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CFD Simulations of Chemical Looping Combustion in a Packed Bed and a Bubbling Bed Fuel Reactor

Guanglei Ma
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WASHINGTON UNIVERSITY IN ST. LOUIS
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CFD Simulations of Chemical Looping Combustion in a
Packed Bed and a Bubbling Bed Fuel Reactor
By
Guanglei Ma

A thesis presented to the School of Engineering of
Washington University in St. Louis in partial fulfillment of the
Requirements for the degree of
Master of Science

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ABSTRACT OF THE THESIS

CFD Simulations of Chemical Looping Combustion in a Packed Bed and a Bubbling Bed Fuel Reactor

by

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Master of Science in Mechanical Engineering

Washington University in St. Louis, 2017

Research Advisor: Professor Ramesh K. Agarwal

Chemical-looping combustion (CLC) is a next generation combustion technology that has shown great promise in addressing the need for high-efficiency low-cost carbon capture from fossil fueled power plants to address the rising carbon emissions. Although there have been a number of experimental studies on CLC in recent years, CFD simulations have been limited in the literature on CLC. The development and confidence in high-fidelity simulations of the CLC process is a necessary step towards facilitating the transition from laboratory-scale experiments to deployment of this technology on an industrial scale. In this research, first the CFD simulations of a CLC packed bed fuel reactor with ilmenite and carbon monoxide are conducted and compared with the experiments of Galucci; the simulations are performed for hot flow with chemical reactions simulating the exact experimental conditions. The previous simulations for this case were conducted for cold flow without chemical reactions. Simulations are performed for the entire sixty minutes of the experimental process and are in good agreement with the experimental data. The second simulation is conducted for a CLC bubbling bed reactor with hematite and methane corresponding to the experiment performed by Weber of NETL. Seventy-five thousand particles are injected to
form the bed and the reactor model is sized to the scale to realize the bed height of the experiment. In order to simulate the bubbling phenomenon and fluid process from beginning to the steady combustion state, Discrete Element Method (DEM) is employed to determine the coordinate & velocity of every particle individually. The entire process is simulated reasonably well when compared to the experiment.
Chapter 1: Introduction

Meeting the energy needs of the people worldwide has been one of the most challenging problems of our time due to rapid increase in population, with needs for rapid economic development. Currently, the annual global energy consumption is nearly equivalent of nine billion tons of crude oil per year, with 1.6% annual growth, of which 90% is fossil fuel. At present, fossil fuels are a primary source of electricity generation. They release a great amount of CO$_2$ in atmosphere, which is the main contributor to the greenhouse effect. In 1896, Arrhenius[1] found the relationship between the global surface temperature of the earth and the concentration of CO$_2$ in the atmosphere. CO$_2$ levels in the atmosphere have risen by almost 30% since then. Since, the dependence on fossil fuel now can not be changed in the near future, Therefore the exploration of alternate combustion technologies that can capture CO2 before is release into the atmosphere has become of vital importance. Chemical looping combustion (CLC) is one Such technology that allows almost pure CO2 capture with low cost and high efficiency.

In traditional combustion, fuel and air are mixed directly and complete the combustion process in the reactor, which releases the complex syngas and makes it harder to separate CO2 from other combustion products. CLC on the other hand employs two reactors to replace the traditional boiler to realize fuel combustion, of which one is the air reactor and the other is the fuel reactor as shown in Fig. 1.1.
An oxygen carrier is needed that circulates between the two reactors; it is reduced in the fuel reactor after combustion and then is re-oxidized in the fuel reactor. Generally, the oxygen carrier consists of a metal oxide and a catalyst. The metal oxide is used to provide oxygen for combustion of fossil fuel in the fuel reactor and the catalyst speeds up the reaction. Metal oxide first goes through reduction reaction with fuel in fuel reactor, which creates CO\textsubscript{2}, H\textsubscript{2}O and reduced metal, as Eq. (1.1) shows. Then it is transferred into the air reactor to have oxidation reaction and gets oxidized, given in Eq. (1.2). The oxidized carrier is then transferred to the fuel reactor completing the loop. Eq. (1.3) shows the combustion of fossil fuel in CLC process. He is the heat released in the combustion.
In the CLC process, the exhaust gases released from the fuel reactor are CO₂ and H₂O. Thus, a high concentration almost pure CO₂ is captured in CLC with high efficiency and reduced cost which can then be sent for sequestration and for creation of chemical products.

To date, majority of research on CLC has been conducted in laboratory scale experiments. There have been very few pilot scale experiments and hardly any industrial scale plants. There are very few process simulations studies reported using ASPEN Plus and detailed simulation of reactor hydrodynamics and multiphase flow are even fewer.

It is time therefore to employ the computational fluid dynamics technology (CFD) to simulate the CLC process and validate the methodology against the experimental data so that the validated CFD tools can be used for evaluating the performance of industrial scale CLC plants. In this thesis, CFD simulations are performed corresponding to the experiment of Gallucci et al.[2] and the experiment of Weber et al.[3]. It is expected that the results of this work should provide a deeper understanding of CLC process and help in future design of CLC reactors.
Chapter 2: Simulation of Packed Bed with Hematite and CO

2.1 Introduction

Packed bed is one kind of bed used in a CLC fuel reactor, in which the reactor is filled with solid particles of diameters of 2~15mm. The inlet gas velocity is very low so that the particles almost don’t move. Thus, the internal flow is laminar and steady. Generally, the reactions in experiments with CLC take a long time, for example, in Galucci et al.’s [2] experiment, most reaction takes about an hour. CFD simulations for this experiment are performed. It should be noted that it is hard to simulate the entire reaction process in the CFD simulations due to the limitations on the computational resources. Nevertheless, with some minor simplifications, it is possible to obtain excellent results as described below.

2.2 Modeling Approach and Numerical Solution Procedure

2.2.1 Modeling Equations

The geometry of the reactor and the mesh inside it are built using the WORKBENCH. The simulations are conducted with the commercial CFD simulation package ANSYS FLUENT, release version 17.0. The flow in the packed bed experiences both the chemical reactions and heat transfer. As a result, all equations of fluid dynamics, the Navier-Stokes equations, the energy equation and the continuity equation need to be solved in the simulation. The solid particles are packed and are considered non-moving for simplification, thus the equations for the solid motion are not employed.
The fluid physics is modeled using the hydrodynamics equations described below:

**Continuity Equation**

The volume fraction of each phase is calculated from the continuity equation:

\[
\frac{1}{\rho_{rq}} \left( \frac{\partial}{\partial t} (\alpha_q \rho_q) + \nabla \cdot (\alpha_q \rho_q \vec{v}_q) \right) = \sum_{p=1}^{n} (\dot{m}_{pq} - \dot{m}_{qp})
\]  

(2.1)

where \(\rho_{rq}\) is the phase density or the volume averaged density of the \(q\)th phase in the solution domain. The solution of this equation for each phase along with the condition that the volume fractions sum to one, allows for the calculation of the primary-phase volume fraction. This treatment is common to all fluid-fluid and granular flows.

**Species Transport Diffusion**

In ANSYS Fluent, the local mass fraction \(i\) of each specie is determined by solving the convection-diffusion equation for the \(i\)th specie as shown below:

\[
\frac{\partial}{\partial t} (\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + R_i + S_i
\]  

(2.2)

where \(R_i\) is the net rate of production of specie \(i\) by chemical reaction (described later in section 2.2.5) and \(S_i\) is the rate of creation by the dispersed phase and external sources. \(\vec{J}_i\) is the diffusion flux of specie \(i\). Eq. (2.2) is solved for N-1 species where N is the total number of fluid phase chemical species present in the system. Since the mass fraction of the species must sum to unity, the mass fraction of \(N_{th}\) specie is determined as one minus the sum of the N-1 species mass fractions. To minimize numerical error, the \(N_{th}\) specie is selected as the specie with the largest mass fraction, e.g. \(N_2\) when the oxidizer is air.
Mass Diffusion in Laminar Flows

\( J_i \) is the diffusion flux of species \( i \), which arises due to gradients of concentration and temperature.

By default, ANSYS Fluent uses the dilute approximation (also called Fick’s law) to model mass diffusion due to concentration gradients, under which the diffusion flux can be written as:

\[
\vec{J}_i = -\rho D_{i,m} \nabla Y_i - D_{T,i} \frac{\nabla T}{T}
\]

Here \( D_{i,m} \) is the mass diffusion coefficient for specie \( i \) in the mixture, and \( D_{T,i} \) is the thermal diffusion coefficient.

Energy Equation

The energy equation can be expressed as:

\[
\frac{\partial}{\partial t} (\rho E) + \nabla \cdot (\vec{v}(\rho E + p)) = \nabla \cdot (k_{eff} \nabla T - \sum h_j J_j + \tau_{eff} \cdot \vec{V}) + S_h
\]

The energy equation is shared among the phases, where \( E, T, k_{eff}, \vec{v} \) and \( \rho \) are the energy, mass-averaged temperature, effective thermal conductivity, velocity and density. \( h_j \) and \( J_j \) are the enthalpy and diffusion flux of species \( j \). \( S_h \) is the source term, which contains contributions from radiation and other volumetric heat sources.

Species Transport in the Energy Equation

For many multicomponent mixing flows, the transport of enthalpy due to species diffusion can have a significant effect on the enthalpy field and should not be neglected. The conservation equation for enthalpy can be written as:

\[
\nabla \cdot \left[ \sum_{i=1}^{n} h_i \vec{J}_i \right] = 0.
\]
Here the $h_i$ is the sensible enthalpy for specie $i$, and $J_i$ is the diffusion flux of the species $i$ due to concentration gradients in the flow field.

In particular, when the Lewis number

$$Le_i = \frac{k}{\rho c_p D_{i,m}}$$

(2.6)

for any species is far from unity, neglecting this term can lead to significant errors. ANSYS Fluent will include this term by default. In Eq. (2.1), $k$ is the thermal conductivity, $\rho$ is the density, $C_p$ is the specific heat at constant pressure and $D_{i,m}$ is the difference coefficient of species $i$. 
2.2.2 Model Parameters

Figure 2.1 shows the geometry of the packed bed reactor used in the experiment of Gallucci et. al [2]. The simulation model is built according to the experiment with 1:1 ratio. The simulation parameters are listed in Table 2.1. In this model, the central blue space in Fig. 2.1 is filled with the oxygen carrier G11 containing 75% ilmenite and 25% Mn$_2$O$_3$. The upper and lower spaces are filled with inert material (clay pellets) of the same size and shape as ilmenite. Since the G11 oxygen carrier in the middle is of pellet shape, according to density calculation it takes about 27.04% of the whole volume in the middle of the reactor.

<table>
<thead>
<tr>
<th>Table 2.1 Modeling parameters for packed bed reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>internal height of reactor</td>
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<tr>
<td>internal diameter of reactor</td>
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<tr>
<td>particle mass</td>
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<tr>
<td>particle composition</td>
</tr>
<tr>
<td>particle size</td>
</tr>
<tr>
<td>ilmenite density</td>
</tr>
<tr>
<td>Mn$_2$O$_3$ density</td>
</tr>
<tr>
<td>primary phase</td>
</tr>
<tr>
<td>secondary phase</td>
</tr>
<tr>
<td>inlet gas composition</td>
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<tr>
<td>gas volume flux</td>
</tr>
<tr>
<td>inlet boundary condition</td>
</tr>
<tr>
<td>outlet boundary condition</td>
</tr>
<tr>
<td>time step size</td>
</tr>
<tr>
<td>models</td>
</tr>
<tr>
<td>numerical scheme</td>
</tr>
</tbody>
</table>

Figure 2.1 Reactor geometry
2.2.3 Mesh Parameters

The computational model is meshed with 3mm square structured mesh, as shown in Fig. 2.2. Every grid cube is 9e-6 m³ with same shape and size. Since the target CLC experiment lasts for about one hour, the number of mesh cell should be minimum without compromising accuracy. The total number of mesh elements is 11067. Table 2.2 shows the mesh parameters.

Table 2.2 Mesh parameters

<table>
<thead>
<tr>
<th>Volume statistics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>minimum volume (m³)</td>
<td>9.000000e-06</td>
</tr>
<tr>
<td>maximum volume (m³)</td>
<td>9.000000e-06</td>
</tr>
<tr>
<td>total volume (m³)</td>
<td>9.954000E-02</td>
</tr>
<tr>
<td>minimum face area (m²)</td>
<td>2.996390E-03</td>
</tr>
<tr>
<td>maximum face area (m²)</td>
<td>3.000000E-03</td>
</tr>
<tr>
<td>Nodes</td>
<td>11616</td>
</tr>
<tr>
<td>Elements</td>
<td>11067</td>
</tr>
</tbody>
</table>

2.2.4 Boundary Conditions

Since the reactor is heated and then dynamically operated with a sequence of reduction and oxidation steps, the initial temperature is set at 1123K and the wall boundary condition is set as adiabatic (heat flux = 0 w/m²). The gas enters at the bottom of reactor and exits from the top of the reactor. The inlet boundary condition is velocity-inlet with magnitude 0.053466 m/s, which is calculated from the experimental data of flow rate = 40L/min, in a direction normal to boundary. The species concentrations are: 30%CO+15%CO₂+55%N₂. The gage pressure is 0 Pa. The outlet boundary condition is set as pressure outlet.
2.2.5 Reaction Rate

Zhao and Shadman[4] conducted a series of experiments on reaction between FeTiO₃ and CO and obtained the rate coefficient curve with temperature as shown in Fig. 2.3.

Using the Arrhenius equation, the pre-exponential factor and activation energy can be calculated as 3 and 4.13E+07 J/kgmole respectively. However, in Gallucci et. al's experiment[2], a mixture of FeTiO₃ and Mn₂O₃ is packed, in which Mn₂O₃ serves as a catalyst for the reaction as noted by Zhang et. al [5]. Depending on the catalyst effect of Mn₂O₃ and after doing some calibration, the five times the pre-exponential factor of Arrhenius shows great consistency with the experimental data. Therefore, the pre-exponential factor of 15 and activation energy 4.13E+07 J/kgmole are needed in the final simulation.
2.3 Simulation Results

Figure 2.4 shows the comparison of outlet gas mole fraction between the experiment and the simulation. As shown in the experimental plot in Fig. 2.4, there is an about two-minute horizontal line, which is the time for gas to go through the whole reactor from bottom inlet to top outlet. After that, as a product of reaction, the CO₂ comes out first and reaches its peak. It reacts with FeTiO₃, but can’t use up all the CO as it passes through the reactor and then exhausts it at about 30 minutes. During the reaction, the CO goes up gradually and reaches a stable value of 23%. On the other hand, CO₂ goes down gradually and reaches a stable value at about 14%. The reason the curves of CO and CO₂ look very similar is that one mole of CO creates one mole of CO₂. The simulation curves show good agreement with the experimental data. The CO and CO₂ curves cross each other at about 23 minutes and become stable at about the same time and acquire a constant value.

![Figure 2.4 Outlet gas mole fractions of CO and CO₂ in experiment and simulation](image-url)
Since the reaction takes place during the first 30 minutes, the detailed reaction process is shown in Fig. 2.5 only for the first thirty minutes. Fig. 2.5 shows the mass fraction of FeTiO$_3$ in the reactor, illustrating the process of FeTiO$_3$ depletion during the reaction. FeTiO$_3$ pellets are fixed at the middle part of reactor. The CO gas comes from the bottom and consumes the lower portion of FeTiO$_3$ first. Then, the upper part of FeTiO$_3$ also begins to disappear, and almost all FeTiO$_3$ is consumed by 30 minutes. Since a phase diffusion model is applied in this case, FeTiO$_3$ doesn't finally disappear at the upper black line, which is the boundary between the fuel area and the clay.

![Figure 2.5 Mass fraction of FeTiO$_3$](image)

Figure 2.5 Mass fraction of FeTiO$_3$
Figure 2.6 shows the mass fraction of Fe. It shows how Fe, as the product of reaction, appears at the bottom of the fuel area and accumulates at the top. By examining Fig. 2.4 and Fig. 2.5, it can be determined what happens to the solid phase in the whole reaction process. The simulation is in reasonable agreement with the experimental data.

![Figure 2.6 Mass fraction of Fe](image)
Figure 2.7 shows the mole fraction of CO. It shows that the CO is almost all consumed once it reacts with the FeTiO₃ at the bottom of fuel area. This is the reason why the mole fraction of CO doesn’t show any change for about 2 minutes in the experiment. As time goes on, the FeTiO₃ inside two reactor continues to be consumed and finally additional CO can’t be further used up when passing through the reactor. Thus, the curve of mole fraction of CO in Fig. 2.4 goes up gradually. At about 30 minutes, mole fraction of CO in the reactor doesn’t change any more, which indicates the end of the reaction.

![Figure 2.7 Mole fraction of CO](image)
Figure 2.8 shows the mole fraction of CO$_2$. At the beginning of the reaction, there is a sharp change in CO$_2$ at the bottom of the fuel reactor. The reason is that there is enough FeTiO$_3$ inside the reactor which is able to turn all the CO into CO$_2$ immediately reacting with it. As the times goes on, the FeTiO$_3$ disappears gradually but it can’t consume all the CO passing by, as a result the mole fraction of CO increases while the mole fraction of CO$_2$ gradually decreases, and finally reach the same value same at the inlet.
Figure 2.9 shows the temperature of the fluid phase. The reaction between FeTiO$_3$ and CO is an exothermic reaction which absorbs heat. Thus, the temperature of fluid phase can provide a good development of the reaction process. As Fig. 2.9 shows, the temperature begins to drop first at the bottom of the fuel area. Then it keeps on increasing finally covering the whole fuel area. This verifies that the reaction begins at the bottom of fuel area, then covers larger gradually, and finally ends at about 30 minutes. The colder fluid area at the bottom also rises up. The reason for it is that the gas at the inlet is preheated to 1273K. Thus, all the gas passing through the reactor cools down by the reaction first, then warm up again before exiting the reactor.
Figure 2.10 shows the fluid temperature change at different heights in the reactor. Since 0.2 m height is below the fuel area and is not affected by the reaction, the temperature doesn’t change and remains at 1273K, which is the same as the inlet gas temperature. At higher heights, the temperature decreases first and then increase with time. The reason is that the gas firstly cools down at the start of the reaction, then warms up by the following gas after FeTiO₃ is used up gradually. The higher the height, the larger amount of gas is affected by the exothermic reaction, and therefore the temperature decreases for a larger time before increasing as shown in Fig. 2.10. Thus, if the experiment continues for a long enough time, the reactor will eventually warm to the inlet gas temperature 1273K. Therefore, all temperature curves at different heights in Fig. 2.10 show the trend of finally reaching a temperature of 1273K.
2.4 Conclusion

At the outlet of the reactor, the simulation results show great consistency with the experimental data, from the start of the reaction to the steady state at the end of the reaction. The analysis of maps of fluid phase and solid phase in the reactor demonstrates the reaction process and shows great consistency in the evolution of fluid and solid phase in time. The simplified packed bed model is able to simulate the experimental data with good accuracy and provides the computer calculations in a cost effective manner.
Chapter 3: Simulation of Bubbling Bed with Ilmenite and CH$_4$

3.1 Introduction

In this chapter, simulations are conducted for a bubbling bed reactor with ilmenite and CH$_4$. Compared to the packed bed, bubbling bed has more complex fluid process. The gas inlet velocity in bubbling bed is over the UMF (Minimum Fluidization Speed) and reaches the minimum bubbling speed, which causes the solid particles to continuously create bubbles at the bottom of the reactor. The bubbling greatly increases the mixing rate between the gas and the solid phase and accelerates the reaction process.

Thus, the simulation of the reaction process in a bubbling bed is much more difficult and complex, since it includes multiphase reaction, species diffusion, particles collision, heat transfer and other factors.

3.2 Modeling Approach and Numerical Solution Procedure

For simulations, a fuel reactor of National Energy Technology Laboratory (NETL) is modeled for which the experimental data is available[3][6]. The geometry is modeled in 3D using the ANSYS Workbench, and simulations are conducted with ANSYS FLUENT 17.1.
Discrete Element Method (DEM)

Solid particles in a bubbling bed have complex movement trajectories and affect the hydrodynamic processes. To achieve the accurate simulations, the solid particles need to be tracked separately as a part of the gas-solid multiphase flow. To achieve this, Discrete Element Method (DEM) is employed, which is able to track the position and velocity of every particle individually, and calculates the collision between the particles and that of the particles with the walls.

Fluid Equations

The equations of fluid motion are slightly modified to account for the presence of the solid particles. This is done by including the porosity which is defined to be equal to the volume fraction of the fluid $\alpha_f$ in the computational cell to which the equations are applied. Furthermore, source terms are added in the equations to account for the transfer of mass, momentum, and energy between the phases. Hence, the volume-averaged continuity equation, Navier–Stokes equations, and energy equation for CFD/DEM simulation can be written as:

$$
\frac{\partial}{\partial t} (\alpha_f \rho_f) + \nabla \cdot (\alpha_f \rho_f u_f) = \dot{m}_{sg}
$$

$$
\frac{\partial}{\partial t} (\alpha_f \rho_f u_f) + \nabla \cdot (\alpha_f \rho_f u_f u_f) = -\alpha_f \nabla p_f - \nabla \cdot \tau_f + \alpha_f \rho_f g - K_{sg}
$$

$$
\frac{\partial}{\partial t} (\alpha_f \rho_f E_f) + \nabla \cdot (\alpha_f u_f (\rho_f E_f + p_f)) = \nabla \cdot (k_f \nabla T_f - \sum h_j J_j + (\tau_f \cdot u_f)) + S_h
$$

where $\rho_f$, $u_f$, $p_f$, $E_f$, and $T_f$ are the density, velocity, pressure, internal energy, and temperature of the fluid, respectively, $g$ is the acceleration due to gravity, $k_f$ is the thermal conductivity, and $h_j$ and $J_j$ are the enthalpy and diffusion flux of species $j$. The source term in the momentum equation, $K_{sg}$, is used to couple the solid and gas phases by accounting for the solid–gas momentum exchange from the interphase drag due to the presence of the solid particles. The source
terms in the continuity and energy equations, $\dot{m}_{sg}$ and $S_h$, capture the mass and heat fluxes from the solid to the gas phase due to chemical reactions in the multiphase flow. For a Newtonian fluid, the shear stress tensor, $\bar{\tau}_f$ can be written as

$$\bar{\tau}_f = \mu_f (\nabla \mathbf{u}_f + \nabla \mathbf{u}_f^T) + \left( \lambda_f + \frac{2}{3} \mu_f \right) \nabla \mathbf{u}_f \hat{I} \tag{3.4}$$

where $\mathbf{u}$ is the fluid viscosity.

**Particle Motion Equation**

In the CFD/DEM simulation, each solid particle is tracked individually. The motion of each solid particle is obtained by summing all the forces on the particle and applying the Newton’s second law of motion. The resulting force balance equation, which is integrated to obtain the motion of the solid particle, is given by

$$m_s \frac{d\mathbf{u}_s}{dt} = \sum F_i = F_{gra} + F_{buo} + F_{drag} + F_{pre} + F_{Saf} + F_{Mag} + F_{con} \tag{3.5}$$

where $F_{gra}$ and $F_{buo}$ are bulk forces due to gravity and buoyancy, respectively, $F_{drag}$, $F_{pre}$, $F_{Saf}$, and $F_{Mag}$ are hydrodynamic forces due to momentum transfer between the solid particles and the surrounding fluid, namely, the drag force due to fluid viscosity, the pressure force due to pressure gradient, Saffman lift force due to interparticle friction, and the Magnus force due to particle spin, respectively. Owing to the large difference between the solid particle density and the fluid density, the pressure force can be dropped from Eq. (3.5) without loss of accuracy. The Magnus force can also be dropped because of negligible particle rotation. $F_{con}$ is the contact force on the particles due to collision with other particles or walls. In this work, this contact force is computed using the soft-sphere model, which decouples its normal and tangential components[7]. The normal force on any particle involved in a collision is given by

$$F_{con}^n = (k\delta + \gamma (u_{12} e)) e \tag{3.6}$$
where $k$ is the spring constant of the particle, $\delta$ is the overlap between the particle pair involved in the collision, $\gamma$ is the damping coefficient, $\mathbf{u}_{12}$ is the relative velocity vector of the colliding pair, and $\mathbf{e}$ is the unit vector. Previous research has demonstrated that for large values of $k$, the results with the soft-sphere model are interchangeable with those obtained using a hard-sphere model[11]. The tangential contact force is calculated based on the normal force as

$$F_{\text{con}}^t = \mu F_{\text{con}}^n$$

(3.7)

where $\mu$ is the coefficient of friction is a function of the relative tangential velocity $v_r$ given as

$$\mu(v_r) = \begin{cases} 
\mu_{\text{stick}} + (\mu_{\text{stick}} - \mu_{\text{glide}}) \left( \frac{v_r}{v_{\text{glide}}} - 2 \right) \left( v_r/v_{\text{glide}} \right) & \text{if } v_r < v_{\text{glide}} \\
\mu_{\text{glide}} & \text{if } v_r \geq v_{\text{glide}} 
\end{cases}$$

(3.8)

The contact force of a collision pair is evaluated as shown in the Fig. 3.1.

![Figure 3.1 Schematic of particle collision model for DEM](image)

**Interphase Momentum Exchange**

For multiphase flow modeling using the coupled CFD/DEM solver, it is crucial to evaluate the momentum exchange between the solid and fluid phases. This is done by considering the drag force. The transfer of momentum from the fluid to a solid particle as it moves through each cell in the
computational domain is attributed to the drag force exerted on the particle by the fluid, and is modeled as

$$F_{\text{drag}} = F_D(u_f - u_p)$$  \hspace{1cm} (3.9)

where $u_f$ is the fluid velocity, $u_p$ is the particle velocity, and $F_D$ is the net drag coefficient. The net drag coefficient can be obtained from

$$F_D = \frac{18\mu}{\rho_p d_p^2} \frac{C_D \text{Re}_p}{24}$$  \hspace{1cm} (3.10)

where $\mu$, $\rho_p$, and $d_p$ are the viscosity of the gas, the density, and the diameter of the solid particle, respectively. $C_D$ and $\text{Re}_p$ are the particle drag coefficients for a sphere and the relative Reynolds number based on the particle diameter, respectively. $\text{Re}_p$ is defined as:

$$\text{Re}_p = \frac{\rho_f d_p |u_f - u_p|}{\mu}$$  \hspace{1cm} (3.11)

The corresponding momentum transfer from the solid phase to the gas phase is incorporated by adding the source term $K_{sg} = \beta_{sg}(u_f - u_p)$ in the momentum equation for the gas phase. $\beta_{sg}$ is the solid–gas exchange coefficient and is obtained by using the relation

$$\beta_{sg} = \frac{\alpha_p \rho_p}{\tau_p} f$$  \hspace{1cm} (3.12)

where $\alpha_p$ is the volume fraction of the solid phase in the cell, $\tau_p$ is the particulate relaxation time defined as $\tau_p = \rho_p d_p^2 / 18 u_f$ and $f$ is the drag coefficient. The drag coefficient can be modeled using various empirical relations. The Wen-Yu drag law[7] is chosen in this work.

**Parcel Concept**

To track each individual particle is computationally very demanding in a conventional CFD/DEM approach. The total number of particles increases exponentially as the particle size becomes smaller. For instance, in a lab-scale CLC system, the particle number is around $7 \times 10^{11}$, which is far beyond
the capacity of current computational resources[8]. Therefore, the parcel methodology proposed by Patankar[11] is employed in this thesis to overcome this problem.

According to the parcel concept, one parcel of particles can represent a group of particles with the same properties (e.g. size and density). The mass used in collisions is the whole parcel rather than a single particle. By summing the mass and volume of each individual particle, the total mass \( m \) and volume \( V_p \) of the parcel can be obtained. The radius of the parcel is thus determined by the mass of the entire parcel and the particle density.

For a given point in the fluid flow, the driving force of a parcel due to fluid forces is assumed to be the same as the sum of the fluid forces acting on the group of particles the parcel represents, the force is given by:

\[
    f_{f,p} = \sum_{i=1}^{N_p} f_{f,i}
\]  

where \( N_p \) is the number of particles contained in a parcel, and \( f_{f,i} \) is the total fluid force acting on a particle “\( i \)”. The acceleration due to inter-particle collision forces and particle-wall collisions forces are calculated according to the properties of the parcel of particles.
### 3.2.1 Model Parameters

Figure 3.2 shows the geometry of the bubbling fuel bed, the experiment for which were conducted by Weber at NETL (National Energy Technology Laboratory)[6]. The reactor is a 1.543m high cylinder with 0.203m inner diameter. There is a 0.08m diameter pipe on its side as the gas outlet. In the experiment, there are two tubes plugged in the reactor for particles inlet and outlet as shown in Fig 3.2. However, since research focuses only on the fluid process for the first 3 second of the experiment, the tubes are not considered here. Table 3.1 shows physical and numerical parameters used in the simulation.

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>internal height of reactor</td>
<td>1543 mm</td>
</tr>
<tr>
<td>internal diameter of reactor</td>
<td>0.203 mm</td>
</tr>
<tr>
<td>particle mass</td>
<td>3.3 kg</td>
</tr>
<tr>
<td>particle composition</td>
<td>100% hematite (Fe₂O₃)</td>
</tr>
<tr>
<td>particle size</td>
<td>238 μm</td>
</tr>
<tr>
<td>Fe₂O₃ density</td>
<td>5240 kg/m³</td>
</tr>
<tr>
<td>Mn₃O₅ density</td>
<td>7870 kg/m³</td>
</tr>
<tr>
<td>primary phase</td>
<td>fluid: CH₄ and N₂</td>
</tr>
<tr>
<td>secondary phase</td>
<td>solid: Fe₂O₃, Fe</td>
</tr>
<tr>
<td>inlet gas composition</td>
<td>7%CH₄+93%N₂</td>
</tr>
<tr>
<td>inlet gas pressure</td>
<td>17500 Pa</td>
</tr>
<tr>
<td>gas inlet velocity</td>
<td>0.3 m/s</td>
</tr>
<tr>
<td>inlet boundary condition</td>
<td>velocity-inlet</td>
</tr>
<tr>
<td>outlet boundary condition</td>
<td>pressure-outlet</td>
</tr>
<tr>
<td>time step size</td>
<td>0.001 s</td>
</tr>
<tr>
<td>models</td>
<td>Eulerian model, implicit formulation, energy equation, laminar viscous flow model, species transport model, volumetric reactions, diffusion energy source, thermal diffusion, bubbling bed, DEM Collision</td>
</tr>
<tr>
<td>numerical scheme</td>
<td>phase coupled SIMPLE least squares cell based for gradient, second order upwind for momentum, QUICK for volume fraction</td>
</tr>
</tbody>
</table>

![Figure 3.2 Geometry of the reactor](image)
ANSYS Fluent 17.1 is used in the simulation. Since all the parameters in Table 3.1 can be easily included in Fluent as input parameters except Fe₂O₃ and Fe, the required properties of Fe₂O₃ and Fe are directly from the data available from NIST (National Institute of Standards and Technology).

DEM Collision model is employed in Fluent which enables the simulation to track and calculate the coordinate and velocity of every particle in the reactor individually, which is necessary to track the bubbling due to particles. The DEM model enables the simulation to compute the reaction between the fluid phase and the solid particle, which is necessary for the simulation of reaction in this case.
3.2.2 Mesh Generation and Parameters

The geometry is built in ANSYS Workbench, and structured mesh is generated in the reactor except in the outlet region where an unstructured mesh created. Figure 3.3 shows the geometry of reactor and structured mesh used in the simulation. Since the parcel diameter is 0.002, and the mesh size must be limited to 5 to 10 times of the parcel size, the mesh is generated automatically in ANSYS Workbench by limiting the sizing to 0.01m to keep the accuracy in the simulation. Table 3.2 shows the parameters of the generated model.

<table>
<thead>
<tr>
<th>Table 3.2 Mesh parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volume statistics</strong></td>
</tr>
<tr>
<td>minimum volume (m3)</td>
</tr>
<tr>
<td>maximum volume(m3)</td>
</tr>
<tr>
<td>total volume (m3)</td>
</tr>
<tr>
<td><strong>Face area statistics</strong></td>
</tr>
<tr>
<td>minimum face area (m2)</td>
</tr>
<tr>
<td>maximum face area (m2)</td>
</tr>
<tr>
<td><strong>Nodes</strong></td>
</tr>
<tr>
<td><strong>Elements</strong></td>
</tr>
</tbody>
</table>

3.2.3 Boundary Conditions

The composition of inlet syngas consists of 7%CH₄ and 93%N₂, of which CH₄ is the main gas that participates in the reaction. According to Weber et. al's[3] paper, the initial CH₄ max conversion is set to 50%. For the inlet velocity, there is no formula that can calculate the minimum bubbling velocity at present. Girimonte et. al[8] have conducted a series of experiments to determine the
relationship between the minimum fluidized velocity and the minimum bubbling velocity, and found that the latter is about 1.2~1.5 times to former depending on the particle diameter[8]. Since only the minimum fluidized velocity is mentioned in Weber et. al’s[3] paper, which is about 0.15m/s after rescaling, the inlet velocity is taken to be 0.3 m/s here. In the experiment, the syngas was preheated before injection, its temperature is therefore set at 1273K, same as the temperature inside reactor. From the pressure plot in [6], the gauge pressure is 17500 Pa. The boundary condition on the wall of the reactor is set as adiabatic (heat flux = 0 w/m2).

3.2.4 Reaction Rate

Monazamk et. al[9] conducted a series of experiments to determine rate of reaction between Fe₂O₃ and CH₄. The temperature dependence curve of the reaction rate is shown in Fig 3.4. Using the Arrhenius equation, the pre-exponential factor is calculated as 133 and activation energy as 3.93E+07 J/kgmol.
3.3 Simulation Results

Figure 3.5 CH₄ mole fraction at outlet in experiment

Figure 3.5 shows the CH₄ mole fraction at the outlet of the reactor in the experiment. Since the experimental data has slight oscillations, a fitting curve is applied to the experimental data. The reaction rate reaches its peak at the beginning, when Fe₂O₃ is at its highest fraction. After that, the reaction rate keeps falling down till the end of the experiment.
Figure 3.6 shows the mole fraction of CH$_4$ at reactor outlet. Due to limitation of computational resources, only first 3 seconds of simulation are conducted. As a result, it is difficult to compare the results with the orange experimental data line in Fig. 3.6. Therefore, the red line in Fig 3.6 showing fitting curve to the experimental data is used to compare the simulation shown in blue line; a satisfactory agreement between the red experimental data line and blue simulation line can be noticed.

![Figure 3.6 Comparison of mole fraction of CH$_4$ between the experiment and simulation](image-url)
Figure 3.7 shows the initial volume fraction of solid phase. About 75k particles are injected at a height of 0.2m from the bottom at 1E-08s. The simulation begins after 0.8s, which is the time needed for the particles to settle down at the bottom of reactor. As shown in Fig 3.7, almost all particles settle down naturally and achieve greater than 50% concentration, which is necessary for particles to create a bubbling bed.
Figure 3.8 shows the volume fraction of solid phase, which is the best way to show the bubbling phenomenon. Since the volume fraction of solid phase is relatively high after initial particles settling down period of 0.8s, the bubbling bed takes about 0.5s after initialization to reach its steady bubbling state. After that, bubbles keep forming at the bottom and breaking at the upper surface of the bubbling bed as shown in Fig 3.8.
Figure 3.9 shows the pressure variation of the solid phase in time. The pressure has the biggest change before 0.5s which is the time required for the when bubbling bed to become steady. It can be seen that the bubbling phenomenon doesn’t have significant effect on the pressure of the solid phase inside the reactor. The pressure decreases with height as expected since it is a result of the gravity of the particles.
Figure 3.10 shows the velocity magnitude of the solid phase. The highest velocity in the reactor occurs before the formation of the steady bubbling bed. After that, the high velocity appears during the bubbling. This is because the bubbles rise faster than rest of the fluid.
Figure 3.11 shows the net force acting on the solid phase. Since the formation of bubbles pushes other particles away, the force is always concentrated between the bubbles and the reactor wall. Since the area occupied by bubbles has large volume of gas, the particles inside them do not collide with the other particles in a significant manner. As a result, there is lower force concentration in these areas.
Figure 3.12 shows the pressure variation of gas phase in time. As the Figure shows, there is higher gas pressure always at the bottom, due to denser concentration of particles at the bottom. As the particles rise the pressure increases with height. However, it appears that the bubbling phenomena doesn’t have a significant effect on gas phase pressure.
Figure 3.13 shows the velocity of the fluid phase. At the bottom part of the reactor, there is higher velocity and formation of bubbles. Highest velocity occurs at the gas outlet due to much smaller exit area compared to the cross-sectioned area of the reactor.
Figure 3.14 shows the temperature of the fluid phase. The reaction is an exothermic reaction. Therefore, temperature decreases at the bottom of the reactor first, as \( \text{Fe}_2\text{O}_3 \) and \( \text{CH}_4 \) get in contact. Then as the reaction proceeds, the temperature begins to decrease in upper parts of the reactor gradually, while the gas reaches the outlet in 3s. Since there is highest concentration of \( \text{Fe}_2\text{O}_3 \) and \( \text{CH}_4 \) at the bottom of the reactor, reaction is highest there and the temperature is lowest.
Figure 3.15 shows the mole fraction of CO\(_2\). CO\(_2\) is produced due to reaction between CH\(_4\) and Fe\(_2\)O\(_3\); thus it appears at the bottom of the reactor first, then rises up gradually, and finally reaches the gas outlet. In Fig. 3.15, one can notice some bubbles at the bottom of the reactor. Although bubbles constitute volume fraction of fluid, however there are not enough Fe\(_2\)O\(_3\) particles in there, which limits the reaction inside the bubbles. Thus, the bubbles in have lower concentration of CO\(_2\). In the upper part of the reactor, there is formation of a vortex which transfers CO\(_2\) to lower part of the reactor due to recirculating motion. However, most CO\(_2\) escapes from the gas outlet and as a result the upper vortex has lower concentration of CO\(_2\).
Figure 3.16 shows the mole fraction of $N_2$. The reactor contains 100% $N_2$ before the reaction begins, thus the upper part of the reactor is full of high concentration of $N_2$. As the reaction proceeds, $N_2$ is pushed up gradually, and most escapes through the gas outlet. Only the part of the reactor that is higher than the gas outlet contains $N_2$, and the vortex there pushes $N_2$ to a lower level again.
Figure 3.17 shows the streamlines of the fluid phase velocity. At the bottom of the reactor, the particles create disturbance in the fluid, which generates velocity that accelerates the mixing between the solid and the fluid phase. In the central part of the reactor, the gas moves steadily upward can be seen by the straight streamlines and the characters of the flow in laminar. In the upper part of the reactor, a vortex is formed, which moves the gas that cannot escape through the gas outlet to a lower level in the reactor.
3.4 Conclusion

The simulations of bubbling bed reactor using the CFD/DEM model are in good agreement with the experimental data. The CFD/DEM model reactions and the multi-phase model are taken into consideration. The 3D simulations provide detailed results for the reaction process as well as the hydrodynamics inside the reactor, which is not easily obtained by the experimental methods. It is expected the simulation research done in this chapter should be helpful in future work on bubbling bed reactors.
Chapter 4: Conclusion

In this thesis, the simulation results for two typical chemical looping combustion reactors are obtained using ANSYS Fluent 17.1. The first case considered is the two dimensions simulation of a packed bed reactor. By taking the advantage of the fact that in packed bed the velocity at the inlet is low and therefore can hardly move the particles inside the packed bed, the simulation ignores the individual particle characteristics and treats the solid phase as a whole block; this packed bed model simplifies the simulation and greatly accelerate the calculation speed. Due to the simplification, compared to the traditionally simulation which can only be conducted for a few seconds, the present simulation is able to cover the entire 60 minutes of the experimental process and keep the high accuracy against the experimental data at the same time.

The second case considered is the three dimensions simulation of a bubbling bed reactor. To simulate the bubbling phenomena in the reactor, the CFD/DEM is employed to track the coordinate and velocity of every particle individually, and 75k particles are injected in the reactor to create a suitable height for the bubbling bed. The outlet gas composition obtained from the simulation is very close to the experimental data. All results for fluid and solid phase composition, and pressure and velocity field show great consistency with each other during the entire reaction process. the details of flow field could not be compared because of lack of experimental data.
References


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Degrees

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