Modeling 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 (FR) in chemical looping combustion systems. This model considers both the hydrodynamic of the fluidized bed (dense bed and freeboard) and the reduction kinetics of the oxygen carrier (OC). The main outputs of the model are solid conversion and gas composition at the reactor exit, the axial profiles of gas composition, and the fluidodynamics structure of the reactor. The FR model was validated using the experimental data obtained from the CH₄ combustion in a 10 kWth prototype built at the “Instituto de Carboquímica” (ICB-CSIC, Spain) using a Cu-based OC. The influence of OC circulation rate, fuel gas load, reactor temperature and OC particle size were analyzed. Combustion efficiency predicted by the model showed a good agreement with experimental results. Once the FR model was validated, important consequences for the design and optimization of the FR in a CLC system were obtained.

© 2008 Elsevier Ltd. All rights reserved

Keywords: Type your keywords here, separated by semicolons ; Keywords:

1. Introduction

Chemical Looping Combustion (CLC) is a combustion process with inherent CO₂ separation 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 (OC) in the form of a metal oxide. Solid particles based on Fe, Ni and Cu have been extensively investigated as feasible oxygen carriers to be used in CLC systems [2]. In CLC systems, the conventional combustion reaction is replaced by two successive reactions forming a chemical loop. The solid circulates between two interconnected reactors, the fuel (FR) and the air reactor (AR). In the FR, the metal oxide reacts with the gaseous fuel to produce CO₂ and H₂O. Pure CO₂, ready to compression and storage, is obtained after steam condensation. The OC is regenerated with air in the AR, and it is ready to start a new cycle. The most common design of a CLC plant includes a high-velocity riser for the AR and a low-velocity fluidized bed for the FR [3]. A fundamental part of the reliability of a CLC system is based on the behavior of the FR in order to obtain high

* Corresponding author. Tel.: +34 976 73 39 77; fax: +34 976 73 33 18.
E-mail address: abad@icb.csic.es.

doi:10.1016/j.egypro.2009.01.053
combustion efficiency. In this line, the modeling of the reactor would be helpful for the design, optimization, and scale-up of the process. A few works have been presented in the literature for the modeling of the reactors involved in a CLC system throughout several strategies. Adánez et al. [4] and García-Labiano et al. [5] modeled the FR using empirical correlations for the hydrodynamic of a fluidized bed based on the two phases 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 fluidodynamic of the AR and FR and an efficiency factor for the gas-solid contact. Jung and Gamwo [8] developed a multiphase CFD-based model to predict the first 10 seconds of the reduction with methane of a Ni-based oxygen carrier in a batch fluidized bed reactor. However, no models have been validated until now against experimental data.

This work is focused on the basic design of a bubbling fluidized bed FR to set up the range of operating conditions to reach high fuel conversion. A model has been developed taking into account both the hydrodynamic of the fluidized bed, considering both the dense bed and the freeboard, and the kinetics of the oxygen carrier reduction. The work has been focused in the combustion of CH$_4$ by means of a CuO-based OC, although the model could be used for any other metal/gas system. The FR model was validated using the experimental data obtained from the operation of a 10 kW$_{th}$ prototype built at the “Instituto de Carboquímica” (ICB-CSIC, Spain).

2. Experimental

To validate the model of the fuel reactor, experimental data obtained during methane combustion in a 10 kW CLC prototype was used, see Figure 1. In this experimental work, the oxygen carrier was a CuO-based material prepared by the impregnation method. The more relevant results of this work can be found elsewhere [9,10].

![Figure 1. Schematic diagram of the 10 kW$_{th}$ CLC prototype.](image)

2.1. Oxygen carrier

A CuO-based oxygen carrier –here denoted as Cu14Al-I– prepared by impregnation was selected as a promising oxygen carrier based on results of a previous work [11]. A detailed description of the preparation method can be found elsewhere [9]. Two different particle sizes were used: 0.1-0.3 and 0.2-0.5 mm. 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.
For kinetic determination, the shrinking core model (SCM) with control by the chemical reaction in the grain was used. The equations that describe this model under chemical reaction control in the grain are the following:

\[
\frac{1}{\tau} = 1 - \left(1 - X_s\right)^{1/3} \quad \tau = \frac{r_{\text{CuO}}}{b V_{\text{CuO}} k C^n}
\]  \hspace{1cm} (1)

The kinetics parameters for the reduction of the oxygen carriers with CH\(_4\), H\(_2\) and CO are shown in Table 2.

<table>
<thead>
<tr>
<th>Table 1. Properties of the Cu14Al-I oxygen carrier.</th>
<th>dp = 0.1-0.3 mm</th>
<th>dp = 0.2-0.5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>After 100 h</td>
</tr>
<tr>
<td>Active material, x\text{CuO} (%)</td>
<td>14</td>
<td>9.5</td>
</tr>
<tr>
<td>ROC (%)</td>
<td>2.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Apparent density (kg/m(^3))</td>
<td>1500</td>
<td>1620</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Kinetic parameters for reduction of Cu14Al-I with CH(_4), CO and H(_2).</th>
<th>CH(_4)</th>
<th>CO</th>
<th>H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(_g) Grain radius (\text{m})</td>
<td>(2 \times 10^{-7})</td>
<td>(2 \times 10^{-7})</td>
<td>(2 \times 10^{-7})</td>
</tr>
<tr>
<td>(V_{\text{CuO}}) Molar volume of CuO (\text{cm}^3/\text{mol})</td>
<td>12.4</td>
<td>12.4</td>
<td>12.4</td>
</tr>
<tr>
<td>b Stoichiometric coefficient (\text{mol CuO/mol gas})</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>n Reaction order</td>
<td>-</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>(k_0) Pre-exponential factor (\text{mol}^{1-n} \text{m}^{3n-2} \text{s}^{-1})</td>
<td>30.0</td>
<td>0.01</td>
<td>1.0</td>
</tr>
<tr>
<td>E Activation energy (\text{kJ/mol})</td>
<td>106</td>
<td>25</td>
<td>60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3. Main operating and modeling parameters of the FR.</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor geometry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Height (H_r)</td>
<td>1.2</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>Bottom bed height (h_b)</td>
<td>0.5</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>Diameter (D_r)</td>
<td>0.1</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>Operational conditions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (T)</td>
<td>973-1073</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Pressure drop (\Delta P)</td>
<td>(\approx 4500)</td>
<td>Pa</td>
<td></td>
</tr>
<tr>
<td>FR solids inventory (m_s)</td>
<td>(\approx 4)</td>
<td>kg</td>
<td></td>
</tr>
<tr>
<td>Solids circulation rate (Q_s)</td>
<td>80-250</td>
<td>kg/h</td>
<td></td>
</tr>
<tr>
<td>Inlet fuel flow (Q_f)</td>
<td>0.6-1.2</td>
<td>Nm(^3)/h</td>
<td></td>
</tr>
<tr>
<td>Inlet gas velocity (u_g)</td>
<td>(\approx 0.1)</td>
<td>m/s</td>
<td></td>
</tr>
<tr>
<td>Oxygen carrier-to-fuel ratio (\phi)</td>
<td>0.7-2.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>AR solids conversion (X_{\text{AR}})</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
2.2. 10 kWth CLC prototype

The 10 kWth CLC prototype –Figure 1– consists in two interconnected bubbling fluidized bed reactors, the FR (1) and AR (2). In the FR the fuel gas, CH₄, reacts with the oxygen carrier to give CO₂ and H₂O. The solids previously reduced in the FR were then transported to the AR through a loop seal fluidized bed reactor (3a). Complete oxidation of the reduced carrier was achieved in the AR. The fully oxidized carrier was taken up by a pneumatic system (4), and sent to a solid reservoir (6) setting the solid ready to start a new cycle. A detailed description of the prototype can be found elsewhere [9,10]. In this work, the FR behavior was modeled using the parameters showed in Table 3. The behavior of the CLC was evaluated calculating the combustion efficiency, \( \eta_c \), defined as

\[
\eta_c = \frac{2y_{\text{CO}} + y_{\text{CO}_2} + y_{\text{H}_2\text{O}}}{4y_{\text{CH}_4}} \cdot \frac{F_{\text{in}}}{\text{F}_{\text{re}}}
\]  

where \( F_{\text{in}} \) and \( F_{\text{out}} \) are the molar flows at the inlet and outlet of the FR, respectively, and \( y_i \) is the molar fraction of gas i. The oxygen carrier-to-fuel ratio (\( \phi \)) was defined by eq 3, where \( F_{\text{CuO}} \) and \( F_{\text{CH}_4} \) are the molar flow rates of the CuO and CH₄ in the FR, respectively. A value of \( \phi = 1 \) means the stoichiometric condition for full reaction between CuO and CH₄.

3. FR modeling

The developed model describes the behavior of a bubbling fluidized bed to process a fuel gas with continuous circulation of an oxygen carrier. The hypotheses considered for the model were: steady state, isotherm bed at macroscopic level, no existence of particle fragmentation or attrition, and no elutriation. The model is one-dimensional, based on empirical and semi-empirical expressions and takes into account lateral exchange of gas in the bottom bed between bubbles and emulsion. The modelling of the fluidized-bed reactor was divided in two fields: fluidodynamics and chemical reactions. Because the gas velocity variation is governed by the methane reaction rate with the OC, the fluidodynamics and mass balance in the reactor should be solved simultaneously.

3.1. Fluidodynamics of the reactor

The reactor can be divided into two vertical zones with respect to concentration of solids: 1) a bottom bed with a high and roughly constant solids concentration; and 2) freeboard or a dilute region above the bottom bed.

The gas flow in the bottom bed is considered by a modified two phase flow as proposed by Johnsson et al. [12]. The total gas flow is divided in three parts: 1) the flow in the particulate or emulsion phase at the minimum fluidization velocity, \( u_{\text{mf}} \); 2) the visible bubble flow, \( u_{\text{vis}} \), related to the gas in the bubbles at the rising velocity of the bubbles; and 3) the gas throughflow, \( u_{\text{tf}} \), 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:

\[
u_0 = (1 - \delta_b) u_{\text{mf}} + u_{\text{vis}} + u_{\text{tf}}
\]

At this point, it is remarkable that the gas velocity \( u_0 \) is not constant with the reactor height because the gas expansion during methane conversion. The bed porosity at a fixed position in the dense bed can be obtained as

\[
\epsilon_b = (1 - \delta_b) \epsilon_{\text{mf}} + \delta_b
\]

where \( \delta_b \) is the bubble fraction in the bottom bed and \( \epsilon_{\text{mf}} \) is the porosity at the minimum fluidization conditions.

The freeboard start from the upper limit of the bottom bed, and it is characterized by a decrease in the solids concentration with the reactor height [6] given by

\[
\frac{dC_s}{dh} = -aC_s
\]
After a sensibility analysis to this parameter, a value for $a \approx 12$ was used to fit the experimental data in this work. Finally, the mixing gas behaviour in the freeboard region has been considered. This phenomenon was taking into account by the use of a contact efficiency $\eta_{g-s}$ between gas and solid in the freeboard [13] calculated as

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

where $C_s$ and $C_{s,b}$ are the solids concentration in the freeboard and in the upper limit of the bottom bed, respectively.

3.2. Mass balances into the reactor

Mass balances for the different reacting compounds and products were developed for these two phases in the bottom bed and the freeboard regions. Plug flow for the gas was considered in each phase, i.e. the emulsion and bubbles in the bottom bed, and the freeboard, whereas solids in bottom-bed and freeboard were in perfect mixing. The pathway for methane reaction with the oxygen carrier was considered to happen in two steps, first towards CO and H$_2$ and later these intermediates products react to give CO$_2$ and H$_2$O:

$$\text{CH}_4 + \text{CuO} \rightarrow \text{CO} + 2 \text{H}_2 + \text{Cu}$$

$$\text{CO} + \text{CuO} \rightarrow \text{CO}_2 + \text{Cu}$$

$$\text{H}_2 + \text{CuO} \rightarrow \text{H}_2\text{O} + \text{Cu}$$

In the dense phase, a gas exchange between bubbles ($u_{vis}$ and $u_{uf}$) and emulsion ($u_{mf}$) is considered allowing the exchange of products and reactants between these phases by diffusive mechanism. 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. Moreover, it was assumed that the reaction products (CO, H$_2$, CO$_2$ and H$_2$O) reach instantaneously the water-gas shift (WGS) equilibrium in all phases into the reactor. Thus, the mass balances for every gas (CH$_4$, CO, H$_2$, CO$_2$ and H$_2$O) in each zone in the reactor are the following:

Emulsion in the bottom bed

$$\frac{dF_{ch,i}}{dV} = \frac{d \left[ \left( 1 - \delta_b \right) u_{mf} C_{ch,i} \right]}{dV} = -\left( 1 - \delta_b \right) \sum (\bar{\tau}_{F,i})_b - \delta_b k_{he} \left( C_{ch,i} - C_{s,b} \right) y_{e,i} \frac{dF_{e,i}}{dV} - \frac{dF_{WGS}}{dV}$$

Bubble in the bottom bed

$$\frac{dF_{ch,i}}{dV} = \frac{d \left[ \left( u_{vis} + u_{uf} \right) C_{ch,i} \right]}{dV} = \delta_b k_{he} \left( C_{ch,i} - C_{s,b} \right) y_{e,i} \frac{dF_{e,i}}{dV} - \frac{dF_{WGS}}{dV}$$

Freeboard

$$\frac{dF_{ch,i}}{dV} = \frac{d \left[ u_{e,i} C_{ch,i} \right]}{dV} = -\sum (\bar{\tau}_{F,i})_b \frac{dF_{WGS}}{dV}$$

The first term in the right side on eq 11 represents the amount of gas $i$ consumed in the differential volume element $dV$, where $(\bar{\tau}_{F,i})_b$ is the average reaction rate of the gas $i$ in the bottom bed, and $\sum (\bar{\tau}_{F,i})_b$ is the net consumption rate of the gas $i$, following the scheme given in eqs 8-10. The second term is the gas flow of gas $i$ from the emulsion to the bubble. The third term refers to the excess of gas in the emulsion that move to the bubbles because the expansion of gas in the element $dV$. 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 (eq 12) and the freeboard (eq 13). These equations allow determining the concentration of gas $i$ in emulsion, bubbles and freeboard.

The average reaction rate of gas is related to the reaction rate of the oxygen carrier in the reactor. Assuming perfect mixing of the solids in the bottom bed and the freeboard zone, the average reactivity is calculated as
\[
\frac{-\tau_{r,i}}{b_i} = \frac{-\tau_{s,i}}{b_i} = \rho_{\text{CuO},p} \frac{1 - \epsilon_s}{b_i} \int_0^t \frac{dX_{s,i}(t)}{dt} E(t) dt
\]

where \(t_{\text{mr}}\) is the mean residence time of particles in the reactor, \(\rho_{\text{CuO},p}\) is the molar density of the active phase (CuO) in the particle (\(\rho_{\text{CuO},p} = \rho_{\text{m},\text{CuO}} X_{\text{CuO}}\)), and \(b_i\) the stoichiometric coefficient for the reacting gas \(i\) (CH\(_4\), CO or H\(_2\)) showed in reactions 8-10, i.e. \(b_i = 1\). The reactivity of the particles, \(dX_s/dt\), is obtained from derivation of eq 1.

4. Results and discussion

Predictions from the model were obtained at different operating conditions. The main outputs of the model consist of the fluidodynamics structure of the reactor, e.g. solids concentration profiles and gas flow distribution between bubbles and emulsion phases, axial profiles of gases composition and flow (CH\(_4\), CO, H\(_2\), CO\(_2\) and H\(_2\)O), and solids conversion in the reactor. As example, Figure 2 shows the solids and concentration of gases profiles in the FR for a reference case. As it can be seen there are a difference in the profiles behaviour in the dense bed and in the freeboard. This fact is due to the differences in the fluidodynamics of these zones. The bottom bed is characterized by a roughly constant porosity, which have a height \(H_b = 0.5\) m. The combustion efficiency reached at this height was \(\eta_c = 0.72\), and was limited by the gas transference between bubble and emulsion in the two-third upper part of the bottom bed. Above the bottom bed, the solids concentration decreases with the reactor height. However, the combustion efficiency increases faster in this zone because the gas-solid contact is better in this zone than in the bottom-bed. It can be seen that full conversion of gas was reached at \(h = 0.65\) m from the distributor plate. Moreover, H\(_2\) and CO concentrations are maintained at low values because they disappear faster by reactions 9 and 10 than they are generated by reaction 8.

![Figure 2. Longitudinal profiles of gas and solids concentration and combustion efficiency in the FR. dp = 0.2-0.5 mm; TFR=1073 K; Qf = 0.8 Nm\(^3\)/h; Qs = 170 kg/h; \(\phi = 1.5\).](image-url)

Figure 3 shows the comparison between experimental results and predictions of the model for different operating conditions. As it can be seen, in all cases the model predict adequately the results obtained in the 10 kW prototype. In general, the use of the stoichiometric oxygen carrier-to-fuel ratio \(\phi = 1\) produced low combustion efficiencies, ranging from 75 to 90%. In this case, although the oxygen available in the FR was exactly the oxygen needed to fully convert CH\(_4\) into CO\(_2\) and H\(_2\)O, not all particles have the chance to transfer the oxygen to the fuel. This was because the FR 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. This behavior was predicted in a previous work [14], where it was showed that when the oxygen carrier-to-fuel ratio goes-down towards 1, the solids inventory to fully convert the fuel gas noticeably increased. The combustion efficiency increases as the oxygen carrier-to-fuel ratio increases because the availability of oxygen in the FR increases and the average reactivity of the oxygen carrier in the FR also increases.
Figure 3. Comparison among the combustion efficiencies experimentally obtained (symbols) and predicted by the model (---) as a function of the oxygen carrier-to-fuel ratio, $\phi$, for different operating conditions: (a) effect of temperature using $d_p = 0.2-0.5$ mm, (b) effect of flow gas using $d_p = 0.2-0.5$ mm, and (c) effect of temperature using $d_p = 0.1-0.3$ mm.

In general, a $\phi$ value of $\approx 1.4$ was needed to fully convert the methane at 1073 K. The effect of the FR temperature also is noticeable. An increase in the FR temperature produced an increase in the combustion efficiency. This increase is related to the reaction rate through an increase in the kinetic constant value of the reduction rate. The model predicts that the decrease in the combustion efficiency is more important in the freeboard than in the bottom-bed. The reason for this is that the reaction in the bottom-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 weight of the chemical reaction in the freeboard, which has a higher dependency on the temperature. Lower relevance on the combustion efficiency has the fuel flow and the particle size. Some increase in the combustion efficiency is obtained when the fuel flow decreases. This effect is common understanding because there is the same amount of oxygen carrier to convert lower amount of methane. Moreover, the model predicts that the gas-solid contact in the bottom-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 contact with the solids. Thus the fuel conversion in the bottom-bed is increased. Regarding the effect of the particle size, some increase in the combustion efficiency can be observed when the particle size of the carrier is increased, mainly at the lower temperature. This difference is attributed to the different contact efficiency between gas and solid in the bottom-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 bottom-bed on the fuel conversion is higher at lower temperatures, as it was above stated.

Figure 4. Solids inventory of Cu14Al-I per MW of CH$_4$ as a function of the oxygen carrier-to-fuel ratio, $\phi$. T$_{FR}$=1073 K; $d_p = 0.2-0.5$ mm; $Q_f = 0.8$ Nm$^3$/h.
Once the model has been validated using experimental data from the 10 kW prototype, the model can be used to optimize and design the FR. Figure 4 shows the minimum solids inventory to fully convert the fuel gas as a function of the oxygen carrier-to-fuel ratio when similar fluidization conditions were used to the existing in the 10 kW prototype. It can be seen that a minimum solids inventory of 70 kg per MWth was needed when the \( \phi \) value was >2 at 1073 K. However, the solids inventory increases rapidly when the \( \phi \) value approach the unity, as previously was reported [14].

5. Conclusions

A model to describe the fuel reactor (FR) of a CLC process burning CH\(_4\) with a CuO-based oxygen carrier has been developed. 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. Two zones are considered for modeling the reactor, a dense bed with a bubble-emulsion phase structure with gas exchange between them and the freeboard with a typical decay in the solids concentration with the reactor height. The kinetic model considers the oxygen carrier reaction with CH\(_4\), CO and H\(_2\) together with the water gas shift reaction at equilibrium condition. The main outputs of the model consist of the fluidodynamics structure of the reactor, e.g. solids concentration profiles and gas flow distribution between bubbles and emulsion phases, axial profiles of gases composition and flow (CH\(_4\), CO, H\(_2\), CO\(_2\) and H\(_2\)O), gas composition at the reactor exit, and solids conversion in the reactor.

For model validation purposes, predictions of the model were compared to experimental results obtained in a 10 kW CLC prototype. The oxygen carrier was a highly reactive CuO-based material containing 14% wt CuO. Good agreement was found between predicted and experimental data. CH\(_4\) conversion was highly dependent on the OC-to-fuel ratio, \( \phi \), and reactor temperature, being of low significance the effect of fuel load and particle size. Moreover, the model predicts the fuel conversion profiles in the reactor. It was determined that the OC-fuel reaction in the freeboard had decidive importance to obtain high combustion efficiency. With the developed model, simulations on the solids inventory of the CuO-based OC in order to obtain high combustion efficiency were carried out at similar conditions than those existing during 10 kW CLC prototype operation. A minimum solids inventory of 75 kg per MWth was needed to reach a combustion efficiency of 99.9% when the \( \phi \) value was >2 at 1073 K.

References