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THEORY OF GRANULAR FLOW

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HYDRODYNAMICS ON CHEMICAL LOOPING COMBUSTION USING MULTIPHASE CFD WITH KINETIC THEORY OF GRANULAR FLOW

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ABSTRACT

The fundamental knowledge of multiphase reactive hydrodynamics of the gas-solid flow is essential for the design, optimization, and operation of industrial reactors. The multiphase computational fluid dynamics (CFD) model with the kinetic theory of granular flow, MFIX, developed earlier at the National Energy Technology Laboratory have been adapted to describe a fuel reactor of chemical looping combustion (CLC) processes. To understand hydrodynamics the chemical kinetics and mass transfer in the fuel reactor have been developed, where the reduction reaction is the first order of methane gas and the oxygen in metal oxygen carriers transfer to gas phase. The fuel conversion rate can be varied by reaction temperature, initial static bed height, and inlet velocity of fuel. The reaction temperature in our earlier work was an important factor for the efficient design of the fuel reactor. In this study, the increase of the initial static bed height for catalyst in the fuel reactor results in the enhancement of the fuel conversion rate at a constant temperature. Successful development of validated CLC models will provide the needed base for the development of such a technology.

INTRODUCTION

The world consumption of energy continues to increase at a rate of about 2% per year. This trend is expected to increase apace with the economic growth through the 21st century even if the efficiency of energy conversation is increased. The forecast of future energy demand shows that the worldwide energy system will rely mainly on fossil fuels at least at short or medium term. Hence, it is important to develop new technologies during this decade that will reduce the impact of the global climate change on the continued fossil energy use while cleaner energy source are being developed. Chemical looping combustion (CLC), having potential for realizing very efficient and low cost CO₂ capture, is a good candidate for fossil fuel combustion in power plants. This basic concept for CO₂ capture can be extended to industrial areas such as cement plants, iron-steel making works, refinery plants, ethanol plants, etc.

CLC produces a relatively pure stream of CO₂ ready for compression and storage in geological settings. Furthermore, CLC also minimizes NO_x emissions since the fuel combustion is flameless in the absence of nitrogen. Hydrogen as a co-product can be obtained from CLC.

Recent studies in this novel technology (1-7) have been focused in three distinct areas: techno-economic evaluations, integration of the system into power plant concepts, and experimental development of oxygen carrier metals. Reactor design, modeling, and hydrodynamics are critical issues that must be solved before a reliable scale-up is possible. Jung and Gamwo (8) showed that the multiphase CFD fluid dynamic modeling is a useful tool for the systematic analysis of the fuel reactor in CLC. The grid independency of the numerical simulation using MFX code has been extensively studied (8, 12). This study is an extension for estimating the reactive hydrodynamics using the multiphase CFD model. We found that the initial static bed height for catalyst is an important factor for a methane fuel conversion, hence for an optimum process in the fuel reactor.

MULTIPHASE HYDRODYNAMIC MODEL

The hydrodynamic approach to multiphase flow systems is based on the principles of mass conservation, momentum balance and energy conservation for each phase (9). The code used in this research is a public domain computer program MFX (Multiphase Flow with Interphase eXchanges; 10) developed at the National Energy Technology Laboratory (NETL) and is available on the internet at <http://www.mfix.org>. The hydrodynamic equations for gas phase and solid phase solved in the MFX code for transient and isothermal fluid-solids are given as follows:

Continuity equations(k = gas, solids):

$$\frac{\partial(\rho_k \epsilon_k)}{\partial t} + \nabla \cdot (\rho_k \epsilon_k v_k) = \dot{m}_k \quad (1)$$

$$\frac{\partial(\rho_k \epsilon_k y_k^{jx})}{\partial t} + \nabla \cdot (\rho_k \epsilon_k v_k y_k^{jx}) = \dot{m}_k^{jx} + r_k^{jx} \quad (2)$$

Momentum equations(k = gas, solids):

$$\frac{\partial(\rho_k \epsilon_k v_k)}{\partial t} + \nabla \cdot (\rho_k \epsilon_k v_k v_k) = \epsilon_k \rho_k F_k + \nabla \cdot \bar{\tau}_k + \beta_{km} (v_m - v_k) + \dot{m}_k v_k \quad (3)$$

where, \dot{m}_k^{jx} is the rate of mass transfer of j xth species between the phase and r_k^{jx} is the rate of production of the j xth species in each phase by homogeneous or heterogeneous reactions. The sum of all reactions at each phase and total mass transfer between the phases must be zero. The sum of weight fraction of all chemical species at each phase must be one. The volume fraction of each phase must be sum to one.

To allow closure of the above equations the constitutive closure models are used in the MFX code, as described in (8). Where, the fluctuating energy equation based on kinetic theory of granular flow (9, 11) was added to calculate the motion in solid

phase. The granular temperature $(\theta = \frac{1}{3} \langle C^2 \rangle)$ is defined as the mean of the squares

of a particle velocity fluctuation(C). Granular temperature in this study was estimated from an algebraic expression based on the kinetic theory of granular flows derived by Lun *et al.* (11). Neglecting the convection and diffusion contributions of granular flows and by assuming that the granular temperature is dissipated locally, the sum of the generation and dissipation terms of granular flows (10) can be written as

$$\left(\overline{PI} + \tau_s\right) : \nabla \vec{v}_s - \gamma = 0 \tag{4}$$

where, P (solid pressure), τ (solids phase granular stress tensor), and γ (dissipation) are a function of granular temperature described in the MFI code (10). The stress tensor for the bubbling beds is given by viscous terms described in references (8, 10). A review of the literature (1, 2, 3, 5) showed that the endothermic chemical reaction in the fuel reactor is generally accepted for metal oxygen carrier with methane gas as fuel.



The reduction reaction produces only carbon dioxide and water vapor, CO_2 can be easily separated and collected by cooling the exhaust gas. The reactions rate of j th species in the species equations are given by

$$r_i^{jx} = \sum_{i=1}^{IX} \alpha^{jx} M^{jx} r \tag{6}$$

We assumed that the reaction rate is first order with respect to CH_4 and is given as follows:

$$-r = \kappa S_o \varepsilon_g \frac{\rho_g x_{CH_4}}{M^{CH_4}} \left(\frac{mol}{cm^3 \cdot sec}\right) \tag{7}$$

where, α^{jx} represents the stoichiometric coefficient of j th species in the fuel reactor, M^{jx} represents the molecular weight of j th species, and x_{jx} represents the weight percent of j th species in each phase.

The reaction rate constant (2) is

$$k = 3.27 e^{\left(\frac{-8854.1}{RT}\right)} \left(\frac{cm}{s}\right) \tag{8}$$

The surface area for reaction in the metal oxygen carrier is

$$S_o = \frac{6.0}{d_p} \varepsilon_s x_{O_2} \left(\frac{1}{cm}\right) \tag{9}$$

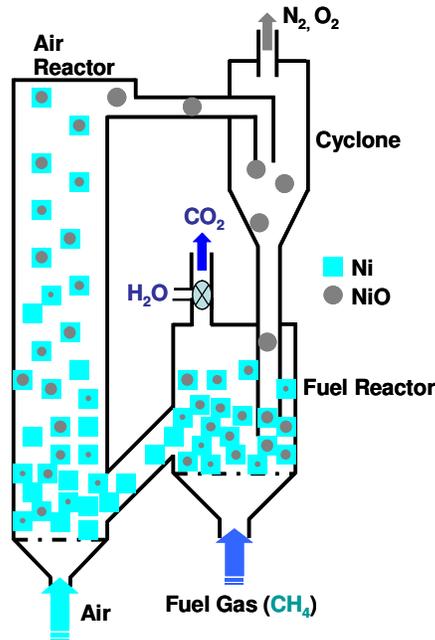
R is the gas constant of $1.987 \text{ (Kcal} \cdot \text{K}^{-1} \cdot \text{Kg} \cdot \text{mol}^{-1}\text{)}$.

Overall reduction rate in the fuel reactor is controlled by chemical reaction resistance (2). Hence, in the shrinking core model for a metal oxygen carrier, external diffusion and internal diffusion are neglected, the mass transfer to the gas phase from the metal oxide (Eq.1) is considered only for O_2 species in this study.

$$\dot{m}_g = \alpha^{O_2} M^{O_2} r = -\dot{m}_s \left(\frac{g}{cm^3 \cdot s}\right) \tag{10}$$

The model geometry defined in simulation was based on the dimensions of the experimental test bed (4, 5), including the initial and boundary conditions. Figure 1 show a layout of CLC process with two separated reactors and the initial condition and system properties for the fuel reactor simulation. The fresh metal oxygen carrier of NiO (57.8 wt%) supported on Bentonite (42.2 wt%) was filled in the bed with solid volume fraction of 0.58 with an inert gas of N_2 until the bed height of 25 cm. The

reactor was initially fluidized with an introduction of 100% N₂ gas. After 5 sec, the fuel gas with methane of 90 wt% and N₂ gas of 10 wt% was fed in the reactor to initiate the reaction. The simulations were run for 15 seconds.



Initial condition and system properties

Width of bed (cm)	25
Height of bed (cm)	60
Temperature (°C)	680 ~ 950
Viscosity of Nitrogen (g/cm-s)	2.3×10^{-4}
Inlet fuel gas velocity (cm/s)	10
Diameter of catalyst (μm)	120
Density of catalyst (g/cm^3)	3.589
Minimum fluidization velocity (cm/s)	1.34
Initial static catalyst height (cm)	20 ~ 40
Initial catalyst volume fraction	0.58
Restitution coefficient (e)	0.8
Time interval (s)	$10^{-3} - 10^{-5}$
Grid size ($\text{dx} \times \text{dy}$) (cm)	0.25×0.25

Figure 1. Layout of chemical looping combustion process with two separated reactors and the simulation conditions for a fuel reactor in this study.

SIMULATION RESULTS AND DISCUSSIONS

The hydrodynamics in the fuel reactor was investigated by bubble growth, solid velocity analysis, and methane conversion with the initial static bed height. The powder of oxidized metals was suspended in a mixed gas. The upward flowing gas bubbles provide the energy to keep the oxide metal and fuel gas highly mixed. The reactant (CH₄) from the gas phase reacted with oxygen (O₂) of the metal oxygen carrier and was converted to gas products CO₂ and H₂O.

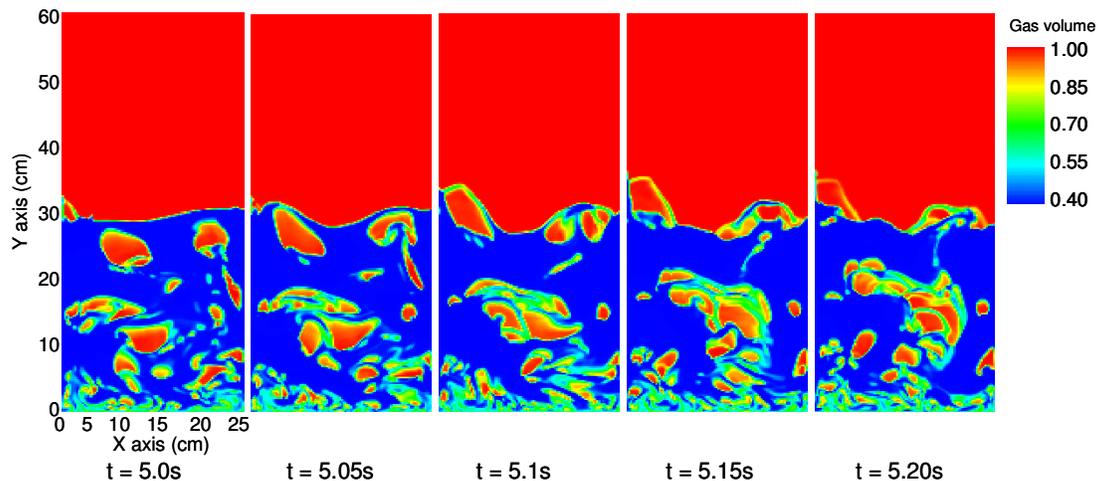


Figure 2. Bubble growth in the fuel reaction captured at a continuous time. Gas volume fraction is represented by the color bar.

Figure 2 shows the bubble growth captured by our CFD simulations, where red represents pure gas and blue mimics dense (60% by volume) gas-solid mixture. We see most of salient bubble features such as formation and rise. The simulated frames showed a clear interface between the fluidized regimes and the free board regimes. We found that a solid re-circulation pattern occurs in the lower portion of the fluidized bed. Then the solid slowly moved to the upper portion. The small gas bubbles formed at the bottom of bed grow, coalesce and then burst at the top of the bed. It generally agrees with the hydrodynamics observed from experiments of bubbling fluidized beds. The computed flow patterns due to the bubble predicted a global mixing between the gas phase and solid phase in the fuel reactor. These features relate the maximum production rates in the reactor.

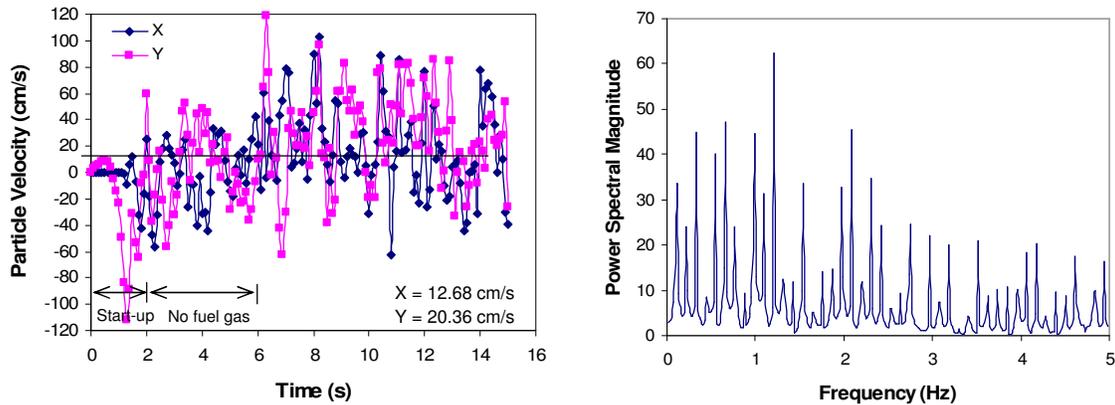


Figure 3. Catalyst velocity as a function of time and frequency at a point of fluidized bed regime: 12.5cm (x) and 25 cm (y).

Figure 3 shows typical time series of vertical and tangential hydrodynamic velocities for catalyst predicted in the simulation. The hydrodynamic velocity in the computation is defined as

$$v_i(r,t) = \frac{1}{n} \int cf(c)dc \quad (11)$$

where, c is the instantaneous particle velocity over velocity space. The computed hydrodynamic velocity oscillates with bubble flows. The flow was non-isotropic in the fluidized beds. Velocity fluctuation was unstable with a slug formation at the initial time of start-up and no fuel gas. After 5sec, the simulation showed more stable quasi-steady state condition, in this time, the fuel was introduced into the reactor. The main frequency for the vertical direction was between 0.5 Hz and 3 Hz as shown in the Figure 3. The frequency is in the range of the dominant frequency (f) of porosity oscillations in the bubbling beds given by Gidaspow (9). In this study, the hydrodynamic velocity and frequency predicted from the simulation shows a reasonably good agreement with the results in the bubbling fluidized beds from Jung et al (12).

The particle granular temperatures due to the random motion of particles were predicted from the fluctuating energy equation for particles. Figure 4 shows the granular temperature estimated from an algebraic expression for the particle granular temperature in this study. The high granular temperatures were at the wake region of gas bubble and at the interface between the free board regime and the bubbling regime. The computed particle granular temperature varies with time and position as

shown in Jung et al (12). Such granular temperature is due to an oscillation of particles in the small space. As shown in Figure 4, the granular temperature predicted at a point of fluidized bed regime oscillated with the computed time and predicted the rheological properties of particles. The high granular temperatures were observed with a passing of gas bubble.

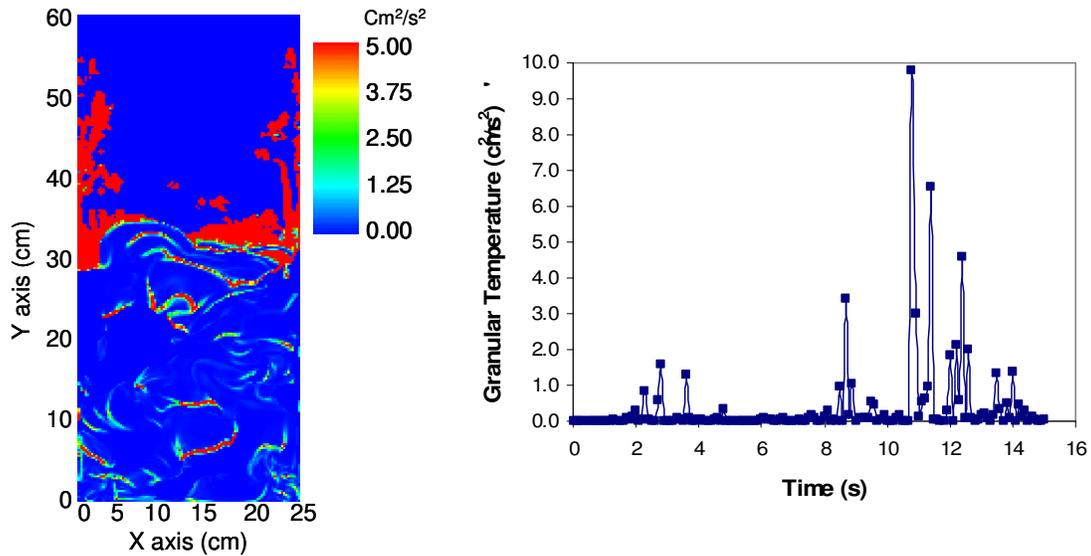


Figure 4. Granular temperature in the fuel reactor at a simulation time of 12s and granular temperature as a function of time at a point of fluidized bed regime: 12.5cm (x) and 25 cm (y).

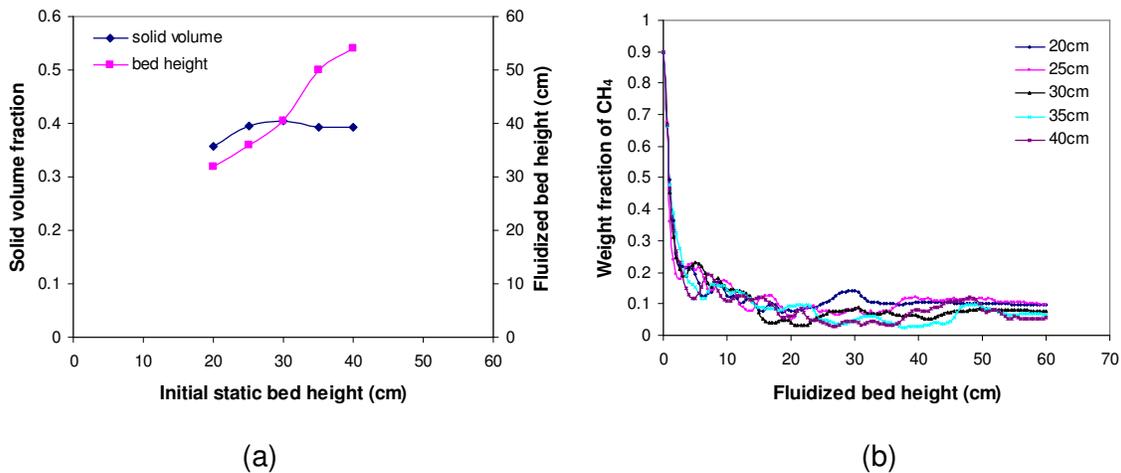


Figure 5. (a) Solid volume fraction and fluidized bed height as a function of the initial static bed height. (b) Weight fraction of methane averaged in the fuel reactor as a function of the fluidized bed height at a simulation time of 14s.

The hydrodynamics with the initial static bed height for catalyst in the fuel reactor was studied at a constant reaction temperature of 950°C. The solids were filled in the range of the bed height between 20 cm and 40 cm with solid volume fraction of 0.58. The constant temperature was determined by Jung and Gamwo (13). They showed that the methane conversion varied with reaction temperature and increased with

temperature. The temperature was an important factor in the fuel reactor simulation. Figure 5 shows the solid volume fraction, the fluidized bed height, and the weight fraction of methane with a variation of the initial static bed height for catalyst. With the increase of the initial static bed height, the fluidized bed height was expanded. We found that the difference between the initial static bed height and the fluidized bed height in all simulated cases is in a range between 10cm and 15cm. The solid volume fraction averaged in the bubbling regime at a simulation time of 14s was a constant value of about 0.4. The weight fraction of methane averaged in the radial direction as a function of the fluidized bed height showed a sharp falling curve to the fluidized bed height of 20cm followed by a slower decline, where the simulation time was 14s. Most of reduction was under the fluidized bed height of 5cm. The weight fraction of methane observed in the free board was gradually decreased with the increase of the initial static bed height. It determines the conversion of methane in the fuel reactor.

Methane conversion as shown in Figure 6 increased with the increase of the initial static bed height. It means that the contact time between fuel reactant and catalyst should increase for a complete reaction in the fuel reactor.

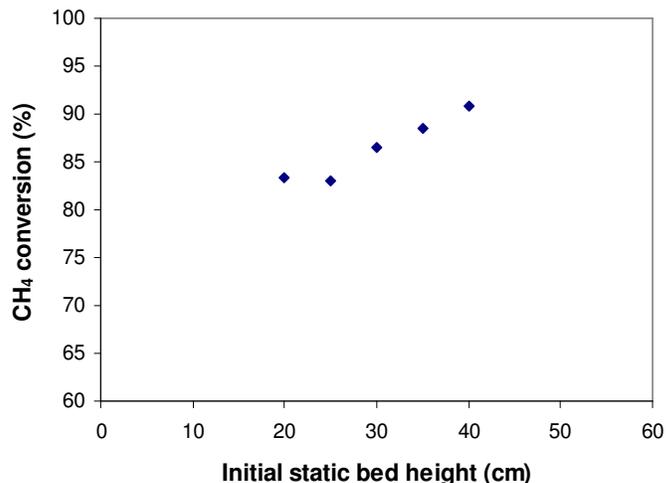


Figure 6. Methane conversion as a function of the initial static bed height at a simulation time of 14s.

CONCLUSION

We have incorporated the kinetic of the oxidized metal reduction into the MFX code to model reactive fluid dynamic in the fuel reactor. Our simulation predicted hydrodynamics behavior on bubble growth, solid velocity, and methane conversion with the initial static bed height in the reactor. The conversion of fuel gas increased with the increase of the initial static bed height for catalyst at a constant temperature. Future effort should extend the model to complete loop system.

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NOTATION

Abbreviation	Term
c	Instantaneous particle velocity
C	Particle velocity fluctuation or Peculiar particle velocity
d_p	Solid phase diameter
F	Force, $(-\nabla P_{\text{gas}}/\rho_k)+g$
i	x or y coordinates
k	Gas phase or solid phase
P	Gas or Solid phase pressure
v	Hydrodynamic velocity
x	Weight fraction of species in each phase
y	Mole fraction of species in each phase

Greek Letters

α	Stoichiometric coefficient
β	Gas-solid drag force
ε	Volume fraction
γ	Energy dissipation due to inelastic particle collision
θ	Granular temperature
ρ	Density
τ	Stress

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