]

(17)

3.1.2. Fluid dynamics in the freeboard

The freeboard region starts from the upper limit of the dense bed, and it is characterized by a decrease in the solids concentration with the reactor height. It must be remembered that particles in the freeboard are in perfect mixing with the solids present in the dense bed. In this work, the freeboard model proposed by Kunii and Levenspiel [6] was used. The decay in solids concentration, \( C_s \), is given by the decay factor \( a \):

\[
\frac{dC_s}{dz} = -aC_s
\]

(18)

Finally, the mixing gas behaviour in the freeboard region has been considered. This phenomenon was taken into account by the use of a contact efficiency parameter, \( \xi_{g-s} \), between gas and solids in the freeboard, calculated by the equation proposed by Furusaki [19]

\[
\xi_{g-s} = 1 - 0.75 \left( \frac{C_s}{C_{s,b}} \right)^{0.4}
\]

(19)

\( C_s \) being the solids concentration in the freeboard given by Eq. (18) and \( C_{s,b} \) the solids concentration in the upper limit of the dense bed. The contact efficiency parameter is applied on the reaction rate calculated at each axial position into the freeboard.
3.2. Mass balances into the reactor

Mass balances for the different reacting compounds and products were developed for the two phases considered in the dense bed and for the freeboard region. Plug flow for the gas was considered in all cases. The reactor model was solved from the distributor plate towards the upper part of the reactor, following the differential equations showed below. Because the volume of gases increases as the CH₄ is converted, the change in the gas velocity along the reactor height was also considered.

The pathway for methane reaction with the oxygen-carrier was considered to happen in two steps, first towards CO and H₂ and later these intermediate products react with the oxygen-carrier to give CO₂ and H₂O:

\[
\begin{align*}
\text{CH}_4 + \text{CuO} & \rightarrow \text{CO} + 2 \text{H}_2 + \text{Cu} & (20) \\
\text{CO} + \text{CuO} & \rightarrow \text{CO}_2 + \text{Cu} & (21) \\
2 \text{H}_2 + 2 \text{CuO} & \rightarrow 2 \text{H}_2\text{O} + 2 \text{Cu} & (22)
\end{align*}
\]

Therefore, the kinetic parameters previously determined for each reaction were used in the model. At this point it is necessary to point out that the reaction rate for the solids with CH₄ obtained from TGA can not be directly used into the model. From the mass variation in TGA experiments it was observed the rate of oxygen transference from the solid sample to the reducing gas, i.e. the reaction rate of the oxygen-carrier, \( \left( -r_{\text{c,CH}_4} \right) \). However, the reaction rate for methane depends on the reaction products considered, i.e. either H₂ and CO or H₂O and CO₂. Because of TGA experiments were carried out at differential conditions, the amount of CH₄ reacted with the solid sample is relatively low compared to the contained CH₄ in the gas flow. At these conditions, and considering that the reaction rate of H₂ and CO is faster than the reaction rate of CH₄, we assumed
that the reaction products in the TGA experiments are H₂O and CO₂. Thus, the reaction rate observed in TGA is the sum of the rates of reactions 20, 21 and 22, and it is limited by the rate of methane conversion. But in the fuel-reactor model the reaction pathway considers the conversion of CH₄ towards H₂ and CO. The reaction rate of CH₄ disappearance is that obtained by TGA and calculated by Eq. (5), and the reaction rate of the oxygen-carrier only with CH₄ following the scheme in reactions 20-22 is 

\[ (-r^*_s,CH_4) = c_{CH_4} \left( -r_{g,CH_4} \right) \]

where \( c_{CH_4} \) is the stoichiometric coefficient for CH₄ in reaction 20, i.e. \( c_{CH_4} = 1 \). The effect on the fuel-reactor behaviour of considering either H₂ and CO as intermediate products or the direct CH₄ conversion into CO₂ and H₂O is later discussed.

3.2.1. Mass balances in the dense bed

In the dense bed, a gas exchange between bubbles (\( u_{vis} \) and \( u_g \)) and emulsion (\( u_{mf} \)) is considered allowing the exchange of products and reactants between these phases by diffusive and/or bulk flow mechanism. Indeed, as the gas suffers a volumetric expansion during methane reaction, some of the gas in the emulsion must move to the bubble phase to maintain the minimum fluidization condition in the emulsion phase. Moreover, it was assumed that the reaction products (CO, H₂, CO₂ and H₂O) reach instantaneously the water-gas shift (WGS) equilibrium in all phases of the reactor, as it was previously discussed. Considering all the above assumptions, the mass balances were given by the following differential equations for each gas i (CH₄, CO, H₂, CO₂, and H₂O) in the emulsion and bubble phases, respectively:

\[
\frac{dF_{e,i}}{dV} = \frac{d}{dz} \left[ \left( 1 - \delta_b \right) u_{mf} C_{e,i} \right] = -\left( 1 - \delta_b \right) \sum \left( -r_{g,i} \right)_e - \delta_b k_{be} \left( C_{e,i} - C_{b,i} \right) - y_{e,i} \frac{dF_{exc}}{dV} - \frac{dF_{WGS}}{dV} \tag{23}
\]

\[
\frac{dF_{b,i}}{dV} = \frac{d}{dz} \left[ \left( u_{vis} + u_g \right) C_{b,i} \right] = \delta_b k_{be} \left( C_{e,i} - C_{b,i} \right) + y_{e,i} \frac{dF_{exc}}{dV} - \frac{dF_{WGS}}{dV} \tag{24}
\]
The first term in the right side on Eq. (23) represents the amount of gas $i$ consumed in the differential volume element $dV$, where $(-\bar{r}_{\text{g},e})$ is the average reaction rate of the gas $i$ in the emulsion phase, and $\sum(-\bar{r}_{\text{g},e})$ is the net consumption rate of the gas $i$, following the scheme given in reactions 20-22. The second term is the net gas amount of gas $i$ flowing from the emulsion to the bubble. The third term refers to the excess of gas in the emulsion that moves to the bubbles because of the gas expansion produced in the differential volume. Finally, the fourth term is the amount of gas $i$ reacted to fulfil the WGS equilibrium. Similar descriptions can be done for the mass balance in the bubble phase, see Eq. (24), excepting that in this phase there is not gas-solid reaction, i.e. $\sum(-\bar{r}_{\text{g},b}) = 0$. These equations allow determining the concentration of gas $i$ in both phases: emulsion and bubbles. The gas exchange between bubbles and emulsion was determined by the bubble-emulsion gas exchange coefficient, $k_{be}$.

3.2.2. Mass balances in the freeboard

Above the dense bed starts the freeboard or dilute region, characterized by a strong decay on solids concentration, as it is described in Eq. (18). In the dilute region, the mass balance for each gas in a differential element of bed yields

$$\frac{dF_{\text{c,}e}}{dV} = \frac{d\left[u_{\text{g},e}C_i\right]}{dz} = -\sum \xi_{\text{g,s}} (-\bar{r}_{\text{g},e})_f - \frac{dF_{\text{WGS}}}{dV}$$

(25)

In this case, the first term in the right side on Eq. (25) represents the amount of gas $i$ consumed in the differential volume element $dV$, where $(-\bar{r}_{\text{g},e})_f$ is the average reaction rate of the gas $i$ corresponding to the gas concentration at the location considered, and $\xi_{\text{g,s}}$ is the efficiency contact between gas and solids in the freeboard given by Eq. (19). The second term is the amount of gas $i$ reacted to fulfil the WGS equilibrium.
3.2.3. Oxygen-carrier reactivity

The average reaction rate of the particles at each height in the reactor to be used in eqs 23 and 25, $(-\tau_{g,i})$, was calculated from the average reaction rate of solids following the scheme given by reactions 20-22. Thus, the average reaction rate of every reducing gas is obtained as

$$(-\tau_{g,i}) = \frac{(-\tau_{s,i})}{c_i} = \frac{(-\tau_{s,i})}{b_i}$$  \hspace{1cm} (26)

c_i being the stoichiometric coefficient for the reacting gas $i$ (CH₄, CO or H₂) showed in reactions 20-22, i.e. $c_i = 1$.

To obtain the average reaction rate of the particles, $(-\tau_{s,i})$, it was assumed a perfect mixing of the solids in the dense bed and the freeboard regions. Thus, the residence time distribution curve of the solids, $E(t)$, is given by the following equation:

$$E(t) = \frac{1}{t_{mr}} e^{-t/t_{mr}}$$  \hspace{1cm} (27)

where $t_{mr}$ is the mean residence time of particles in the whole reacting zone of the fluidized-bed reactor. The conversion as a function of the residence time is obtained taking into account for the mean conversion of the carrier at the reactor inlet and the kinetics of reaction

$$X_{s}(t) = \bar{X}_{s,in} + \frac{t}{\tau_m}$$  \hspace{1cm} (28)

and the mean conversion of the particles, $\bar{X}_{s,out}$, can be obtained as

$$\left(1 - \bar{X}_{s,out}\right) = \int_{0}^{t_{in}} (1 - X_{s}(t)) E(t)dt$$  \hspace{1cm} (29)
The mean reacting time, \( \tau_{m} \), is determined by an iterative process to obtain from eqs 28-29 the corresponding mean conversion at the reactor outlet, \( \overline{X}_{s,out} \), that fit the mean conversion obtained from a mass balance to the whole reactor

\[
F_{\text{CuO}} \Delta X_s = F_{\text{CuO}} \left( \overline{X}_{s,out} - \overline{X}_{s,in} \right) = b_g \eta_c F_{CH_4}
\]  

(30)

\( b_g \) being the stoichiometric coefficient to fully convert CH4 into CO2 and H2O (\( b_g = 4 \)). Once the distribution of the conversions was obtained, the average reaction rates of the oxygen-carrier in the reactor can be obtained as

\[
\left( -r^*_{s,i} \right) = \frac{c_i}{b_i} \rho_{m,p} \left( 1 - \epsilon_s \right) \int_0^{r_i} \frac{d \left( X_s(t) - \overline{X}_{s,in} \right)}{dt} E(t) dt
\]

(31)

where \( \rho_{m,p} \) is the molar density of the active phase (CuO) in the particle (\( \rho_{m,p} = \rho_{CuO} X_{CuO} \)).

The external diffusion through the gas film around the particle was considered to obtain the gas concentration at the particle’s exterior, \( C_{ex} \). Thus, the reaction rate is should be different than the bulk gas concentration at a height \( z \) in the reactor, \( C_z \). It is worth noting that the concentration was assumed to be constant over the entire particle, as it is above discussed (Section 2.1.1.), being \( C_{ex} = C_p \). The reaction rate of the particles, \( dX_s/dt \), was calculated from Eq. (3) at the concentration in the particle, \( C_p \). The gas concentration in the particle’s exterior, \( C_{ex} \), can be obtained by a mass balance to the whole particle at each height in the bed and particle conversion

\[
\left( -r^*_{s,i} \right) = \frac{c_i}{b_i} \rho_{m,p} \left( \frac{4}{3} \pi r_p^3 \right) \frac{d \left( X_s(t) - \overline{X}_{s,in} \right)}{dt} = c_i \ k_{g,i} \left( 4 \pi r_p^2 \right) \left( C_z - C_{ex} \right)
\]

(32)

where the second term in Eq. (31) is the fuel gas reacted in the whole particle and the third term is the gas flow from the bulk gas to the particle. The mass transfer coefficient for each gas, \( k_{g,i} \), was
obtained with equations proposed by Palchonok [20] and Chakraborty and Howard [21] for the dense bed and the freeboard, respectively.

Dense bed: 
\[
\text{Sh} = \frac{k_{g,i} d_p}{D_{g,i}} = 2\bar{e}_{mf} + 0.117 \text{Ar}^{0.39} \text{Sc}^{1/3}
\]

Freeboard: 
\[
\text{Sh} = \frac{k_{g,i} d_p}{D_{g,i}} = 2\bar{e}_{h} + 0.69 \text{Re}^{1/2} \text{Sc}^{1/3}
\]

Moreover, Eq. (30) has been expressed to consider that the oxygen-carrier is introduced into the reactor with a mean conversion of the carrier for the reduction reaction, \( \bar{X}_{s,in} \), higher than 0, i.e. the oxygen-carrier could be not fully oxidized in the air-reactor. The values of \( t_r \) were defined as the reacting time of an oxygen-carrier particle from zero conversion until the maximum variation possible in conversion of the carrier, i.e. \( 1 - \bar{X}_{s,in} \). This fact assumes that the reaction rate of a particle entering to the fuel-reactor goes from the reaction rate at conversion 0 to the reaction rate at the maximum conversion that can be reached, i.e. \( 1 - \bar{X}_{s,in} \). This assumption considers that the oxidation in the air-reactor of the Cu grains inside the oxygen-carrier particles starts from its outlet part, and progress towards the interior of the grain following the SCM. On the contrary, the reaction rate should be considered from that corresponding to \( \bar{X}_{s,in} \) to \( X_s = 1 \). Thus, the \( t_r \) value can be obtained as

\[
t_r = \tau (1 - \bar{X}_{s,in})
\]

Nevertheless, it was found that samples of particles taken from the outlet of the riser at the 10 kW CLC plant at different operation times were fully oxidized [10,11]. Thereby, \( \bar{X}_{s,in} \) was zero in this work.
3.2.4. Calculation procedure

To solve the mathematical model developed with the above equations, convergence of the mass balance for solids and gases must occur simultaneously. For its solution, the model was solved using a Visual Fortran © code. The flow diagram for the overall solution of the model is shown in Fig. 3. To obtain the variation of the gases concentration with the height, the entire reactor was divided into compartments with a height of $\Delta z$. The reactor model has the following calculation flow structure:

- **Input data:** The input data are the reactor characteristics and the operating conditions, as it is shown in Table 3.

- **Firstly,** it is necessary to make an assumption of the average variation of the solids conversion in the reactor, $\Delta X_s$. For this purpose, it was assumed that the fuel gas is fully converted into CO$_2$ and H$_2$O, i.e. $\eta_c = 1$ in Eq. (30).

- **The solids conversion distribution in the reactor** is calculated to obtain the average variation of the solids conversion in the reactor, $\Delta X_s = \bar{X}_{s,\text{out}} - \bar{X}_{s,\text{in}}$, as it is obtained from Eq. (28) and (29). For this purpose, the residence time distribution (RTD) of oxygen-carrier particles in the fuel-reactor is considered taking into account for the amount of solids in the reactor and the recirculation rate of solids.

- **Methane conversion:** The system of differential equations for the mass balance in every compartment was solved using a Runge-Kutta method over the entire reactor and starting from the distributor plate. In the dense bed, at each height there is a compartment for the emulsion phase and other compartment for the bubble phase. The gas in each type of compartment is considered as plug flow and there is a gas exchange between the bubble and the emulsion phases, calculated using the $k_{be}$ obtained with the Eq. (40) or (41).
fluid dynamical characteristics of the reactor (solids concentration and gas flow) are calculated simultaneously with the mass balance. Methane reacts with the oxygen-carrier particles, given as products CO, H₂. CO and H₂ generated also react with the oxygen-carrier given CO₂ and H₂O. The gas mixture is considered to be at equilibrium conditions for the WGS reaction. The mass balance for each gas (CH₄, CO, H₂, CO₂ and H₂O) was calculated in every segment for the emulsion and bubble phases in the dense bed and the freeboard.

- Output data: when the mass balance for all the species is solved, the concentration profiles of the gas species were obtained along the entire reactor, as well as the variation with the height of fluid dynamical properties, e.g. gas flow distribution, solids concentration and dense bed properties. Eventually, the amount of solids in the reactor, and the gas concentration of gases and solids conversion at the reactor exit are determined.

- The variation of the solids conversion, ΔXₛ, obtained with the model is compared to the assumed value. If the calculated ΔXₛ is not the same as the input value, the mass balance is repeated until the two values agree.

4. Results

The developed model has been used to simulate the behaviour of the fuel-reactor in the 10 kWₑ CLC plant located at ICB-CSIC using a Cu-based oxygen-carrier. The main design parameters are shown in Table 3, and the operating conditions and experimental results have been described in previous works [10,11]. Predictions from the model were obtained at different operating conditions. The main outputs of the model consist of the fluid dynamical structure of the reactor – solids concentration profiles and gas flow distribution between bubbles and emulsion phases–, axial profiles of flow and gas composition (CH₄, CO, H₂, CO₂ and H₂O), gas composition at the
reactor exit, and conversion of the carrier in the reactor. As an example, Fig. 4 shows the axial profiles of gas and solids concentration in the fuel-reactor for a reference case. As it can be seen there is an important change in the profiles between the dense bed and the freeboard regions. This fact is mainly due to the differences in the fluid dynamics of these two regions. The dense bed is characterized by a roughly constant porosity, which in the 10 kW<sub>th</sub> CLC plant have a fixed height \( H_b = 0.5 \) m. The combustion efficiency reached at this height was \( \eta_c = 0.72 \). The conversion rate of methane was particularly reduced in the two-third upper part of the dense bed. In this zone, most of unconverted gas is going through the bubble phase, and the gas conversion was mainly limited by the gas transfer between bubble and emulsion. Thus, the contact efficiency between gas and solids become poor in this zone. In the freeboard, the solids concentration decreases with the reactor height. However, the combustion efficiency increases faster in this zone because the gas-solids contact is better in this zone than in the dense bed. It can be seen that full conversion of gas was reached in the first 0.15 m of the freeboard. Moreover, H<sub>2</sub> and CO concentrations are maintained at low values because they disappear faster by reactions 20 and 21 than they are generated by reaction 19.

Prior to use the model to predict the experimental data obtained in the 10 kW<sub>th</sub> CLC prototype a sensitivity analysis was done regarding to some model parameters: the bubble diameter in the dense bed, \( d_b \), the bubble-emulsion gas exchange coefficient, \( k_{be} \), the decay factor for solids concentration in the freeboard, \( a \), and the contact efficiency between gas and solid particles in the freeboard, \( \xi \), which depends on the value of \( a \). It was found that the combustion efficiency predicted by the model was very sensitive to the values of \( k_{be} \) and \( a \), and at lower extension to the value of \( \xi \). An increase in the \( k_{be} \) value or a decrease in the \( a \) value produced an increase in the combustion efficiency. However, the value of \( d_b \) had no significant effect on the efficiency predictions.
Table 4 shows different equations found in the literature for each parameter. Similar values were found for the bubble diameter in the dense bed, $d_b$, and the bubble-emulsion gas exchange coefficient, $k_{be}$, and small differences were found in the model predictions. However, the value for the decay factor for solids concentration in the freeboard, $a$, was very different depending on the correlation used. The value for $a$ using the Eq. (42) was $a \approx 6.5$, whereas using the Eq. (43) was $a \approx 25$. In Fig. 5, predictions of the model are compared to experimental results obtained during methane combustion using Cu14Al-I oxygen-carrier in the 10 kW prototype [10] as a function of the ratio of oxygen-carrier to fuel, $\phi$. It can be observed that the values from experimental tests are found between those predicted by the model using equations (42) and (43), being an intermediate value of $a$ necessary to predict the experimental results. To fit the experimental results, a value for $a \approx 12$ was needed. Therefore, this value will be used from now on the model predictions.

4.1. Model validation

Model validation was carried out using the experimental data obtained in the 10 kW th CLC plant located at ICB-CSIC [10,11]. Fig. 6 shows the comparison between the combustion efficiencies experimentally obtained and predicted by the model for different operating conditions such as fuel flow, temperature, ratio of oxygen-carrier to fuel and particle size. As it can be seen, in all cases the model predicts adequately the experimental results obtained in the 10 kW prototype. The use of the sub-stoichiometric ratio of oxygen-carrier to fuel, $\phi < 1$, produced low combustion efficiencies. Even for $\phi = 1$ the combustion efficiency ranged from 75 to 90%, although the oxygen available in the fuel-reactor was exactly the oxygen needed to fully convert CH$_4$ into CO$_2$ and H$_2$O. This was because the fuel-reactor was considered to be in a perfect mixing for the solids, where there are a fraction of particles with low residence time in the reactor and high reactivity. This behaviour was predicted in a previous work about the CLC design [27], where it was showed that when the ratio of oxygen-carrier to fuel goes-down towards 1, the inventory of solids to fully
convert the fuel gas noticeably increased. Although the inventory of solids would be increased, not all particles could have the chance to transfer the required oxygen to the fuel. As consequence, the $\phi$ value should be always higher to 1 to fully convert the fuel gas. The combustion efficiency increases as the ratio of oxygen-carrier to fuel increases because the availability of oxygen in the fuel-reactor increases and the average reactivity of the oxygen-carrier in the fuel-reactor also increases. In general, a $\phi$ value of $\approx 1.4$ was needed to fully convert the methane at 1073 K with the Cu14Al-I oxygen-carrier used in this work.

The effect of the fuel-reactor temperature also is noticeable. An increase in the fuel-reactor temperature produced an increase in the combustion efficiency. This effect is related to the increase of the reaction rate due to the higher rate constant value of the reduction rate. The fluidized-bed model used in this work predicts that the decrease in the combustion efficiency is more important in the freeboard than in the dense bed. The reason for this is that the reaction in the dense bed is mainly controlled by the mass transfer between the bubble and the emulsion, which has a low dependency on the temperature, whereas there is a major effect of the chemical reaction in the freeboard, which has a higher dependency on the temperature.

The fuel flow and the particle size have lower relevance on the combustion efficiency than temperature. A slightly increase in the combustion efficiency is obtained when the fuel flow decreases. This effect is of common understanding because there is the same amount of oxygen-carrier to convert lower amount of methane. Moreover, the model predicts that the gas-solids contact in the dense bed improves as the gas velocity decreases, because at lower velocities there is a lower amount of gas in the bubble phase or the throughflow, which are not in direct contact with the solids. Thus the fuel conversion in the dense bed is increased. Regarding the effect of the particle size, some increase in the combustion efficiency can be observed for higher particle size of the carrier. This difference can be attributed to the different contact efficiency between gas and
solids in the dense bed. An increase in the particle size produces an increase in the minimum fluidization velocity and, thus, a decrease of gas flow in the bubble phase. This effect is more noticeable at lower temperatures because the relevance of the dense bed on the fuel conversion is higher at lower temperatures, as it was above stated.

4.2. Fuel-Reactor design

Once the model has been validated, it can be used to design a new fuel-reactor and to optimize the operation of an existing CLC plant. A basic design parameter is the inventory of solids needed to obtain high combustion efficiency depending on the operating conditions. In this work the inventory of solids as a function of the ratio of oxygen-carrier to fuel and the conversion of the oxygen-carrier at the fuel-reactor inlet have been analyzed using CH₄ as fuel gas and the Cu14Al-I oxygen-carrier. Fig. 7 shows the minimum inventory of solids per MWth of fuel to fully convert the CH₄ as a function of the ratio of oxygen-carrier to fuel and temperature (solid lines). It can be seen that the inventory of solids is lower than 80 kg per MWth when the \( \phi \) value was > 2 at 1073 K. However, the inventory of solids increases rapidly when the temperature decreases or the \( \phi \) value approach the unity, as previously Abad et al. reported [27]. fuel-reactor temperature has an important effect on inventory of solids because the oxygen-carrier reactivity decreases with decreasing temperature. Indeed, the reactivity of the Cu14Al-I particles with methane at 1073 K is 1.75 times higher than the reactivity at 1023 K and 3.2 times higher than that at 973 K. Thus, for \( \phi = 3 \) the inventory of solids should be increased up to 280 kg/MWth at 1023 K and 1200 kg/MWth at 973 K to reach a combustion efficiency of 99.9%.

The secondary abscise axis in Fig. 7 shows the circulation rate of solids necessary to fulfil the oxygen mass balance in the CLC system for each value of the ratio of oxygen-carrier to fuel, ranging from 4 kg/s per MWth at \( \phi = 1 \) to 12 kg/s per MWth at \( \phi = 3 \). To know if these values are realistic in a CLC system it is also necessary to consider other aspects related with the fluid
dynamical behaviour and with the energy balance in the system. The energy balance can limit the minimum circulation rate needed in a CLC system, mainly if the reaction of the fuel gas with the oxygen-carrier is endothermic, as it is the case for Ni-based oxygen-carriers. In this case, the energy needed in the fuel-reactor is supplied by the circulating solids coming from the air-reactor at higher temperature. However, for Cu-based oxygen-carriers the reduction reactions of CuO with CH₄, CO or H₂ are exothermic ($\Delta H^{0}_{c,CH_4} = -178$ kJ/mol; $\Delta H^{0}_{c,H_2} = -86$ kJ/mol; $\Delta H^{0}_{c,CO} = -127$ kJ/mol), and the circulation rate of solids is not limited by the heat balance.

Regarding to the fluid dynamical behaviour, the CLC design concept is similar to that of a circulating fluidized bed reactor (CFB), being the riser the air-reactor and placing the fuel-reactor in the return loop of solids. The circulation rate depends on the operating conditions and configuration of the riser. From results showed in a previous work [27], the maximum circulation rate feasible in a CLC plant could be around 80 kg m⁻² s⁻¹ and the average value of the cross section area of the riser was determined to be about 0.2 m²/MWth. Thus, the circulation rate of solids would be about 16 kg s⁻¹ per MWth in a CLC system. Therefore, for the Cu14Al-I oxygen-carrier the maximum ratio of oxygen-carrier to fuel could be $\phi \approx 4$. From the results showed in this work, it can be concluded that a inventory of solids lower than 100 kg/MW was enough to obtain high combustion efficiency at 1073 K for the ratio of oxygen-carrier to fuel $\phi > 1.75$. As the ratio of oxygen-carrier to fuel must be lower than 4 because of fluid dynamical limitations, optimal operation conditions could be reached operating in the range of $\phi = 1.75$-4 in a CLC system using the Cu14Al-I oxygen-carrier.

Another operating condition to be considered is the oxygen-carrier conversion at the fuel-reactor inlet, $\bar{X}_{s,in}$, which is determined by the oxidation conversion in the air-reactor, defined as $\bar{X}_{o,AR} = 1 - \bar{X}_{s,in}$. Fig. 8 shows the inventory of solids needed in the fuel-reactor to obtain a combustion
efficiency $\eta_c = 99.9\%$ as a function of the oxidation degree reached in the air-reactor, $\chi_{o,AR}$, and temperature (solid lines). The ratio of oxygen-carrier to fuel was fixed at $\phi = 2$. At this condition, the oxygen-carrier should be oxidized at least a 50% in the air-reactor, i.e. $\chi_{o,AR} > 0.5$, in order to transport enough oxygen from the air-reactor to the fuel-reactor to get full conversion of fuel gas.

It can be seen that the inventory of solids increases as the oxidation degree in the air-reactor decreases, because of the lower oxygen availability in the fuel-reactor. It is remarkable the strong increase in the inventory of solids for values of $\chi_{o,AR} < 0.7$. From Fig. 8 it seems that the optimum oxidation degree in the air-reactor to minimize the inventory of solids would be $\chi_{o,AR} > 0.75-0.8$. However, at this point it is necessary to consider that an increase in the conversion of the carrier in the air-reactor must be related to an increase in the inventory of solids in the air-reactor. Thus, as $\chi_{o,AR}$ increases the inventory of solids needed in the air-reactor increases, but decreases in the fuel-reactor, and vice versa, as it was shown in previous works [13,27,28,29]. As a result, the total inventory of solids in the system (air- and fuel-reactors) has a minimum value for a determined value of the oxidation degree reached in the air-reactor, $\chi_{o,AR}$. The optimum operating conditions to minimize the inventory of solids in the system should be a configuration where the oxygen-carrier was not fully oxidized in the air-reactor, and it must be determined by a coupled analysis of both fuel-reactor and air-reactor.

5. Discussion

5.1. Relevance of the reaction pathway

From an analysis of the experimental results obtained during the methane combustion with Cu14Al-I oxygen-carrier in the 10 kWth prototype, it was concluded that the methane conversion likely goes through of H$_2$ and CO as intermediate products. To estimate the relevance of the reaction rate of these intermediate products, an evaluation of the combustion efficiency predicted
by the fuel-reactor model was done assuming different reaction rates for CO and H2, i.e. \((-r_{g,CO})\) and \((-r_{g,H2})\), but maintaining constant the reaction rate for CH4, \((-r_{g,CH4})\). Fig. 9 shows the combustion efficiency obtained by the model for different reactivity ratios between CO or H2 and CH4, i.e. \((-r_{g,CO}) / (-r_{g,CH4})\) or \((-r_{g,H2}) / (-r_{g,CH4})\) and oxygen-carrier to fuel ratios. At previously have been shown, the combustion efficiency increases as the ratio of oxygen-carrier to fuel increases. Moreover, for \((-r_{g,i}) / (-r_{g,CH4}) > 3\) the combustion efficiency is roughly affected by the CO and H2 reactivity for all oxygen-carrier to fuel ratios, but when the ratio \((-r_{g,i}) / (-r_{g,CH4})\) decreases below values of 3, the predicted combustion efficiency decreases noticeably. Fig. 10 shows the unburnt gases, i.e. CH4, H2 and CO, as a function of the ratio \((-r_{g,i}) / (-r_{g,CH4})\) for two different values of the ratio of oxygen-carrier to fuel. These values have been chosen to have one case (\(\phi = 1.5\)) that permits to fully convert the fuel gas at high \((-r_{g,i}) / (-r_{g,CH4})\) values and another case (\(\phi = 1.2\)) which is not possible to reach full fuel conversion even at high \((-r_{g,i}) / (-r_{g,CH4})\) values. In both cases, the concentration of CO and H2 increases as the reaction rates for CO and H2 are decreased. Regarding to the methane, for \(\phi = 1.5\) it is always fully converted. On the contrary, for \(\phi = 1.2\) the CH4 concentration increases as the ratio \((-r_{g,i}) / (-r_{g,CH4})\) increases. At this condition, the most unburnt compound is CH4 for \((-r_{g,i}) / (-r_{g,CH4}) > 3\), obtaining smaller amounts of CO and H2 as unconverted products.

Although the methane reactivity was maintained constant, for \((-r_{g,i}) / (-r_{g,CH4}) < 3\) methane concentration decreases because of the combustion efficiency decreases and then the average reactivity of the solids in the fuel-reactor increases.
Thus, for ratios \( \frac{-r_{g,\text{CH}_4}}{-r_{g,i}} > 3 \) the gas conversion is limited by the conversion rate of CH\(_4\), and the reactivity of the oxygen-carrier with CO and H\(_2\) has only a residual effect on the fuel conversion. In these cases, the CH\(_4\) conversion can be considered directly towards CO\(_2\) and H\(_2\)O, and it would be not necessary to obtain the kinetic parameters for these intermediate products. On the contrary, for \( \frac{-r_{g,\text{CH}_4}}{-r_{g,i}} < 3 \) a relevant concentration of CO and H\(_2\) is obtained, and the reactivity of the oxygen-carrier with these gases has an important effect on the combustion efficiency. At these conditions, it is important to know the kinetic of reaction for CO and H\(_2\) and it is necessary to include them into the reactor model. For the CuAl14-I oxygen-carrier, the reactivity ratio \( \frac{-r_{g,\text{CH}_4}}{-r_{g,i}} \) was \( \approx 2 \) at 1073 K, being necessary to consider H\(_2\) and CO as intermediate compounds in the fuel-reactor model.

5.2. Relevance of the gas-solids contact

The developed model is relatively complex because considers all the processes affecting to the reaction of fuel gas with the oxygen-carrier, such as reactor fluid dynamics, reactivity of the oxygen-carrier and the reaction pathway. For the same purposes of this work, a simplified model can be built without consider any restriction for the gas-solids contact, i.e., the resistance to gas diffusing between bubble and emulsion phases in the dense bed, the efficiency of contact between gas and solid particles in the freeboard and the gas diffusion throughout the gas film around the particle. In this case, the differential mass balance on the oxygen atoms between the height \( z \) and \( z + dz \) yields [30]

\[
\frac{1}{\Delta H^0_{c,\text{CH}_4}} \frac{\partial y_{\text{CH}_4}}{\partial m_{\text{OC}}} + \frac{R_{\text{OC}}}{2dM_o} \left[ \frac{\Phi_{FB}}{3} \frac{\partial X_i}{\partial t} \bigg|_{X_i=0} \right] = 0 \quad (44)
\]

and the bed mass in the fuel-reactor reactor per MW of fuel can be calculated as
The parameter \( \Phi_{FR} \) is the characteristic reactivity in the fuel-reactor. With the assumption of perfect mixing of solid particles in the air- and fuel-reactors, the parameter \( \Phi_{FR} \) can be expressed as a function of conversion of the carrier at the inlet of fuel-reactor, \( \bar{X}_{s,in} \), and the conversion variation in the reactor, \( \Delta X_i \) [27]

\[
\Phi_{FR} = 1 - \exp \left( - \frac{(1 - \bar{X}_{s,in}) \Phi_{FR}}{\Delta X_i} \right)
\]

For the reaction model in the particle proposed in this work, the value of characteristic reactivity, \( \Phi_{FR} \), is limited between 1 and 0. The value \( \Phi_{FR} = 1 \) is obtained when \( \Delta X_i \approx 0 \) and \( \bar{X}_{s,in} = 0 \), i.e. \( \bar{X}_{n,AR} = 1 \), which is the case for the minimum inventory of solids, and \( \Phi_{FR} \) decreases as \( \bar{X}_{n,AR} \) decreases and/or \( \Delta X_i \) increases.

The parameter \( \tau_m \) is the time needed for the complete conversion of particles in the fuel-reactor obtained at an average gas concentration. Assuming gas plug flow in the reactors and no resistance to the gas exchange between the bubble and emulsion phases in the fluidized bed, the average reacting gas concentration in the air and fuel-reactors can be obtained by the equation,

\[
\overline{C^g} = \frac{\Delta X_g C_0^n}{\int_{X_{g,in}}^{X_{g,eq}} \left[ \frac{1+\varepsilon_g X_g}{I-X_g} \right]^n dX_g}
\]

Considering 100% CH₄ and a final gas conversion of 0.999, the value of \( \varepsilon_g \) is 2 and the average CH₄ concentration is 11.7%.
Abad et al. [27] introduced this simplified method to calculate the inventory of solids in a CLC system for comparison purposes between different oxygen-carriers. Thus, the inventory of solids can be obtained as a function of the conversion of the carrier at the inlet of fuel-reactor, $\bar{X}_{x,\text{in}}$, and the conversion variation in the reactor, $\Delta X_s$. It is necessary to point out that the simplified method only use the kinetic of reduction with CH$_4$, and it does not consider CO and H$_2$ as intermediate products. However, when the reactivity for H$_2$ and CO are higher than reactivity for CH$_4$, the estimated error should be of lower relevance, as it has been previously discussed.

Together with the solids inventories predicted by the model, Fig. 7 and 8 also show the solids inventories obtained from Eq. (45), i.e. the simplified model (dashed lines). The solids inventories obtained in this way underpredict the solids inventories showed by the model because the resistance to the exchange of gas between the bubble and emulsion phases is not considered by the simplified method. These results reveal the importance of considering the mechanisms limiting the gas-solids contact in the fluidized bed fuel-reactor. The solids inventories given by the model are between 2 and 10 times higher than those given by the simplified method, depending on the operational conditions. For example, the solids inventories given by the simplified method should be multiplied by a factor of 2 to obtain the solids inventories predicted by the model when the temperature is 1073 K, the ratio of oxygen-carrier to fuel $\phi > 1.75$ and $\bar{X}_{x,\text{AR}} > 0.8$. In this way, the simplified method only allows us to know the order of magnitude for the inventory of solids, applying the correction that the value predicted from Eq. (45) should be multiplied by a factor of 2-10.

Although important errors can be made in the inventory of solids calculated by the simplified method, this method can be used to give an easy and fast evaluation of the solids inventories in a CLC system. Moreover, the inventory of solids calculated by this simple method is an interesting value to be used for comparison purposes between different oxygen-carrier particles [27-29].
Nevertheless, the fluidized-bed model developed in this work must be used to give a more accurate evaluation of the inventory of solids needed in the fuel-reactor.

6. Conclusions

A model to describe the behaviour of the fuel-reactor of a CLC process has been developed. The model can be used to simulate the behaviour of the fuel-reactor bubbling fluidized bed type, for the combustion of different fuel gases (CH$_4$, syngas, etc.) using any oxygen-carrier (CuO, NiO, Fe$_2$O$_3$, etc.). The model considers all the processes affecting to the reaction of fuel gas with the oxygen-carrier, such as reactor fluid dynamics, reactivity of the oxygen-carrier and the reaction pathway. The main outputs of the model consist of the fluid dynamical structure of the reactor, e.g. solids concentration profiles and gas flow distribution between bubbles and emulsion phases, axial profiles of flow gases and composition (CH$_4$, CO, H$_2$, CO$_2$ and H$_2$O), gas composition at the reactor exit, and solids conversion in the reactor. The pathway of the CH$_4$ reaction was considered to be through CO and H$_2$ as intermediate products. Only for reactivity ratios between CO or H$_2$ and CH$_4$ higher than 3 could be assumed the direct reaction of CH$_4$ to give CO$_2$ and H$_2$O.

For the validation of the model, model predictions were compared to experimental results of CH$_4$ combustion obtained in a 10 kW$_{th}$ CLC prototype. The oxygen-carrier was a highly reactive CuO-based material containing 14%wt CuO. Good agreement was found between model predictions and experimental data. It was determined that the reaction of fuel gas with the oxygen-carrier in the freeboard had decisive importance to obtain high combustion efficiency. CH$_4$ conversion was highly dependent on the ratio of oxygen-carrier to fuel, $\phi$, the oxidation conversion of the oxygen-carrier in the air-reactor, $\overline{X}_{v, AR}$, and reactor temperature, being of low significance the effect of fuel load and particle size. Considering the inventory of solids and the mass and energy balances in the CLC system, the optimal ratio of oxygen-carrier to fuel was found to be 1.7 to 4 for the
Cu14Al-I oxygen-carrier. To reach a combustion efficiency of 99.9%, the inventory of solids was lower than 130 kg per MWth when the $\phi$ value was $> 1.75$ and $\bar{X}_{o,AR} > 0.8$ at 1073 K.

The bubble-emulsion gas exchange coefficient, $k_{be}$, the decay factor for solids concentration in the freeboard, $a$, and the contact efficiency between gas and solids in the freeboard, $\xi$, were the parameters more affecting to the combustion efficiency predicted by the model. These results reveal the importance of considering the mechanisms limiting the contact between gas and solids in the fuel-reactor model. When these restrictions to the gas-solids contact were neglected in a simplified method, the solids inventories were 2-10 times less than considering them. Simplified methods can be interesting only to compare among different oxygen-carrier particles although a fluidized-bed model, as the developed in this work, must be used to give a more accurate evaluation of the inventory of solids needed in the fuel-reactor.
References


25. F. Johnsson F and B. Leckner, Proceedings of the 13th International Conference on Fluidized
Table 1. Properties of the Cu14Al-I oxygen-carrier.

<table>
<thead>
<tr>
<th></th>
<th>$d_p = 100$-$300 , \mu m$</th>
<th>$d_p = 200$-$500 , \mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>After 100 h</td>
</tr>
<tr>
<td>Active material, $x_{CuO}$ (%)</td>
<td>14</td>
<td>9.5</td>
</tr>
<tr>
<td>$R_{OC}$ (%)</td>
<td>2.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>54.8</td>
<td>52.1</td>
</tr>
<tr>
<td>Apparent density (kg/m$^3$)</td>
<td>1500</td>
<td>1620</td>
</tr>
<tr>
<td>BET specific surface area (m$^2$/g)</td>
<td>80.5</td>
<td>34.9</td>
</tr>
</tbody>
</table>

Table 2. Kinetic parameters for reduction of Cu14Al-I with CH$_4$, CO and H$_2$.

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$</th>
<th>CO</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b$</td>
<td>Stoichiometric coefficient mol CuO/mol gas</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>$n$</td>
<td>Order of the reaction -</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Pre-exponential factor mol$^{1-n}$ m$^{3n-2}$ s$^{-1}$</td>
<td>480</td>
<td>2.21*10$^{-4}$</td>
</tr>
<tr>
<td>$E$</td>
<td>Activation energy kJ/mol</td>
<td>106</td>
<td>11</td>
</tr>
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Table 3. Main operating and modeling parameters of the fuel-reactor.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reactor geometry</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Height</td>
<td>$H_r$</td>
<td>1.2</td>
</tr>
<tr>
<td>Dense bed height</td>
<td>$h_b$</td>
<td>0.5</td>
</tr>
<tr>
<td>Freeboard height</td>
<td>$h_f$</td>
<td>0.7</td>
</tr>
<tr>
<td>Diameter</td>
<td>$D_r$</td>
<td>0.1</td>
</tr>
<tr>
<td>Number of nozzles</td>
<td>$N_{nz}$</td>
<td>68</td>
</tr>
<tr>
<td><strong>Operational conditions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>973-1073</td>
</tr>
<tr>
<td>Pressure at the outlet</td>
<td>$P$</td>
<td>101325</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>$\Delta P$</td>
<td>$\approx 4500$</td>
</tr>
<tr>
<td>Inventory of solids in the fuel-reactor</td>
<td>$m_s$</td>
<td>$\approx 4.2$</td>
</tr>
<tr>
<td>Circulation rate of solids</td>
<td>$Q_s$</td>
<td>80-250</td>
</tr>
<tr>
<td>Inlet fuel flow</td>
<td>$Q_f$</td>
<td>0.6-1.2</td>
</tr>
<tr>
<td>Inlet gas velocity</td>
<td>$u_g$</td>
<td>0.075-0.15</td>
</tr>
<tr>
<td>Ratio of oxygen-carrier to fuel</td>
<td>$\phi$</td>
<td>0.7-2.2</td>
</tr>
<tr>
<td>Thermal power</td>
<td>$P_{th}$</td>
<td>6-12</td>
</tr>
<tr>
<td>Air-reactor solids conversion</td>
<td>$X_{\alpha,in}$</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 4. Correlations for the bubble diameter in the dense bed, $d_b$, the bubble-emulsion gas exchange coefficient, $k_{be}$, and the decay factor for solids concentration in the freeboard, $a$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_b$</td>
<td>Darton et al. [22]</td>
<td>$d_b = 0.54 \left( u - u_{mf} \right)^{0.4} \left( h + 4 \sqrt{A_0} \right)^{0.8} g^{-0.2}$ (36)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d_b = d_{bm} - (d_{bm} - d_{bo}) e^{-0.3h/D_r}$ (37)</td>
</tr>
<tr>
<td>$d_b$</td>
<td>Mori and Wen [23]</td>
<td>$d_{bm} = 1.64 \left[ A_0 \left( u_0 - u_{mf} \right) \right]^{0.4}$ (38)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$d_{bo} = 0.872 \left[ A_0 \left( u_0 - u_{mf} \right) \right]^{0.4}$ (39)</td>
</tr>
<tr>
<td>$k_{be}$</td>
<td>Kunii and Levenspiel [6]$^{(1)}$</td>
<td>$k_{be} = 4.5 \left( \frac{u_{mf}}{d_b} \right) + 5.85 \left( \frac{D_g^{1/2} g^{1/4}}{d_b^{3/4}} \right)$ (40)</td>
</tr>
<tr>
<td>$k_{be}$</td>
<td>Sit and Grace [24]$^{(1)}$</td>
<td>$k_{be} = \frac{1}{d_b} \left( 2u_{mf} + 12 \left( \frac{D_g e_{mf} U_h}{\pi d_b} \right)^{0.5} \right)$ (41)</td>
</tr>
<tr>
<td>$a$</td>
<td>Kunii and Levenspiel [6]$^{(2)}$</td>
<td>$a = 315 \frac{d_p^{0.64}}{u_g}$ (42)</td>
</tr>
<tr>
<td>$a$</td>
<td>Johnsson and Leckner [25]</td>
<td>$a = 4 \frac{u_j}{u_g}$ (43)</td>
</tr>
</tbody>
</table>

$^{(1)}$ Gas diffusivity of gas $i$ in the gas mixture was calculated using the equation given by Fuller et al. [26].

$^{(2)}$ Expression obtained by fitting experimental data showing the effect of the particle size on the product $a \cdot u_g$ calculated by several authors.
Caption of Figures

**Figure 1.** Effect of CH$_4$ concentration and temperature on the reduction reaction of Cu14Al-I. $d_p = 100$-300 $\mu$m. (a) $T = 1073$ K; H$_2$O = 30 vol %. (b) CH$_4$ = 10 vol %; H$_2$O = 30 vol %. Model predictions are presented as continuous lines (—).

**Figure 2.** Schematic diagram of the 10 kW$_{th}$ CLC prototype located at ICB-CSIC (Spain).

**Figure 3.** Simplified flow diagram of calculation for the overall solution.

**Figure 4.** Longitudinal profiles of gas and solids concentration and combustion efficiency in the fuel-reactor. $d_p = 0.2$-0.5 mm; $T_{FR}=1073$ K; $Q_f = 0.8$ Nm$^3$/h; $Q_s = 170$ kg/h; $\phi = 1.5$.

**Figure 5.** Comparison among the combustion efficiencies experimentally obtained (o) and predicted by the model as a function of the ratio of oxygen-carrier to fuel, $\phi$, for different equations to obtain the value of the decay constant parameter for solids concentration in the freeboard, $a$: Eq. (42) —— , Eq. (43) ----- ; $a = 12$ ——. $T_{FR}=1073$ K; $Q_f = 0.8$ Nm$^3$/h; $d_p = 0.2$-0.5 mm.

**Figure 6.** Comparison among the combustion efficiencies experimentally obtained (symbols) and predicted by the model (——) as a function of the ratio of oxygen-carrier to fuel, $\phi$, for different operating conditions: (a) effect of temperature using $d_p = 0.2$-0.5 mm, $Q_f = 0.8$ Nm$^3$/h; (b) effect of flow gas using $d_p = 0.2$-0.5 mm, $T_{FR}=1073$ K; and (c) effect of temperature using $d_p = 0.1$-0.3 mm, $Q_f = 0.8$ Nm$^3$/h.

**Figure 7.** Inventory of Cu14Al-I per MW of CH$_4$ as a function of the ratio of oxygen-carrier to fuel, $\phi$, to reach a combustion efficiency $\eta_c = 99.9\%$. $d_p = 0.2$-0.5 mm; $u_0 = 0.1$ m/s. Solid lines:
values predicted by the model; dashed lines: values predicted by a simplified model without any restriction to the gas-solids contact, Eq. (45).

**Figure 8.** Inventory of Cu14Al-I per MW of CH₄ as a function of the average oxidation conversion of the oxygen-carrier in the air-reactcor, $\bar{X}_{O_{2,air}}$, to reach a combustion efficiency $\eta_c = 99.9\%$. $d_p = 0.2\text{–}0.5$ mm; $u_0 = 0.1$ m/s. Solid lines: values predicted by the model; dashed lines: values predicted by a simplified model without any restriction to the gas-solids contact, Eq. (45).

**Figure 9.** Combustion efficiency predicted by the model as a function of the ratio of oxygen-carrier to fuel, $\phi$, for different CO/CH₄ and H₂/CH₄ reactivity ratios, i.e. $\left(-r_{g,i}\right)^{\circ}/\left(-r_{g,CH_4}\right)^{\circ}$. $d_p = 0.2\text{–}0.5$ mm; $T_{FR} = 1073$ K; $u_0 = 0.1$ m/s; $m_{OC,FR} = 500$ kg MW⁻¹.

**Figure 10.** CH₄, CO and H₂ concentration predicted by the model as a function of the CO/CH₄ and H₂/CH₄ reactivity ratios, i.e. $\left(-r_{g,i}\right)^{\circ}/\left(-r_{g,CH_4}\right)^{\circ}$ for $\phi = 1.5$ and $\phi = 1.2$. $d_p = 0.2\text{–}0.5$ mm; $T_{FR} = 1073$ K; $u_0 = 0.1$ m/s; $m_{OC,FR} = 500$ kg MW⁻¹.
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Alberto Abad, Juan Adánez, Francisco García-Labiano, Luis F. de Diego, Pilar Gayán.

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Alberto Abad, Juan Adánez, Francisco García-Labiano, Luis F. de Diego, Pilar Gayán.

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Alberto Abad, Juan Adánez, Francisco García-Labiano, Luis F. de Diego, Pilar Gayán.

Figure 7. Inventory of Cu14Al-I per MW of CH₄ as a function of the ratio of oxygen-carrier to fuel, \( \phi \), to reach a combustion efficiency \( \eta_c = 99.9\% \). \( d_p = 0.2\text{-}0.5 \text{ mm}; u_0 = 0.1 \text{ m/s} \). Solid lines: values predicted by the model; dashed lines: values predicted by a simplified model without any restriction to the gas-solids contact, Eq. (45).

Alberto Abad, Juan Adánez, Francisco García-Labiano, Luis F. de Diego, Pilar Gayán.

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Alberto Abad, Juan Adánez, Francisco García-Labiano, Luis F. de Diego, Pilar Gayán.

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Alberto Abad, Juan Adánez, Francisco García-Labiano, Luis F. de Diego, Pilar Gayán.

Figure 10. CH₄, CO and H₂ concentration predicted by the model as a function of the CO/CH₄ and H₂/CH₄ reactivity ratios, i.e. \( \frac{-r_{\text{g,i}}}{-r_{\text{g,CH₄}}} \) for \( \phi = 1.5 \) and \( \phi = 1.2 \). \( d_p = 0.2-0.5 \) mm; \( T_{FR} = 1073 \) K; \( u_0 = 0.1 \) m/s; \( m_{OC,FR} = 500 \) kg MW⁻¹.