Computational fluid dynamics simulation for chemical looping combustion of coal in a dual circulation fluidized bed

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Computational fluid dynamics simulation for chemical looping combustion of coal in a dual circulation fluidized bed

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A dual circulation fluidized bed system is widely accepted for chemical looping combustion (CLC) for enriching CO₂ from the utilization of fossil fuels. Due to the limitations of the measurement, the details of multiphase reactive flows in the interconnected fluidized bed reactors are difficult to obtain. Computational Fluid Dynamics (CFD) simulation provides a promising method to understand the hydrodynamics, chemical reaction, and heat and mass transfers in CLC reactors, which are very important for the rational design, optimal operation, and scaling-up of the CLC system. In this work, a 5 kWth coal-fired CLC dual circulation fluidized bed system, which was developed by our research group, was first simulated for understanding gas leakage, flow pattern and combustion efficiency. The simulation results achieved good agreement with the experimental measurements, which validates the simulation model. Subsequently, to improve the combustion efficiency, a new operation condition was simulated by increasing the reactor temperature and decreasing the coal feeding. An improvement in the combustion efficiency was attained, and the simulation results for the new operation condition were also validated by the experimental measurements in the same CLC combustor. All of the above processes demonstrated the validity and usefulness of the simulation results to improve the CLC reactor operation.

1. Introduction

Chemical looping combustion (CLC), which has the characteristic of CO₂ inherent separation, is a novel fossil fuel utilization technology [1,2]. Lattice oxygen atoms in the oxygen carrier instead of oxygen molecules in air are used to oxidize the fossil fuel indirectly. In this process, the utilization of chemical energy is cascaded, thereby achieving higher energy conversion efficiency. A typical CLC reactor is composed of an air reactor (AR) and a fuel reactor (FR). The fossil fuel is oxidized via an oxygen carrier with high oxygen potential (usually metal oxide, Me₂O₃) in the FR, and the resulting products are CO₂, H₂O and an oxygen carrier with low oxygen potential (Me₂O₅₋₁). High-purity CO₂ can be easily obtained from the flue gas through a simple condensation process. The high oxygen potential OC is regenerated in the AR as the low oxygen potential OC is re-oxidized by air. Circulation is formed as the high oxygen potential OC is further transferred into the FR.

Due to the complex multiphase reactive flows present in CLC reactors (usually dual-circulation fluidized beds [3–6], also a small amount of fixed bed [7]), a comprehensive understanding to the multiphase reactive flows is important for the rational design, optimal operation and scaling-up of the CLC reactors. As an effective tool, numerical simulation has been used by many researchers. Based on the description of the fluid dynamics of the reactor, two categories of models can be identified [8]: macroscopic fluid dynamics models (MFD) [9–13] and computational fluid dynamics models (CFD). Based on the description to the particle phase dynamics, the CFD models can also be divided into three categories: the two-fluid model, the CFD-DEM (discrete element method) model [14,15], and the CPFD (computational particle fluid dynamics) model [16,17]. In CFD simulation based on the Navier–Stokes equation for describing the fluid flow, less artificial factors existed. Generally speaking, the CFD simulation result is more credible than that of MFD simulation. Among the CFD simulations, the two-fluid CFD model is widely adopted in the literature because it can provide almost all of the details of multiphase reactive flows within an acceptable computational cost. In the present work, we mainly focused on the CLC–CFD simulation using the two-fluid model.

Generally the CFD simulation in this aspect can be distinguished between CLC of gaseous fuels and one using solid fuels. Since the CLC of gaseous fuels is relatively simple on the experimental investigation end as well as on the numerical simulation end, both CFD model (reaction kinetic model for gas–solid heterogeneous reaction and multi-scale hydrodynamics model for particle cluster) development and thermo-chemical performance understanding have been widely investigated for the CLC of gaseous fuels.
The accurate CFD prediction of CLC is first dependent of a reasonable gas–solid heterogeneous reaction kinetics model. Deng et al. [18,19], for the first time, developed the reaction kinetic models for calcium sulfate (CaSO₄, as an oxygen carrier) and hydrogen, and from CFD simulations, they concluded that a high reactor temperature enhances the conversion of hydrogen. Similar simulations were conducted by Jung and Ganwo [20] for the reaction between NiO and methane, Wang et al. [21] for the reaction between NiO and methane, and Wang et al. [22] for the reduction reaction between CuO/Al₂O₃ oxygen carrier and coal gas containing CO, H₂, H₂O and CO₂. Kruggel-Emden et al. [23] investigated the validity of the heterogeneous reaction kinetics models by conducting a CFD simulation in the FR; the results revealed that the empirical polynomial based models proposed by Kruggel-Emden et al. [24] provide an accurate representation to the reaction rate.

On the other hand, describing the heterogeneous particle cluster formed in the circulated fluidized bed reactors is another challenging task for CLC–CFD simulation. Wang et al. proposed a series of models, e.g., CSD drag coefficient model [25], multi-scale chemical reaction model [26] and multi-scale heat transfer model [27], to capture more accurately the local non-uniform characteristics in a dual circulating fluidized bed. The usual parameters of the pressure profile, solid volume fraction distribution and gas compositions at the outlet were investigated. The results indicated that these non-uniform based models can substantially improve the accuracy of simulation result. Recently, a three-dimensional interconnected fluidized bed CFD simulation was conducted by Guan et al. [28]. In this simulation, the effect of the drag models on the computational results was investigated, and the pressure profile and solid volume fraction distribution were studied in detail. The results indicated that the Gidaspow and Syamlal-O’Brien drag models both produced accurate predictions to the reactor. Using CFD simulations, Chen et al. [29] proposed a parameter to correlate the occurrence of bubbles and the dynamic properties; based on the CFD simulation and the proposed parameter, the velocity, volume fraction, formed bubble and the species distributions in the FR were investigated.

Generally speaking, the reliability of CFD simulation for multi-phase CLC processes has been demonstrated. As an example, Mahalatkar et al. [30] simulated the FR experiments by Son and Kim [31], Mattisson et al. [32], Leion et al. [33] and Abad et al. [34]; the simulation results agreed well with the experiments. Based on these achievements, CFD simulation as an effective tool was widely utilized to investigate the thermo-chemical performances of CLC combustors and influencing factors involved in CLC. Harichandan and Shamim [35] conducted a FR CFD simulation using CaSO₄ as the oxygen carrier and H₂ as the fuel to investigate the effects of bed height, bed width, free board height and particle diameter on the fuel conversion rate; the results demonstrated a significant increase in the conversion rate with higher dense bed height, lower bed width, higher freeboard height and smaller oxygen carrier particle. Using the commercial CFD software Fluent, Kruggel-Emden et al. [36] simulated a CLC system that is comprised of an interconnected AR and FR. The spherical shrinking core model and the linear shrinking core model for the reaction kinetics were evaluated and compared; the effects of different kinetic models, oxygen carrier mass flows and reactor bed heights on the methane conversion and bed temperature were investigated. Recently, Wang et al. [37] conducted a multiphase CFD simulation for chemical looping reforming (CLR) in dual circulation fluidized beds; the effects of bed temperature, superficial gas velocity and H₂O/CH₄ ratio on the gas conversion efficiency were investigated.

Note that great achievements in the CLC of gaseous fuels have laid the foundation for the CFD simulation of CLC with solid fuels. Among the CFD simulations using solid fuels, Mahalatkar et al. [38,39], for the first time, utilized FLUENT to simulate the quartz tube reactor that was used in the coal CLC experiments of Leion et al. [40]. With different bed temperatures and different steam inlet concentrations, the CO₂ and CO concentrations in the outlet were found to agree well with the experimental measurements. Wang et al. [41] conducted a simulation of a continuous coal feeding CFB fuel reactor. The results of the outlet gas concentrations were in agreement with the experimental measurements.
However, the oxygen feeding rate was set arbitrarily and may not be in accordance with the rate in practical operation. Most of the existing CLC–CFD simulations are for single bed reactor (mainly the fuel reactor), and for CLC of gas fuels. To the best of our knowledge, there has been still no full reactor CFD simulation of coal-fired CLC until now. However, the full reactor simulation is very important to understand the thermo-chemical performance and hydrodynamics in the entire CLC reactor because the CLC performance depends on many correlated operating parameters: the heat and mass transfer between the air and fuel reactors, the flow pattern and the solid particle circulation. For example, the FR outlet gas concentration is influenced by the solid circulation rate, while the single FR reactor simulation can only be performed based certain assumptions, e.g., a constant solid circulation rate. In this work, the CFD simulation of a 5 kWth dual fluidized bed reactor for coal-fired CLC was performed. From the simulation results, both the outlet gas concentration and the detailed reactive multiphase flow profiles in the reactor were obtained, which provide essential information for the optimal operation of the dual fluidized bed reactors.

2. CFD model

The Eulerian multiphase model has been used to simulate both the fluid phase and the solid phase regarding the exchange of momentum, heat and mass transfer between the two phases. The solid phase is modeled as a continuum fluid, and the kinetic theory of granular flow (KTGF) is used in the transport equation to model the solid phase, considering the particle collision and fluctuations. The governing equations of mass, momentum and energy conservations are solved for each individual phase. An interpenetrating continuum assumption is applied to treat the phase interaction. The conversation equations, constitutive relations and reaction kinetics used in this work are given as below.

2.1. Hydrodynamic model of multiphase flow

The two-fluid model is used in this work. All the equations in the hydrodynamic model of multiphase flow used in this study are listed in Table 1. The model equations consist of continuity equations, momentum equations, energy equations, species transport equations, constitutive equations and other relational expressions. In particular, the dispersed turbulence model, which is a modified $k$–$\varepsilon$ model, is used for the fluid phase, and the Tchen-theory correlation is used for the dispersed phase. The modified $k$–$\varepsilon$ equation can be expressed as follows:

$$\frac{\partial (\rho \phi \mu_k)}{\partial t} + \nabla \cdot (\rho \phi \mu_k \mathbf{u}_k) = \nabla \cdot \left( \frac{\mu_k}{\sigma_k} \nabla k \right) + 2 \Gamma_a G_a - 2 \rho \phi \mu_k \frac{\partial \mu_k}{\partial u}$$

$$\frac{\partial (\rho \phi \mu_\varepsilon)}{\partial t} + \nabla \cdot (\rho \phi \mu_\varepsilon \mathbf{u}_\varepsilon) = \nabla \cdot \left( \frac{\mu_\varepsilon}{\sigma_\varepsilon} \nabla \varepsilon \right) + 2 \rho \phi \mu_\varepsilon \frac{\partial \mu_\varepsilon}{\partial u}$$

Table 1

Governing equations and constitutive correlations in the model.
where $I_1$ and $I_2$ represent the influence of the particle phase on the fluid phase, and $C_0$ is the production of turbulent kinetic energy. The constants have the following values: $C_1 = 1.44$, $C_2 = 1.92$, $\sigma_x = 1.0$, and $\sigma_z = 1.3$ [42].

2.2. Multiphase reactive kinetic model

2.2.1. Coal pyrolysis model

According to the model given by Wang et al. [41], the coal pyrolysis reaction was modified as below, considering the proximate and ultimate analyses of the Chinese bituminous coal used in this work:

$$\text{Coal} + 0.0666\text{CO}_2 \rightarrow 0.4663\text{Char} + 0.05192\text{CH}_4 + 0.00554\text{C}_2\text{H}_6 + 0.1672\text{CO} + 0.0604\text{H}_2 + 0.0269\text{H}_2\text{O} + 0.01007\text{Ash} \quad (1)$$

In the above reaction, partial reforming reaction of CH4 with H2O and CO2 was also considered. The reaction kinetic model can be expressed as:

$$r_{\text{pyroly}} = (Y_A k_1 + Y_B k_2)C_{\text{coal}} \quad (26)$$

where $C_{\text{coal}}$ is the concentration of non-gasified coal in the solid particles. The reaction rate constant $k_1$ can be expressed using the Arrhenius form:

$$k_1 = A \exp(-E_1/RT) \quad (27)$$

The relevant parameters in the simulation are as follows [43]: $A_1 = 2 \times 10^{4} \text{ s}^{-1}, A_2 = 1.3 \times 10^{7} \text{ s}^{-1}, E_1 = 104.6 \text{ kJ/mol}, E_2 = 167.4 \text{ kJ/mol}, Y_0 = 0.3,$ and $Y_0 = 1.0$.

2.2.2. Char gasification model

Everson et al. [44] described the kinetics of the char gasification reaction. The reaction formula and the source term in the mass conservation equation are given as below:

$$\text{Char} + \text{CO}_2 \rightarrow 2\text{CO} \quad (R2)$$

$$\text{Char} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad (R3)$$

$$\dot{m}_{\text{char}} = \rho_{\text{char}} e_{\text{char}} \frac{S_0}{1 - e_0} r (1 - X_{\text{char}})^{2/3} \quad (28)$$

where $\rho_{\text{char}}$ and $e_{\text{char}}$ represent the char density and the char volume fraction, respectively. $S_0 (1 - e_0)$ represents the char initial surface area per kilogram. The value of this variable is related to the coal pyrolysis temperature. $X_{\text{char}}$ is the conversion of char, and $r$ is the reaction rate of the char gasification, given by

Gasification in CO2 atmosphere:

$$r = \frac{k_{\text{CO}} k_{\text{CO}_{2}} P_{\text{CO}}}{1 + k_{\text{CO}_{2}} P_{\text{CO}} + k_{\text{CO}} P_{\text{CO}_{2}}} \quad (29)$$

Gasification in H2O atmosphere:

$$r = \frac{k_{\text{H}_2\text{O}} k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}{1 + k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + k_{\text{H}_2} P_{\text{H}_2}} \quad (30)$$

$P_{\text{CO}_2}, P_{\text{CO}}, P_{\text{H}_2\text{O}},$ and $P_{\text{H}_2}$ represent the partial pressure of CO2, CO, H2O, and H2, respectively. The reaction rate constants $k_{\text{CO}}, k_{\text{CO}_{2}},$ and $k_{\text{H}_2}$ and the equilibrium constants $K_{\text{CO}}$, $K_{\text{CO}_{2}}$, $K_{\text{H}_2\text{O}}$, and $K_{\text{H}_2}$ can be expressed in an Arrhenius form. The parameters we selected in the simulation are listed in Table 2.

2.2.3. Heterogeneous reaction models between the reducible gas and the oxygen carrier

The most important reactions in a coal-fired CLC system are the heterogeneous reactions between the gaseous phase and the oxygen carrier (iron ore with active metal oxide of Fe2O3 here). The relevant reactions are presented here:

$$\text{CH}_4 + 12\text{Fe}_2\text{O}_3 \rightarrow 8\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{CO}_2 \quad (R4)$$

$$\text{C}_2\text{H}_6 + 21\text{Fe}_2\text{O}_3 \rightarrow 14\text{Fe}_3\text{O}_4 + 3\text{H}_2\text{O} + 2\text{CO}_2 \quad (R5)$$

$$\text{CO} + 3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \quad (R6)$$

$$\text{H}_2 + 3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \quad (R7)$$

Because no description of the reaction kinetics of C,H, reacting with a Fe-based oxygen carrier was found in the open literature, we used the reaction kinetics of CH4 instead. The kinetic rate of these reactions can be characterized by the shrinking core model (SCM), and the reaction kinetics can be expressed as follows [30]:

$$\dot{m}_{\text{CH}_4} = \frac{k_{\text{CH}_4} R_0}{2MW_{\text{CH}_4}} \rho_{\text{char}} e_{\text{char}} \frac{Y_{\text{Fe}_3\text{O}_4} + Y_{\text{Fe}_2\text{O}_3} \times \frac{s_{\text{Fe}_2\text{O}_3}M_{\text{Fe}_2\text{O}_3}}{s_{\text{Fe}_3\text{O}_4}M_{\text{Fe}_3\text{O}_4}}}{(1 - X)^{\frac{1}{2}}} \times MW_{\text{CH}_4} \quad (31)$$

$$\dot{m}_{\text{H}_2} = \frac{2k_{\text{H}_2} R_0}{MW_{\text{H}_2}} \rho_{\text{char}} e_{\text{char}} \frac{Y_{\text{Fe}_3\text{O}_4} + Y_{\text{Fe}_2\text{O}_3} \times \frac{s_{\text{Fe}_2\text{O}_3}M_{\text{Fe}_2\text{O}_3}}{s_{\text{Fe}_3\text{O}_4}M_{\text{Fe}_3\text{O}_4}}}{(1 - X)^{\frac{1}{2}}} \times MW_{\text{H}_2} \quad (32)$$

$$\dot{m}_{\text{CO}} = \frac{2k_{\text{CO}} R_0}{MW_{\text{CO}}} \rho_{\text{char}} e_{\text{char}} \frac{Y_{\text{Fe}_3\text{O}_4} + Y_{\text{Fe}_2\text{O}_3} \times \frac{s_{\text{Fe}_2\text{O}_3}M_{\text{Fe}_2\text{O}_3}}{s_{\text{Fe}_3\text{O}_4}M_{\text{Fe}_3\text{O}_4}}}{(1 - X)^{\frac{1}{2}}} \times MW_{\text{CO}} \quad (33)$$

$R_0$ in (31)–(33) represents the oxygen carrying capacity of the oxygen carrier: $R_0 = \frac{m_{\text{ox}} - m_{\text{red}}}{m_{\text{ox}}}, X$ represents the conversion rate of the oxygen carrier: $X = \frac{m_{\text{ox}} - m_{\text{red}}}{m_{\text{ox}}}$.

The kinetic parameters of the above reactions can be expressed as [45]:

For R4 and R5, \( k_{\text{CH}_4} = \frac{3bk_{\text{H}_2} e^{-E/RT}}{\rho_m r_0} \times C_{\text{H}_4} \quad (34) \)

where $\rho_m = 60,627 \text{ mol/m}^3$, $r_0 = 3.29 \times 10^{-7} \text{ m}$, $b = 12$, $k_0 = 8.0 \times 10^{-4}$, $E = 49 \text{ kJ/mol}$, and $n = 1.3$.

For R7, \( k_{\text{H}_2} = \frac{3bk_{\text{H}_2} e^{-E/RT}}{\rho_m r_0} \times C_{\text{H}_2} \quad (35) \)

where $\rho_m = 60,627 \text{ mol/m}^3$, $r_0 = 3.29 \times 10^{-7} \text{ m}$, $b = 3$, $k_0 = 2.3 \times 10^{-3}$, $E = 24 \text{ kJ/mol}$, and $n = 0.8$.

For R6, \( k_{\text{CO}} = \frac{3bk_{\text{CO}} e^{-E/RT}}{\rho_m r_0} \times C_{\text{CO}} \quad (36) \)

where $\rho_m = 60,627 \text{ mol/m}^3$, $r_0 = 3.29 \times 10^{-7} \text{ m}$, $b = 3$, $k_0 = 6.2 \times 10^{-4}$, $E = 20 \text{ kJ/mol}$, and $n = 1.0$.

2.2.4. Water–gas shift reaction model

The influence of the reforming reaction may be remarkable in CLC reactors, so the water–gas shift reaction should be considered in the CFD simulation. The reaction formula is as follows:

\[ \text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2 \]
CO + H₂O → CO₂ + H₂  \hspace{1cm} \text{(RB)}

The reaction rate can be expressed according to Bustamante et al. [46]:

\[
r = -k_0 \left( e^{-E/RT} C_{H_2}^a C_{CO_2}^b - \frac{1}{K_{eq}} e^{-E/RT} C_{H_2} C_{CO} \right)
\]

where \( C_{H_2}, C_{CO_2}, C_{H_2O}, \) and \( C_{CO} \) represent the mole concentrations of \( H_2, CO_2, H_2O, \) and \( CO, \) respectively; \( k_0 = 2.17 \times 10^7; \ E = 192.9 \text{ kJ/mol} \); \( a = 0.5; \ b = 1; \) and the equilibrium constant \( K_{eq} \) is expressed as:

\[
K_{eq} = \exp(-4.33 + (4577.8/T))
\]

\[
r_{O2} = k_{O2} R_0 \rho_i \left( Y_{Fe_2O_3} + Y_{Fe_3O_4} \times \frac{S_{Fe_2O_3} M_{Fe_2O_3}}{S_{Fe_3O_4} M_{Fe_3O_4}} \right)^{2/3} \frac{MW_{O2}}{2}
\]

where \( k_{O2} = \frac{b k_0}{\rho_i} C_{O2}^b, \) with \( \rho_i = 41.523 \text{ mol/m}^3, \) \( R_0 = 1.8 \times 10^{-7} \text{ m}, \) \( b = 4, \) \( k_0 = 3.1 \times 10^{-4}, \) \( E = 14 \text{ kJ/mol}, \) and \( n = 1.0. \)

\[\text{3. Reactor geometry, initial condition and boundary condition}\]

A 5 kWth dual circulation fluidized bed for the CLC of coal was constructed by our research group [6]. Some experiments were conducted on this rig to investigate the effects of the operational parameters, such as the FR temperature, the thermal power and the fluidized gas flow rate, on the combustion efficiency. The highest combustion efficiency of 96.33% was attained under the optimal operation condition (FR temperature = 1273 K and thermal power = 2.25 kWth). The 5 kWth rig was simulated in this study. The geometry of the reactor is shown in Fig. 1. It is noted that the FR riser height in the CFD simulation is artificially increased for the convenience of constructing the model. We considered that this adjustment only has a minor effect on the precision of the simulation results. On the one side, a higher gas velocity exists in the region, which results in a small reaction time. On another side, the concentration of gaseous fuel is relatively low in the region, which does not contribute too much relative to the whole reaction in the FR.

The dual circulation fluidized bed reactor consists of an air reactor (AR), a fuel reactor (FR), an air riser reactor and a fuel riser reactor, cyclones 1 and 2, downcomers 1 and 2, and loop seals 1 and 2. The reactor size is described in Table 3 and is also presented in Fig. 1. Hematite was used as the oxygen carrier in this experiment, whose compositional analysis (as determined using an X-ray Fluorescence apparatus, EAGLE III, EDAX Inc.) is presented in Table 4. For simplicity, in the simulations, we assumed that \( Fe_2O_3 \) and the inert component are the only two components. According to Table 4, the mass fraction of \( Fe_2O_3 \) was 66%. The average diameter of the oxygen carrier particles is 180 μm, and their apparent density is 3472 kg/m³. Chinese bituminous coal was used as the fuel, and the results of the proximate and ultimate analyses of this coal are listed in Table 5. The boundary and initial conditions used in the simulation are listed in Table 6. The temperature of the reactor was maintained at 1223 K with the help of an electric heater and an insulation can. The back pressure of AR loop seal and FR loop seal are quite different due to different operating conditions between AR and FR, and we therefore selected different aeration rates in AR loop seal and FR loop seal to obtain the matched solid circulation rates. A zero velocity and a zero volume fraction
were set for the solid phase at the inlet of loop seal, and the velocity inlet boundary condition was adopted for the gas phase. The distributor configuration has not been taken into account.

4. Results and discussion

4.1. Validation of the simulation models

Before performing the comprehensive research, a pre-calculation was conducted for testing and determining the grid structure, the appropriate cell number and the time step for the simulations. The dependence of CO2 concentration at the FR outlet on the grid number was examined. The results indicated that cell number of 20,689 is appropriate for this two-dimensional calculation and that the simulation result under this condition is grid independent. The time step is set to $2 \times 10^{-5}$ s. In this research, a parallel computer with 16 threads was used, and the actual computation time was approximately 350 h.

At the beginning of the comprehensive research, the computational model was validated by comparing the simulation results with the experimental results. Fig. 2 shows the histogram of FR exhaust gas volume fraction detected in the simulation and experiment. Note that the exhaust gas volume fraction is in dry basis, and N2 was not considered. As shown in Fig. 2, some differences were observed between the simulation and experimental results. The relative errors are 2.45%, 7.05%, 16.8%, 55.8% for CO2, CO, CH4, H2, respectively. However, considering that the simulation models we used are relatively simple, the simulation results are within the range of acceptable errors.

Various methods can be used to improve the model. First, a simple coal pyrolysis model is used in our simulations; however, the coal is known to undergo a complex process in actual CLC reactors. The composition of coal is very complex and is different for each type of reactor. Second, although the Gidaspow drag model is a widely used model, many previous works indicated that the spatially heterogeneous drag model should be considered due to the cluster formation. Finally, the multiphase reactive kinetic model we used in this work is cited from the previous references. However, there are several types of iron based oxygen carriers, each with different properties; in particular, many differences exist between the oxygen carrier prepared in the laboratory and the natural ore.

As shown in Fig. 3, the AR exhaust gas volume fraction obtained from the CFD simulation and the experimental measurements were also comparable (the relative errors are 24.7%, 14.3%, 4.46% for CO2, O2, N2, respectively). CO2 exhausted from the air reactor may originate from the burning of char that was entrained from the fuel reactor to the air reactor and may also originate from gas leakage from the fuel reactor to the air reactor. The gas leakage phenomenon is further discussed in Section 4.2.

Table 3

<table>
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<tr>
<th>Parameters</th>
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<th>Simulation</th>
<th>Unit</th>
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<td>FR riser diameter</td>
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Table 4

Elemental analysis of the hematite.

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<tr>
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Table 5

Proximate and ultimate analyses of the coal used in this simulation.

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<th>Proximate analysis (ad wt.%</th>
<th>Volatiles</th>
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<tr>
<td>Ultimate analysis (ad wt.%</td>
<td>N</td>
<td>0.79</td>
</tr>
<tr>
<td>C</td>
<td>55.26</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>2.12</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>5.39</td>
<td></td>
</tr>
<tr>
<td>Lower heating value (MJ/kg)</td>
<td>24.8</td>
<td></td>
</tr>
</tbody>
</table>

Table 6

Initial and boundary conditions (ambient temperature based).

<table>
<thead>
<tr>
<th>Boundary condition</th>
<th>Air: 30</th>
<th>Operation temperature $T_{\text{button}}$ (°C)</th>
<th>950</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air reactor $F_{\text{AR}}$ (L/min)</td>
<td>N2: 25.0 CO2: 5.0</td>
<td>Coal feeding (g/min)</td>
<td>11.26 (4.75 kWth)</td>
</tr>
<tr>
<td>Fuel reactor $F_{\text{FR}}$ (L/min)</td>
<td>N2: 1.5</td>
<td>Loop seal from FR $F_{\text{Friss}}$ (L/min)</td>
<td>N2: 1.94</td>
</tr>
<tr>
<td>Loop seal from AR $F_{\text{LStran}}$ (L/min)</td>
<td>N2: 1.84</td>
<td>Loop seal from FR $F_{\text{LStran}}$ (L/min)</td>
<td>N2: 2.4</td>
</tr>
<tr>
<td>Initial condition</td>
<td>AR initial bed height (m)</td>
<td>0.35</td>
<td>FR initial bed height (m)</td>
</tr>
<tr>
<td>Downcomer initial bed height (m)</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.2. Analysis of the gas leakage during continuous operation of a CLC reactor

Minimization of the gas leakage between the air reactor and fuel reactor is essential for high-efficiency CO₂ capture and high-concentration CO₂ enrichment in CLC systems. The gas leakage from the FR to the AR can be measured by detecting the AR exhaust gas component; however, the AR exhaust gas component only provides indirect information on the gas leakage. CFD simulation is a powerful method for providing a direct description to the gas leakage between the AR and the FR.

Fig. 4 shows the contour of the instantaneous CO₂ distribution in the full reactor at 15 s. According to this figure, a high concentration of CO₂ exists in the FR downcomer. The main reason for this phenomenon is that some of the char that was not gasified completely in the FR will be converted to CO₂ at this position. The gas and solid residence time in the FR downcomer is sufficiently large to ensure that the char is gasified completely (see Fig. 9). Because the FR downcomer is connected with the FR loop seal, a high concentration CO₂ may leak into the AR along with the oxygen carrier circulation. Fig. 4 illustrates the details of the CO₂ leakage from the FR loop seal to the AR. On the other hand, whether the AR fluidized gas leaks to the FR downcomer or not should also be studied. As shown in the CFD results, the solid volume fraction in the AR is small (see Fig. 6) due to the high superficial gas velocity, resulting in a stable gas–solid flow in the AR. The pressure fluctuation in the AR is small. The oxygen carrier circulation process from the FR loop seal to AR was run smoothly at normal operation conditions. Therefore, the AR fluidized gas did not escape into the FR downcomer through the FR loop seal.

As will be discussed in Section 4.3, the FR ran at two different operation stages: the no coal feeding condition stage and the continuous coal feeding condition stage. The flow patterns in the FR are different for the two stages. In the first stage, a large solid inventory exists in the FR due to the relatively small FR superficial gas velocity. Slugging phenomenon appears, and the gas–solid flow is unstable (see Fig. 6). Meanwhile, the pressure in the FR exhibits a large fluctuation. The AR loop seal was alternately run under a normal condition and an abnormal condition (see Fig. 5). The FR fluidized gas escapes into the AR downcomer under the abnormal condition. In the second stage, the FR superficial gas velocity increases and results in the decrease of the solid inventory. Meanwhile, the slugging phenomenon disappeared. The AR loop seal is run at a normal condition all the time. A small amount of gases in the AR downcomer will leak to the FR along with the oxygen carrier circulation.

4.3. Analysis of the flow pattern

In the simulation and in the continuous experiment, the mixture of N₂ and CO₂ (see Table 6) was first introduced into the fuel reactor as fluidized gas (the first stage), while no coal was fed into the fuel reactor until a stable operation condition was achieved (the second stage). An unexpected phenomenon was observed in the process: the stable core annulus flow changed significantly after feeding of coal initiated. Fig. 6 shows the typical contours of the instantaneous solid volume fraction distribution at 5.6 s (no coal feeding) and 12.5 s (coal continuously feeding from 6.5 s). Fig. 7 shows the comparison of the time-averaged solid volume fraction.
fraction profiles at the FR heights of 0.4 m and 0.8 m. The flow pattern clearly changes significantly after coal feeding, and the bed material in the AR and the FR undergo a re-balance process. The FR solid inventory decreases, while the AR solid inventory increases. Alobaid et al. [47] also observed a similar phenomenon.

In fact, coal will undergo the pyrolysis and gasification process once it is fed into the fuel reactor, which will lead to gas volume expansion and an increase in the superficial gas velocity. According to the simulation results, the gas velocity of the FR outlet increased from 0.8 m/s to 1.7 m/s after coal feeding. The change of the gas velocity contributes to the change of the flow pattern. Note that the coal pyrolysis effect should to be carefully considered in the CLC reactor design and operation.

4.4. Combustion efficiency for the coal-fired CLC reactor

The combustion efficiency is determined based on the carbon balance and the oxygen demand. The combustion efficiency can be calculated through detection of the volume fractions of the exhaust gases as follows [48]:

$$
\eta_{\text{comb, FR}} = 1 - \frac{\Omega_{\text{OD}}}{\Phi_0(\gamma_{\text{CO}} + \gamma_{\text{CH}_4} + \gamma_{\text{H}_2})};
$$

where $\gamma_{\text{CO}}$, $\gamma_{\text{CH}_4}$ and $\gamma_{\text{H}_2}$ are the volume fractions of CO, CH$_4$, and H$_2$ contained in the FR exhaust gas, respectively; $\Phi_0$ is the oxygen/carbon ratio, i.e., the moles of oxygen required to convert the fuel completely per mole of carbon in the fuel.

According to the data of the FR exhaust gas volume fraction represented in Fig. 2, the combustion efficiency is 89.3% for the experiment and 91.3% for the simulation.

Similar to the combustion efficiency analysis for the coal-fired boiler, the coal pyrolysis efficiency and the char gasification efficiency were investigated in this study. These two variables can be defined as follows:

$$
\eta_{\text{pyro}} = \frac{\Delta m_{\text{coal}}}{m_0^{\text{coal}}};
$$

$$
\eta_{\text{gasi}} = \frac{\Delta m_{\text{char}}}{m_0^{\text{char}}};
$$

where $\Delta m_{\text{coal}}$ represents the mass of the coal consumed by the pyrolysis process, and $m_0^{\text{coal}}$ is the total mass of the coal fed into the reactor. $\Delta m_{\text{char}}$ represents the mass of the char consumed by
the gasification process, and $m_{\text{char}}^0$ is the total mass of char generated in the coal pyrolysis process.

According to the ash balance and the chemical formula (R1), the spatially resolved time-averaged coal pyrolysis efficiency and char gasification efficiency can be obtained, as shown in Figs. 8 and 9, respectively. The instantaneous values at 9–15 s were chosen as a statistical sample. Obviously, the coal pyrolysis efficiency reached 100% very quickly after the coal was introduced into the fuel reactor. However, the char gasification efficiency is only 69.2% at the FR outlet, although the value increases with the FR height. The above phenomenon indicates that the overall conversion rate of coal was controlled by the relatively slow char gasification process, which is consistent with previous results [30]. A part of the coal that was not gasified completely in the FR will be transferred into the FR downcomer. As mentioned in Section 4.2, this phenomenon will reduce the carbon capture efficiency.

The CO volume fraction distribution at 15 s is shown in Fig. 10. According to Figs. 8 and 10, the volume fraction of CO reaches the maximum value at the position where the coal pyrolysis efficiency reaches 100% (except the coal entrance region). This phenomenon occurs because the CO generation rate from the coal pyrolysis and the char gasification at the bottom of the reactor is greater than the CO consumption rate from the reduction reaction between CO and the OCs. Downstream of the fuel reactor, the CO volume fraction decreases gradually. This gradual decrease occurs because the char gasification rate is less than the reaction rate of CO oxidation. According to Fig. 6, high concentrations of oxygen carrier particles exist near the reactor wall, while a gas by-pass is formed at the center of the reactor. CO has more opportunity to be oxidized in these high OC concentration regions, resulting in low concentrations of CO in these regions.

The volume fraction distribution of CH$_4$ at 15 s is shown in Fig. 11. In comparison with the CO volume fraction, the volume fraction of CH$_4$ is relatively low because CH$_4$ can only be produced in the coal pyrolysis process, while CO can be produced both in the coal pyrolysis process and in the char gasification process. Another important gas component is H$_2$O. H$_2$O can accelerate the char gasification reaction, which is important to the improvement of the combustion efficiency of coal. The H$_2$O volume fraction
distribution at 15 s, shown in Fig. 12, exhibits an increasing tendency with the reactor height. Because the fluidized gas we used in this work does not include a H$_2$O component (it includes N$_2$ and CO$_2$ instead), the H$_2$O component in the reactor is primarily due to the coal combustion with oxygen carrier. The H$_2$O volume fraction is relatively low at the bottom of the reactor because only a small amount of coal is consumed in this region. If H$_2$O was used as fluidizing agent, it is expected that an increase in the char conversion with the promotion of H$_2$O to char gasification. Since the global reaction rate is limited by the reaction rate of char gasification in an iG-CLC system, these gasification products can be effectively converted by the reduction of oxygen carrier. As a result, it is also expected that the combustion efficiency is improved if using H$_2$O as fluidizing agent.

Not only CO$_2$ produced in the fuel reactor but also a part of CO$_2$ from the downcomer due to the further gasification of unconverted char will be exhausted from the outlet of FR cyclone, and this part of CO$_2$ can also be captured. The carbon capture efficiency ($\eta_{CC}$) was defined as the ratio of carbon containing gas flow leaving the fuel reactor to the total carbon containing gas flow leaving the unit [48]:

$$\eta_{CC} = \frac{(F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR})}{(F_{CO_2,AR} + F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR})}$$  \(\text{(43)}\)

where $F_{CO_2,FR}$, $F_{CO,FR}$ and $F_{CH_4,FR}$ were the mass flow rates of CO$_2$, CO and CH$_4$ at the outlet of fuel reactor, respectively. $F_{CO_2,AR}$ was the mass flow rate of CO$_2$ at the outlet of the air reactor. From Eq. (43), the carbon capture efficiencies are 75.3% for the original case and 79.1% for the optimal case.

4.5. Operation optimization

According to the above analysis, the FR superficial gas velocity will increase after initiation of coal feeding. The higher gas velocity reduces the FR solid inventory and also reduces the residence time of the gas fuel and the oxygen carrier particles, thereby reducing the conversion of the gas fuel originated from the coal. Meanwhile the char residence time is also reduced because the back-mixing effect in the FR is reduced due to the lower solid inventory. To improve the combustion efficiency, the superficial gas velocity in the FR should be adjusted accordingly. At this point, decreasing the thermal power of the reactor by reducing the FR coal feeding may be an effective approach to improve the combustion efficiency. Meanwhile, the reactor temperature is also an important factor. High temperature contributes to the increase of the reaction rate, especially for the OCs reduction rate and the char gasification rate.

Based on the above understanding, a new simulation was conducted with the reactor temperature increased to 1273 K and with the FR coal feeding decreased to 2.25 kW$_{th}$. Fig. 13 shows the comparison of the char gasification efficiency under the old and new operation conditions in the FR. The figure shows that the char gasification efficiency reaches 90% under the new operation condition at the FR outlet. The comparison of the FR solids inventory is shown in Fig. 14. The FR solid inventory under the new operation condition is larger than that under the old operation condition, mainly because the superficial gas velocity decreased due to the reduced FR coal feeding. The comparison of the exhaust gas volume fraction at the outlet is shown in Fig. 15. Except for the CO component, the volume fractions of other gas fuels exhibit a decreasing trend with the change of the operational conditions, while the product gas CO$_2$ increases accordingly. In fact, on one hand, the reactivity of the reactants increase rapidly with the temperature increasing, resulting in more gas fuel being converted to CO$_2$, and on the other hand, the OC volume fraction increases with the FR solid inventory increasing, thus causing the gas and solid residence time to also increase with the decrease of the superficial gas velocity, which provides more opportunity for the gas fuel conversion. The CO volume fraction changed very little. This lack of change is
observed because, although more CO is converted to CO₂, the CO yield also increased in the char gasification process under the new condition. To validate the new simulation results, a new experiment under this new operational condition was conducted. The combustion efficiency obtained in the experiment was 96.33%, which is a good agreement with the simulation result (94.49%). All of the above analysis and optimization process demonstrated that the CFD simulation results can not only enhance the understanding of the thermo-chemical performance and of the hydrodynamics in the coal-fired CLC experiment but also be of benefit for the optimization of the experimental operation.

5. Conclusions

In this work, a coal-fired CLC dual circulation fluidized bed system was comprehensively investigated through CFD simulations using the Eulerian two-fluid model. With the aid of the simulation results, the operational characteristics of the reactor are now deeply understood. The simulation results were used to guide the operational optimization of the coal-fired CLC experiment. The main conclusions of this study are listed as follows:

1. The char that is not gasified completely in the FR is the main source of CO₂ leaked into the AR. The overall conversion rate of coal was controlled by the relatively slow char gasification process. Thus the rational design of the reactor is very important for a coal-fired CLC system.

2. Thermal power is one of the most important factors in a coal-fired CLC reactor. The coal feeding rate has a great impact on the superficial gas velocity, which has an obvious effect on the flow pattern. The influence of the coal pyrolysis reaction and the char gasification reaction on the operation of the coal-fired CLC reactor should be reasonably considered during the coal-fired CLC reactor design process.

3. High temperature can effectively improve the gas fuel conversion efficiency and the char gasification efficiency, which contributes to the complete conversion of the fuel.

4. CFD simulation can truly provide the important information of the hydrodynamics and chemical reactions in CLC reactors, which was helpful for optimizing the operation condition.

Acknowledgement

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References


