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A DEM STUDY OF THE REDUCTION OF VOLUMETRIC FLOW IN BUBBLING FLUIDIZED BED METHANATION REACTORS

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ABSTRACT

The methanation reaction kinetics is incorporated into a DEM model to investigate the effect of the decrease of gas volumetric flow on the dynamics of a bubbling catalytic fluidized bed. The influence of particles with different physical properties and superficial velocity are studied. The results showed that for Geldart B particles the change of volumetric flow has a minor influence on the expansion of the emulsion phase, while, for Geldart A particle, a profound contraction of the emulsion phase was observed. The contraction degree linked closely with the superficial velocity.

INTRODUCTION

Natural gas is a clean energy carrier with high-heating value that can be used in various industries. China is rich in coal and biomass but poor in natural gas. Methanation of synthesis gas from coal or biomass steam gasification can produce synthetic natural gas (SNG) (Kopyscinski *et al* (1) , Gassner *et al* (2)), which is of great importance in improving China's energy structure. So far many SNG production processes have been developed, based on either fixed bed or fluidized bed reactors (Kopyscinski *et al* (1)). The methanation reaction, usually catalyzed by nickel, is fast and highly exothermic:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \text{（}\Delta H_r^0\text{=-206KJ/mol)}$$

The methanation reaction is favored at low temperature and high pressure. Efficient remove of the reaction heat is of crucial importance to avoid local hot spots, to prevent the catalyst from sintering, and to achieve high methane selectivity. Compared to fixed bed reactors, fluidized bed reactors are known to be more suitable for heterogeneously catalytic and highly exothermic reactions， duo to the high heat transfer rate. Nevertheless, there remain many challenges in the development of an industrial methanation fluidized bed reactor. For example, the fluidization behavior in the case of decreasing gas volume in a highly exothermic environment is yet to be understood. In the carbon monoxide methanation process, the number of gas molecules is reduced from 4 moles to 2 moles. Since the catalytic methanation reaction mainly proceeds in the emulsion phase, the reduced volumetric flow may have a negative influence on the expansion of the emulsion phase. Yet the fluidization quality is closely associated with the voidage of the emulsion phase. Experiments of carbon dioxide methanation (Kai et al (3,4)) showed a large decrease in fluidization quality in a bubbling fluidized bed reactor， which may cause serious defluidization and eventually lead to failure of the reactor operation. Thus a deep understanding of the fundamentals of the fluidization behavior in the methanation fluidized bed reactor is of significant importance.

In this paper, the fluidization behavior in a bubbling fluidized bed methanation reactor has been studied by use of a CFD-DEM code. The methanation reaction kinetics is coupled to the CFD-DEM source code, which was originally developed by Prof. Han Kuipers' group at Twente University (Hoomans et al.(5), Ye et al. (6,7)). CFD-DEM model has been applied successfully to study various phenomena in gas-solid two-phase flows (Deen et al. (8), Zhu et al. (9)). Wu et al. (10) performed a CFD-DEM simulation for methanation process in a fluidized bed reactor. They observed unwanted defluidization by altering superficial gas velocity. However, in the work by Wu et al. (10) only Geldart B particles have been considered and no detailed information on bubble behavior was reported. In another interesting work by Li and Guenther (11) the effect of gas volume change caused by ozone decomposition on fluidized bed hydrodynamics such as bubble behavior has been studied by 2D MFIX-DEM simulations. It has been found that the gas volume change has an essential impact on the bubble characteristics. Again, their work concentrated on the Geldart B particles. In fact, Geldart A particles have been widely used in catalytic fluidized bed processes as catalyst. In this paper we will investigate and compare the emulsion phase characteristics for both Geldart A and B particles.

MATHEMATICAL MODELS

The gas phase is described by the Navier-Stokes equations, and the particle phase is modeled by a soft-sphere discrete particle model (Ye et al. (6, 7)). The motion of each particle is tracked by solving Newton's second law. The detailed interaction between particles and between particles and boundaries is calculated by a simplified spring-dashpot model. The numerical solution of gas phase is in accordance with the lines of Kuipers et al. (12). A drag model derived from lattice Boltzmann simulation was used to calculate the drag force between the gas and particles (Hill et al. (13)):

$$\mathrm{F_d} = 3\pi\mu_\mathrm{g}\varepsilon^2 d_\mathrm{p}(\vec{U}-\vec{V})\ f(\varepsilon) \tag{1}$$

Where ε is the local void fraction, and *f*(ε) is characterized by

$$f(\varepsilon) = \frac{10(1-\varepsilon)}{\varepsilon^3} + 0.7 \qquad \text{for } \varepsilon<0.6$$

$$f(\varepsilon) = \frac{1+3\sqrt{0.5(1-\varepsilon)}+(135/64)\ (1-\varepsilon)\ln(1-\varepsilon)+17.14(1-\varepsilon)}{1+0.681(1-\varepsilon)-8.48(1-\varepsilon)^2+8.16(1-\varepsilon)^3} \qquad \text{for } \varepsilon>0.6.$$

Here $\vec{U}$ and $\vec{V}$, respectively, denote the local gas velocity and the particle velocity. μ_g is the gas density, and d_p the particle diameter. The methanation reaction kinetics is incorporated into the DEM-CFD source code. The methanation reaction rate is described by a Langmuir-Hinshelwood expression as following

$$r=\frac{kK_{\mathrm{c}}p_{\mathrm{CO}}^{0.5}p_{\mathrm{H_2}}^{0.5}}{\left(1+K_{\mathrm{c}}p_{\mathrm{CO}}^{0.5}+K_{\mathrm{OH}}p_{\mathrm{H_2O}}p_{\mathrm{H_2}}^{-0.5}\right)^2}\ , \tag{2}$$

where the kinetic parameters are taken from the literature (Kopyscinski *et al* (14)). The conversion equations of gas species (CO, H_2, CH_4, CO_2 and H_2O) are considered in the model:

$$\frac{\partial}{\partial t}(\varepsilon\rho_{\mathrm{g}}Y_j)+\nabla(\varepsilon\rho_{\mathrm{g}}\vec{U}Y_j)=\nabla(\varepsilon\rho_{\mathrm{g}}D_j\nabla Y_j)+S_j \tag{3}$$

where ρ_g is the gas density, Y_j the mass fraction of gas component j, D_j the molecular diffusion coefficient, and S_j the source term. The source term is defined as

$$S_j=\varepsilon(1-\varepsilon)\ r\rho_{\mathrm{s}}M_j \tag{4}$$

Here M_j represents the molar mass of each gas component j, ρ_s the particle density.

The current study focuses on the effect of the gas volume reduction caused by the reaction. In real situation, there is a temperature difference in the reactor, and the non-uniformity of temperature might lead to a change of the gas volumetric flow. It should be stressed, however, that the temperature difference in the reactor would be small due to the good heat transfer performance of the fluidized bed. For simplicity, the operating temperature in our study was assumed to be a constant. Therefore, the conservation equation of energy is not taken into account here.

NUMERICAL SETUP

A lab-scale rectangular fluidized bed has been considered in all the simulations. The fluidized bed is 6cm wide and 0.15m high. The thickness of the bed is assumed equal to the diameter of a single particle. Both Geldart A and Geldart B particles were studied (Geldart (15)).The computational domain has been discretized at a uniform grid of 0.5mm for Geldart A particles, or 1.25mm for Geldart B particles. Table 1 shows the simulation conditions and physical properties of particles. The gas density is calculated via the state equation of ideal gas. The Geldart A particles considered here have a particle density of 1300kg/m^3 and diameter of 100μm while the Geldart B particles have a particle density of 2500kg/m^3 and diameter of 250μm.

RESULTS AND DISCUSSIONS

Bed expansion

Fig.1 shows the predicted flow patterns for both Geldart A and Geldart B particles when the simulations reach a quasi-steady-state, which are exclusively taken from the results at 20s real time. It can be seen that, for Geldart A particles the bubbles in the fluidized bed split and coalesce frequently, and the bubble size is relatively small. For Geldart B particles, however, the bubbles are enlarged. The comparison between the simulations with and without methanation reaction indicates that the bed height shows a profound decrease, for both Geldart A and B particles. Apparently this is caused by the reduction of the gas volumetric flow due to the methanation reaction. Clearly, the bubble holdup also becomes smaller when the methanation reaction has been considered regardless of the particle type.

Expansion of the emulsion phase

In the simulation work by Wu et al. (10) and experimental work by Kai et al. (16) (17), the defluidization was observed. In our study, however, the direct defluidization was only found in the simulations where the fluidized bed has a large height-to-diameter ratio. The defluidization is closely related to the small local voidage in the fluidized bed. It is indeed a trivial task to predict the defluidization in a 2D DEM simulation since the solid fraction calculated in 2D simulations differs significantly from that calculated in 3D. It is generally accepted that the fluidization quality increases with the expansion ratio of the emulsion phase (Kai et al (18)). Therefore in this study the voidage of the emulsion phase is used as an important factor indicating the fluidity of catalyst (Weimer et al (19)) rather than direct observation of defluidization in the bed.

Table 1：Parameters used in the simulations.

Parameters	Value	
	Big particle	Small particle
Particle number	76800	480000
Particle diameter	250μm	100μm
Particle density	2500kg/m^3	1300kg/m^3
Constant temperature	600K	600K
Pressure	6bar	6bar
Gas inlet velocity	0.06~0.24m/s	0.025~0.1m/s
Gas inlet composition(mass fraction)		
CO	0. 616	
H_2	0. 132	
CH_4	0	
H_2O	0.05	
CO_2	0.202	

Methanation is a highly exothermic reaction, but this reaction is favored at lower temperature. Therefore, to avoid hot spots in the fluidized reactor, high fluidization quality should be guaranteed to ensure a good heat transfer. The catalytic methanation reaction mainly takes place in the emulsion phase, resulting in a transient decrease of the volumetric flow in this phase. The density and viscosity of the gas mixtures would both increase in the methanation reactor. It has been found (Yates (20), Kai et al (21),) that an increased gas viscosity and density will enhance the expansion of the emulsion phase. If the gas consumed in the emulsion phase can be completely compensated by the gas from bubbles, by which an efficient mass transfer between the emulsion phase and the bubble phase is established, an increase of the expansion ratio of the emulsion phase will be expected. This will certainly improve the fluidity of the catalyst and avoid the defluidization.

Fig.2 refers to the time-averaged frequency distribution of the voidage of the emulsion phase, and the first 20s simulation results are ignored to avoid the start-up effect. It can be seen that, for Geldart B particles, the reduction of volumetric flow has a relatively small influence on the expansion of the emulsion phase. For Geldart A particles, however, the peak voidage in the emulsion phase shifts to lower values, which suggests an apparent emulsion phase condensation. Obviously, the decrease of gas flow in the emulsion phase cannot be completely compensated by the gas flows from the surrounding bubbles. This causes a contraction in the emulsion phase due to the methanation reaction. The contraction of the emulsion phase, in the extreme case, will lead to the defluidization. In fact, even if there is no defluidization, the contraction of the emulsion phase will prompt the effective viscosity of the emulsion phase (Mickley et al (22), King et al (23),), which consequently increases the shear resistance of the emulsion phase and weakens the catalyst mobility. This has a negative impact on solid mixing rate. On the other hand, the contraction of the emulsion phase also causes a significant decrease of the voidage, which increases flow resistance of the gas and limits the gas flow from the bubbles. So the mass transfer between the bubble phase and emulsion phase will also be affected.

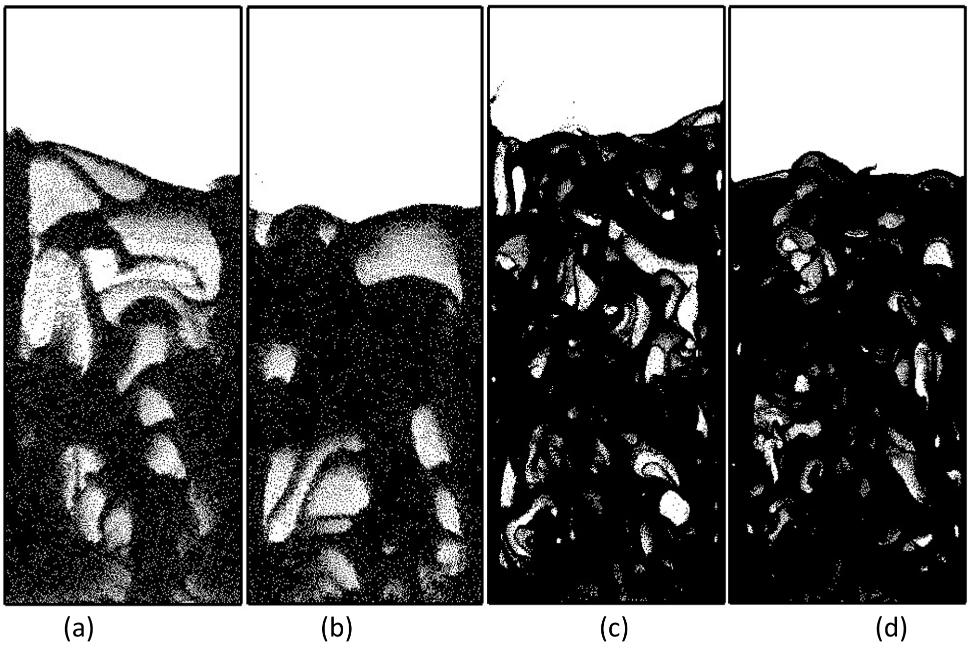
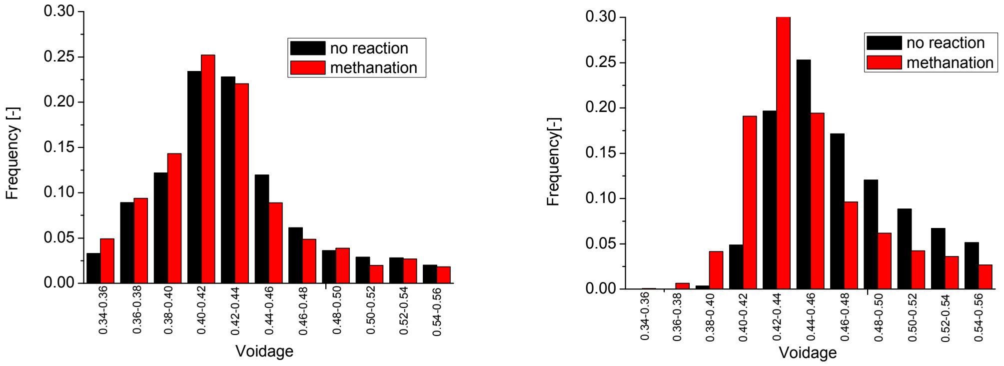

(a) (b) (c) (d)

Fig.1 Flow patterns in the fluidized beds. (a) Geldart B particles, without reaction; (b) Geldart B particles, with methanation reaction; (c) Geldart A particles, without reaction; (d) Geldart A particles, with methanation reaction. The gas inlet velocity: 0.16m/s for (a) and (b), and 0.05m/s for (c) and (d).

Influence of Inlet Gas velocity

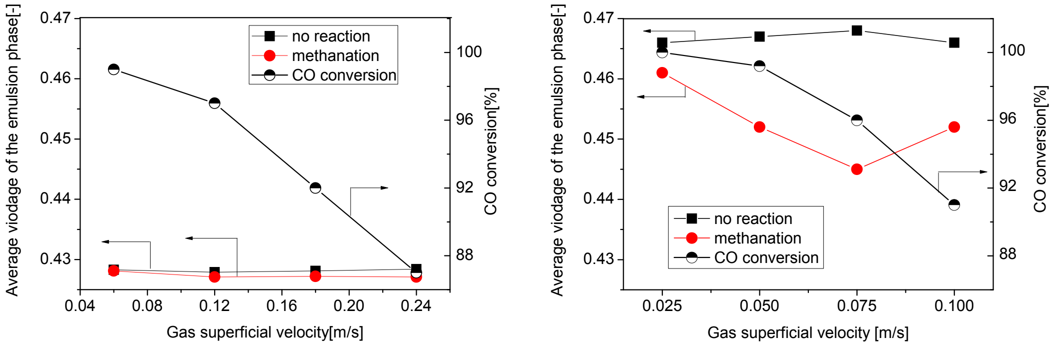
The effect of gas inlet velocity on the emulsion phase voidage was studied. The variations of averaged emulsion phase voidage and CO conversion at different gas superficial velocity were shown in Fig. 3(a). As can be seen, for Geldart B particles the variation of the voidage in emulsion phase is negligible. In general, for bubbling fluidized bed, the bubble size will grow with an increasing superficial gas velocity and the mass transfer coefficient between the bubble and emulsion phase will decline. Thus a part of the fresh gas carried by the bubbles leaves the fluidized bed before being fully converted, which results in a gradual reduction in CO conversion.

Fig.3 (b) shows a distinct contraction of the emulsion phase for Geldart A particles. It can be observed that the degree of contraction is relatively small at a low gas inlet velocity. The possible reason is that at low gas velocity the reaction mainly takes place near the distributor, which is also reflected in Fig.4. The reduction of gas volume in the regime far from the distributor is quite small so that the fluidization quality in the upper bed is not affected. When the gas inlet velocity increases from 0.025 to 0.075m/s, an enhanced contraction of the dense phase has been observed. This is mainly due to the limited mass transfer between the two phases, and the reduced gas volume in the emulsion phase cannot be sufficiently compensated for. However, a further increase of the gas velocity leads the averaged voidage, on the contrary, to shift to a higher value. This means beyond certain gas inlet velocity the contraction of the emulsion phase starts to become less serious. This is not surprised because when the bubbling fluidized bed is operated at a high superficial gas velocity, the local gas velocity will increase accordingly, which is verified in Fig.5. Thus the gas mass flow in the emulsion phase becomes larger. Note that the reaction kinetics keeps unchanged, the local gas volume reduction rate would be smaller at high velocities. Hence when the gas inlet velocity increases from 0.075 to 0.1 m/s, the degree of the contraction diminishes. Though a higher gas inlet velocity can restrain the contraction rate of the emulsion phase, it may lead to a lower conversion, which is well demonstrated in Figs.3 and 4.



(a) (b)

Fig.2 Distribution of the voidage of the emulsion phase for (a) Geldart B particle and (b) Geldart A particle, both with methanation reaction. The gas inlet velocity: 0.16m/s for (a) and 0.05m/s (b).



(a) (b)

Fig.3 Average voidage of the emulsion phase and CO conversion for (a) Geldart B particle, (b) Geldart A particle with different gas inlet superficial velocities.

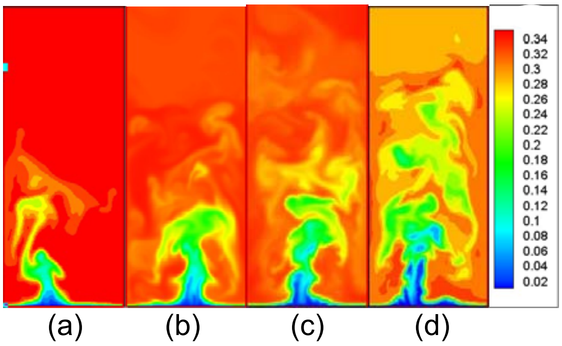


Fig.4 Methane mass fraction distribution maps for Geldart A particles with different superficial velocity, (a)0.025m/s;(b)0.05m/s; (c)0.075m/s;(d)0.1m/s

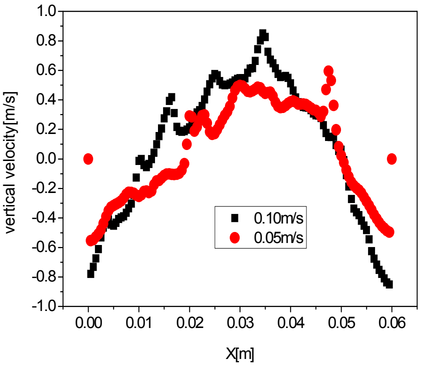


Fig.5 Time-averaged gas vertical velocity at the height of 0.03m above the distributor for small particles.

CONCLUSION

The methanation reaction kinetics model is successfully incorporated into the originated CFD-DEM source code. For Geldart B particles (ρ_s =2500kg/m^3, d_p=250μm), the change of volumetric flow showed minor influence on the expansion of the emulsion phase. However, for Geldart A particle (ρ_s =1300kg/m^3, d_p=100μm), the results showed that the decrease of volumetric flow will make a contraction of the emulsion phase, leading to a decrease of the fluidization quality. Meanwhile, the contraction degree linked closely with the superficial velocity.

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NOTATION

F_d = drag force, N
ε = local porosity
μ_g = gas viscosity, Pa.s
ρ_g = gas density, kg/m^3
U= gas velocity, m/s
V= particle velocity, m/s
Y_j = mass fraction of species i
D_j = molecular diffusion coefficient, m^2/s
S_j =the source term of the conversion equations of gas specie j, kg/m^3/s
M_j = molar mass of gas specie j, kg/mol
r = rate of methanation, mol/kg$_{cat}$/s
d_p = particle diameter, m
k = reaction constant
K_i = absorption constant of species i
p_i =partial pressure of species i, bar/Pa

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