HYDRODYNAMIC MODELS FOR SLURRY BUBBLE COLUMN REACTORS

Final Technical Report

This report also includes the Quarterly Technical Report for period: 01/01/97 - 03/31/97.

Reporting Period: 06/01/94 - 06/01/97

Principal Author: Dimitri Gidaspow

Report Issue Date: 08/15/97

DE-FG22-94PC94208--12

Illinois Institute of Technology
Dept. Of Chemical and Environmental Engineering
10 W. 33rd St.
Chicago, IL 60616

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trademark manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect of the United States Government or any agency thereof.

ABSTRACT

The objective of this study is to develop a predictive experimentally verified computational fluid dynamic (CFD) three phase model. It predicts the gas, liquid and solid hold-ups (volume fractions) and flow patterns in the industrially important bubble-coalesced (churn-turbulent) regime. The input into the model can be either particulate viscosities as measured with a Brookfield viscometer or effective restitution coefficient for particles.

A combination of x-ray and γ -ray densitometers was used to measure solid and liquid volume fractions. There is a fair agreement between the theory and the experiment. A CCD camera was used to measure instantaneous particle velocities. There is a good agreement between the computed time average velocities and the measurements. There is an excellent agreement between the viscosity of 800 μm glass beads obtained from measurement of granular temperature (random kinetic energy of particles) and the measurement using a Brookfield viscometer.

A relation between particle Reynolds stresses and granular temperature was found for developed flow. Such measurement and computations gave a restitution coefficient for a methanol catalyst to be about 0.9.

A transient, two-dimensional hydrodynamic model for production of methanol from syn-gas in an Air Products/DOE LaPorte slurry bubble column reactor was developed. The model predicts downflow of catalyst at the walls and oscillatory particle and gas flow at the center, with a frequency of about 0.7 Hertz. The computed temperature variation in the reactor with heat exchangers was only about 5 $^{\circ}\text{K}$, indicating good thermal management.

The computed slurry height, the gas holdup and the rate of methanol production agree with LaPorte's reported data.

Unlike the previous models in the literature, this model computes the gas and the particle holdups and the particle rheology. The only adjustable parameter in the model is the effective particle restitution coefficient.

EXECUTIVE SUMMARY

The objective of this investigation is to convert our “learning gas-solid -liquid” fluidization model into a predictive design model . This model is capable of predicting local gas , liquid and solids hold-ups and the basic flow regimes: the uniform bubbling , the industrially practical churn-turbulent (bubble coalescence) and the slugging regimes . Current reactor models incorrectly assume that the gas and the particle hold-ups (volume fractions) are uniform in the reactor . They must be given in terms of empirical correlations determined under conditions that radically differ from the reactor operation . In the proposed hydrodynamic approach these hold-ups are computed from separate phase momentum balances . Furthermore , the kinetic theory approach computes the high slurry viscosities from collisions of the catalyst particles . Thus particle rheology is not an input into the model . See Gidaspow, “Multiphase Flow and Fluidization, Continuum and Kinetic Theory Description,” Academic Press, 1994.

Our program was reviewed by DOE and Air products team who visited us January 31 , 1995 . DOE FETC is sponsoring a multi-year program at Air Products and Chemicals on development of alternative fuels from coal derived syngas using slurry bubble column reactors . Air Products use stirred tank reactor models for analyzing their data . Our model predicts the flow patterns .

The new model we developed should help the industry to optimize their reactors, since it predicts the hydrodynamics under operating conditions. Our newly developed CCD camera technique can measure the velocity and the turbulence in a cold model of the reactor. This new method can be used to further verify our hydrodynamic model.

A combination of x-ray and γ -ray densitometers was used to measure solid and liquid volume fractions. There is a fair agreement between the theory and the experiment. A CCD camera was used to measure instantaneous particle velocities. There is a good agreement between the computed time average velocities and the measurements. There is an excellent agreement between the viscosity of 800 μm glass beads obtained from measurement of granular temperature (random kinetic energy of particles) and the measurement using a Brookfield viscometer.

A relation between particle Reynolds stresses and granular temperature was found for developed flow. Such measurement and computations gave a restitution coefficient for a methanol catalyst to be about 0.9.

A transient, two-dimensional hydrodynamic model for production of methanol from syngas in an Air Products/DOE LaPorte slurry bubble column reactor was developed. The model predicts downflow of catalyst at the walls and oscillatory particle and gas flow at the center, with a frequency of about 0.7 Hertz. The computed temperature variation in the reactor with heat exchangers was only about 5 $^{\circ}\text{K}$, indicating good thermal management.

The computed slurry height, the gas holdup and the rate of methanol production agree with LaPorte's reported data.

TABLE OF CONTENT

Abstract	ii
Executive Summary	iii
PHASE I : EXPERIMENTAL STUDIES	1
A Comparison of A Kinetic Theory CFD Model for Gas-Liquid-Solid Fluidization to Experiments with Glass Beads and Methanol Catalyst By: D.Gidaspow, M.Bahary, M.R. Mostofi, U.K.Jayaswal	
Introduction	2
Part I : Hydrodynamic Model	2
Part II : Comparison to Experiment with Glass Beads in Bubbly Coalesced Fluidization Regime	10
Part III : Granular Temperature and Reynolds Stress for Methanol Catalyst	
Conclusions	25
Nomenclature	26
Bibliography	28
PHASE II : SIMULATION	55
Hydrodynamic Simulation of Methanol Synthesis in Gas-Liquid Slurry Bubble Column Reactor By: Y. Wu , D. Gidaspow	
Introduction	56
Hydrodynamic Model	57
Conclusions	66
Nomenclature	66
References	69

A COMPARISON OF A KINETIC THEORY CFD MODEL FOR GAS-LIQUID-SOLID FLUIDIZATION TO EXPERIMENTS WITH GLASS BEADS AND METHANOL CATALYST

by

D. GIDASPOW, M. BAHARY¹, M.R. MOSTOFI and U.K. JAYASWAL¹

Department of Chemical and Environmental Engineering
Illinois Institute of Technology, Chicago, IL 60616

ABSTRACT

The objective of this study is to develop a predictive experimentally verified computational fluid dynamic (CFD) three phase model. It predicts the gas, liquid and solid hold-ups (volume fractions) and flow patterns in the industrially important bubble-coalesced (churn-turbulent) regime. The input into the model can be either particulate viscosities as measured with a Brookfield viscometer or effective restitution coefficient for particles.

A combination of x-ray and γ -ray densitometers was used to measure solid and liquid volume fractions. There is a fair agreement between the theory and the experiment. A CCD camera was used to measure instantaneous particle velocities. There is a good agreement between the computed time average velocities and the measurements. There is an excellent agreement between the viscosity of 800 μm glass beads obtained from measurement of granular temperature (random kinetic energy of particles) and the measurement using a Brookfield viscometer.

A relation between particle Reynolds stresses and granular temperature was found for developed flow. Such measurement and computations gave a restitution coefficient for a methanol catalyst to be about 0.9.

¹ Raytheon Engineers and Constructors, Inc.
Cambridge, MA 02142

INTRODUCTION

Fluidized beds are widely used industrially because the particles can be introduced into and out of a reactor as a fluid and because of good heat and mass transfer in the reactor. The invention of kinetic theory of granular flow by professor Savage and collaborators (Savage & Jeffrey, 1981; Savage, 1983 & 1988; Lun et al, 1984), as reviewed by Gidaspow (1994), provides a plausible explanation for this fluid-like behavior of particles. The particles oscillate randomly. This assumption, supported by measurements (Carlos and Richardson, 1968; Gidaspow and Huilin, 1996 & 1997; Arastoopour and Yang, 1992; Cody, et al, 1996, 1997) allows the definition of granular temperature as one third the sum of the squares in the three directions of the random oscillations of particle velocities. In other words, the granular temperature is the random kinetic energy of particles per unit mass. It is directly related to the turbulent kinetic energy used in single phase flow in the k-epsilon model (Mohammadi and Pironneau, 1994) and extended to multiphase flow by Ahmadi and Cao (1990) and to gas-particle computation flow by Cao and Ahmadi (1995). The distinction is that in the granular flow theory this temperature acts like the thermal temperature in kinetic theory of dense gases and in statistical mechanics of fluids. This analogy allows an easy application of these theories to fluidized beds. For example, the kinematic viscosity of the fluidized beds can be computed from a direct measurement of the particle oscillations, as essentially the product of the mean free path and the oscillating particle velocity. This paper illustrates the application of this theory to gas-liquid-solid fluidized beds. Such computations for gas-solid flow in a riser were performed by Samuelsberg and Hjertager (1996).

Fan (1989) has reviewed three-phase fluidization and its applications. Tarmy and Coulaloglu (1992) show that there exist no hydrodynamic models for three phase fluidization in the literature. Reactor design using slurry bubble columns is usually done using hold-up correlations (Viking Systems International, 1994). Papers presented at the recent Computational Fluid Dynamics (CFD) in Reaction Engineering Conference held in San Diego in October 1996 by the EXXON (Heard, 1996) and the Los-Alamos groups (VanderHeyden, 1996) have described their work in using CFD models to understand the injection of oil into fluidized catalytic cracking risers. The application of interest in this study is the slurry bubble column reactor for making of methanol from synthesis gas. EXXON and other companies are commercializing processes to convert the apparently abundant natural gas into storable liquid fuels. Fluidized beds are often used in such applications. The CFD approach described in this paper should eventually help in the design of more efficient reactors, such as the selection of internals for proper flow patterns and bubble control and optimization of size of catalyst. For such a purpose an experimentally verified CFD model is needed.

PART I : HYDRODYNAMIC MODEL

The physical principles used are the laws of conservation of mass and momentum for the gas, the liquid and the solid phases, as shown in Table 1. The constitutive equations for the stress are also shown in Table 1. This approach is similar to that of Soo (1967) for multiphase flow and of Jackson (1985) for fluidization. The equations are similar to

Bowen's (1976) balance laws for multi-component mixtures. The principle difference is the appearance of the volume fraction of phase "k" denoted by ϵ_k . In the case of phases not all the space is occupied at the same time by all the phases, as it is by components. As in the case of the mixture equations for components, the mixture equations for phases show that the sum of the drag forces is zero. The fluid pressure p_l is in the liquid (continuous) phase.

The corresponding gas and solids (dispersed particulate phases) momentum equations with zero particulate viscosities are the trajectory equations for particulate flow. For gas-solid fluidized beds, Bouillard, et al. (1989) have shown that this set of equations produces essentially the same numerical answers for fluidization as did the earlier conditionally stable model which has the fluid pressure in both the gas and the solids phases. In this model (hydrodynamic model B) the drag and the stress relations were altered to satisfy Archimedes' buoyancy principle and Darcy's law, as illustrated by Jayaswal (1991). The gas-particulate drag coefficients given in Table 1 are for the model B reviewed by Jayaswal (1991). Note that Equation (2a) does not contain the volume fraction in the gravity term, while Equation (2b) has a buoyancy term. This is a generalization of model B for gas-solid systems as discussed by Gidaspow (1994) in section 2.4. For the solid phase, p_s consists of the static normal stress and the dynamic stress, called solids pressure, which arises due to the collision of the particles. The added mass forces and the Saffman's lift forces (Saffman, 1965; Drew, et al., 1979) were assumed to be negligible.

This model is unconditionally well-posed, i.e., the characteristics are real and distinct for one dimensional transient flow. It does not require the presence of solids pressure for stability and well posedness. The details of hydrodynamic equations used in the computer simulation are given in Table 1.

NUMERICAL SCHEME

The governing equations along with the constitutive equations are solved for p_l , ϵ_k , u_k and v_k ($k = g, l, s$) using the Implicit Continuous Eulerian (ICE) method (Rivard and Torrey, 1977, Jayaswal, 1991) with appropriate initial and boundary conditions. Stewart and Wendroff (1984) have critically reviewed the ICE algorithm and related staggered mesh conservative schemes. The computations are carried out using a mesh of finite-difference cells fixed in two-dimensional space (Eulerian mesh). The scalar variables are located at the cell center and the vector variables at the cell boundaries. The momentum equation is solved using staggered mesh, where as for continuity equation a donor cell method was used.

The partial differential equations are well-posed. The time step is chosen to satisfy the Courant stability criterion (Courant, et al., 1952). The numerical stability of the equations can be obtained using the von Neumann stability analysis, as illustrated by Lyczkowski, et al. (1978) and Prosperetti (1982).

**TABLE 1. Governing Equations - Hydrodynamic Model B
for Gas-Liquid-Solid Flows**

In the following equations, the tensor is represented as [].

1. Continuity Equation for Phase k ($= g, l, s$).

$$\frac{\partial}{\partial t} (\epsilon_k \rho_k) + \nabla \cdot (\epsilon_k \rho_k \mathbf{v}_k) = 0$$

2. Momentum Equations.

(a) Liquid Phase (Continuous Phase)

$$\frac{\partial}{\partial t} (\epsilon_l \rho_l \mathbf{v}_l) + \nabla \cdot (\epsilon_l \rho_l \mathbf{v}_l \mathbf{v}_l) = -\nabla p_l + \rho_l \mathbf{g} + \sum_{m=g,s} \beta_{lm} (\mathbf{v}_m - \mathbf{v}_l) + \nabla \cdot [\boldsymbol{\tau}_l]$$

(b) Gas / Solid Phases k ($= g, s$) (Dispersed Phases)

$$\begin{aligned} \frac{\partial}{\partial t} (\epsilon_k \rho_k \mathbf{v}_k) + \nabla \cdot (\epsilon_k \rho_k \mathbf{v}_k \mathbf{v}_k) = & -\nabla p_k + \frac{\epsilon_k}{\epsilon_l} (\rho_k - \sum_{m=l,g,s \text{ } m \neq k} \epsilon_m \rho_m) \mathbf{g} \\ & + \sum_{m=l,g,s \text{ } m \neq k} \beta_{km} (\mathbf{v}_m - \mathbf{v}_k) + \nabla \cdot [\boldsymbol{\tau}_k] \end{aligned}$$

3. Constitutive Equations for Stress.

a) Fluid Phase Stress. k ($= g, l$)

$$[\boldsymbol{\tau}_k] = \epsilon_k \mu_k \left([\nabla \mathbf{v}_k + (\nabla \mathbf{v}_k)^T] - \frac{2}{3} \nabla \cdot (\mathbf{v}_k) [\mathbf{I}] \right)$$

a) Solid Phase Stress.

$$[\boldsymbol{\tau}_s] = \mu_s [\nabla \mathbf{v}_s + (\nabla \mathbf{v}_s)^T] + \left(\xi_s - \frac{2}{3} \mu_s \right) \nabla \cdot (\mathbf{v}_s) [\mathbf{I}]$$

4A. Kinetic Theory Model.

Fluctuating Energy Θ_s ($= \frac{1}{2} \langle C^2 \rangle$) Equation,

$$\frac{3}{2} \left(\frac{\partial}{\partial t} (\epsilon_s \rho_s \Theta_s) + \nabla \cdot (\epsilon_s \rho_s \Theta_s \mathbf{v}_s) \right) = -p_s \nabla \cdot \mathbf{v}_s + \Phi_k - \nabla \cdot \mathbf{q}_s - \gamma_s - 3 \beta_{ls} \Theta_s$$

Collision Energy Dissipation Rate,

$$\gamma_s = 3 (1 - e^2) \epsilon_s^2 \rho_s d_s g_0 \Theta_s \left(\frac{4}{d_s} \left(\frac{\Theta_s}{\pi} \right)^{\frac{1}{2}} - \nabla \cdot \mathbf{v}_s \right)$$

Flux of Fluctuating Energy,

$$\mathbf{q}_s = -\kappa_s \nabla \Theta_s$$

Conductivity of Fluctuating Energy,

$$\kappa_s = \frac{2\kappa_{dil}}{(1+e)g_0} \left[1 + \frac{6}{5} (1+e) g_0 \epsilon_s \right]^2 + 2\epsilon_s^2 \rho_s d_s (1+e) g_0 \left(\frac{\Theta_s}{\pi} \right)^{\frac{1}{2}}$$

Dilute Phase ("Eddy Type") Granular Conductivity,

$$\kappa_{dil} = \frac{25\sqrt{\pi}}{128} \rho_s d_s \Theta_s^{\frac{1}{2}}$$

Solid Phase Shear Viscosity,

$$\mu_s = \frac{2\mu_{dil}}{(1+e)g_0} \left[1 + \frac{4}{5} (1+e) g_0 \epsilon_s \right]^2 + \frac{4}{5} \epsilon_s^2 \rho_s d_s (1+e) g_0 \left(\frac{\Theta_s}{\pi} \right)^{\frac{1}{2}}$$

Solid Phase Bulk Viscosity,

$$\xi_s = \frac{4}{3} \epsilon_s^2 \rho_s d_s (1+e) g_0 \left(\frac{\Theta_s}{\pi} \right)^{\frac{1}{2}}$$

Dilute Phase Solids Viscosity,

$$\mu_{dil} = \frac{5\sqrt{\pi}}{96} \rho_s d_s \Theta_s^{\frac{1}{2}}$$

Solid Phase Pressure

$$p_s = \epsilon_s \rho_s \Theta_s [1 + 2 (1+e) \epsilon_s g_0]$$

Radial Distribution Function,

$$g_0 = \left[1 - \left(\frac{\epsilon_s}{\epsilon_{s,\max}} \right)^{\frac{1}{3}} \right]^{-1}$$

Energy Dissipation Rate

$$\Phi_s = [\tau_s] : \nabla \mathbf{v}_s$$

4B. Empirical Solids Viscosity and Stress Model.

$$\nabla p_k = G(\epsilon_k) \nabla \epsilon_k$$

$$\xi_s = 0$$

$$\mu_s = 5\epsilon_s \text{ (poises)} \quad (\text{example})$$

5. Continuous Phase-Particulate Phase Drag Coefficients. $k (= g, s)$
for $\epsilon_1 < 0.8$, (based on Ergun equation)

$$\beta_{1k} = \beta_{k1} = 150 \frac{(1 - \epsilon_1) \epsilon_k \mu_1}{(\epsilon_1 d_k \psi_k)^2} + 1.75 \frac{\rho_1 \epsilon_k |\mathbf{v}_1 - \mathbf{v}_k|}{\epsilon_1 d_k \psi_k}$$

for $\epsilon_1 \geq 0.8$, (based on empirical correlation)

$$\beta_{1k} = \beta_{k1} = \frac{3}{4} C_D \frac{\epsilon_k \rho_1 |\mathbf{v}_1 - \mathbf{v}_k|}{d_k \psi_k} \epsilon_1^{-2.65}$$

where,

$$C_D = \begin{cases} \frac{24}{Re_k} (1 + 0.15 Re_k^{0.687}) & \text{for } Re_k < 1000 \\ 0.44 & \text{for } Re_k \geq 1000 \end{cases}$$

$$Re_k = \frac{\epsilon_1 \rho_1 |\mathbf{v}_1 - \mathbf{v}_k| d_k \psi_k}{\mu_1}$$

6. Particle-Particle Drag Coefficients. $k, m (= g, l, s)$

$$\beta_{km} = \frac{\alpha (1+e) \epsilon_k \rho_k \epsilon_m \rho_m (d_k + d_m)^2 \left[1 + 3 \left(\frac{\epsilon_{km}}{\epsilon_k + \epsilon_m} \right)^{\frac{1}{3}} \right]}{2 \epsilon_r (\rho_k d_k^3 + \rho_m d_m^3) \left[\left(\frac{\epsilon_{km}}{\epsilon_k + \epsilon_m} \right)^{\frac{1}{3}} - 1 \right]} |\mathbf{v}_k - \mathbf{v}_m|$$

where

$$\epsilon_{km} = \begin{cases} [(\phi_k - \phi_m) + (1-a)(1-\phi_k)\phi_m] [\phi_k + (1-\phi_m)\phi_k] \frac{X_k}{\phi_k} + \phi_m & \text{for } X_k \leq X_{k,o} \\ (1-a) [\phi_k + (1-\phi_k)\phi_m] (1-X_k) + \phi_k & \text{for } X_k > X_{k,o} \end{cases}$$

$$a = \sqrt{\frac{d_m}{d_k}} \quad (d_k \geq d_m)$$

$$X_k = \frac{\epsilon_k}{\epsilon_k + \epsilon_m}$$

$$X_{k,o} = \frac{\phi_k}{[\phi_k + (1-\phi_k)\phi_m]}$$

7. Definitions.

$$\epsilon_g + \epsilon_l + \epsilon_s = 1$$

The liquid, gas, and solid phases are assumed to be incompressible and constant densities are used. The constitutive relations in the kinetic theory model were derived by Gidaspow (1994). The constitutive relations may be easily changed by some program modification.

DISPERSED BUBBLE FLUIDIZATION REGIME

Carlos and Richardson (1968) studied the movement of large particles in the liquid-solid fluidized bed and reported the measurements of the velocity components of particles. They used a cylindrical fluidization column made of standard 10.16 cm diameter Q.V.F. glass 121.92 cm in length and carried out the experimental work with uniform sized glass bead particles with dimethyl phthalate fluid. The diameter of glass bead particles used was 0.889 cm. The densities of glass bead particles and dimethyl phthalate fluid were 2.49 g/cm^3 and 1.19 g/cm^3 , respectively. Liquid was fed at the bottom of the bed. The particles in the bed were filled to a constant bed height of 26 cm. Initial superficial liquid velocity was 4.8 cm/s, which was the minimum fluidization velocity of the 0.889 cm glass beads in dimethyl phthalate.

In the three phase fluidization study, we used the above described fluidization system with gas injection at the bottom of the bed. The gas phase was treated as a particulate phase having 0.4 cm diameter dispersed spherical air bubbles at room temperature (27°C) with constant density.

Hydrodynamic model B with the kinetic theory model was used to simulate this gas-liquid-solid fluidized bed. The governing equations are shown in Table 1. The geometry and dimensions are given in Figure 1.

Uniform finite difference grids were used in computations. It was assumed that angular symmetry existed. The fluidized bed was divided into 154 computational cells. Each cell was 1.016 cm by 2.5 cm size. Numerical computations for fluidization were carried out for 1.5 seconds with a time increment of 5×10^{-6} seconds. The computations were conducted on Cray YMP/4-464 supercomputer at the National Center for Supercomputing Applications (NCSA) at University of Illinois, Urbana-Champaign, Illinois.

Four different cases for gas-liquid-solid fluidization system were simulated in this study. Flow conditions and the volume fractions used in each simulation case are given below in Table 2.

TABLE 2. Flow Conditions for Dispersed Bubble Flow Regime

$U_{mf}=4.8 \text{ cm/s}$; height of fluidized bed=26 cm

Cases	$U_{sup,l} \text{ (cm/s)}$	U/U_{mf}	Bed Volume Fraction	Inlet Gas Volume Fraction	$U_{sup,g} \text{ (cm/s)}$
1	7.6	1.6	0.53	0.03	0.844
2	9.4	2.0	0.58	0.03	0.844
3	9.4	2.0	0.58	0.07	1.968
4	15.1	3.1	0.70	0.07	1.968

The particle terminal velocity ($v_{s,t}$) for glass beads was 53.7 cm/s and gas bubbles terminal velocity ($v_{g,t}$) was 28.1 cm/s.

Results For Dispersed Bubble Regime.

In this regime, no experimental work was performed in our laboratory. A transient three phase fluidized behavior inside the bed was simulated. The phase holdup in the bed for three phase fluidization was computed and compared with the estimated results from a number of existing empirical correlations for phase holdups given by Saberian-Broudjenni, et al. (1984); Sinha, et al. (1984); and Dakshinamurthy, et al. (1972). The correlations are not repeated here as they are summarized in Table 2.1 by Fan (1989). Good comparison was obtained as shown in Table 3.

TABLE 3. Average Gas-Liquid Volume Fraction in Bed

Cases	Computed	Saberian-Broudjenni, et al. (1984)	Sinha, et al. (1984)	Dakshinamurthy, et al (1972)
1	0.572	0.580	0.576	0.486
2	0.623	0.615	0.602	0.552
3	0.639	0.647	0.633	0.591
4	0.752	0.735	0.695	0.785

No bubble coalescence was observed in the simulated three phase fluidization. The gas phase remained dispersed in all four cases. This result is consistent with the predictions from flow regime diagram for concurrent gas-liquid-solid fluidized bed shown in Figure 2.3 (Fan, 1989) for bed diameter of 10.16 cm, and particles terminal velocity of 53.7 cm/s, although care must be taken because Figure 2.3 (Fan, 1989) was prepared for air-water-particle fluidization system.

Figure 2 shows typical computed granular temperature and shear viscosity inside the bed. In general, the local solids shear viscosity varies between 1 and 20 poises for all the simulation cases. The shear viscosity is higher at the lower section of the bed and close to the wall and decreases to zero in the top section of the bed. In the top section the shear viscosity is almost constant across the cross-section of the bed. The granular temperature inside the bed also shows considerable fluctuations in the lower section of the fluidized bed.

Earlier, for the gas-solid systems, solid shear viscosity was computed from experimental measurements to be of the order of $5\epsilon_s$ poises (Gidaspow, 1986). Song and Fan (1986) measured apparent viscosity for air-water-glass beads system and obtained values ranging from 0.5 to 15 poises. The apparent viscosity correlation for three phase fluidized bed developed by Song and Fan (1986) gives values ranging from 15 to 20 poises. These values compare favorably with the solids viscosity shown in Figure 2.

The computed velocity patterns for each of the four simulation runs are similar and only the velocity patterns for Case 1 (see Table 2) is shown in Figure 3. There is considerable scatter in computed velocities. A general velocity pattern within the bed is upward movement of particles in the center and downward movement at the walls. There is marked inward radial movement near the bottom of the bed and outward radial movement higher in the bed.

In the dispersed bubble three phase fluidization regime, no comparison with the experiment is available. However, in the same fluidization system with no gas flow, i.e., for liquid-solid fluidization, fair comparison between experimentally measured (Carlos and Richardson, 1968) and computed solid velocities (both axial and radial components) were obtained, as reported elsewhere (Gidaspow, et al., 1991).

PART II: COMPARISON TO EXPERIMENT WITH GLASS BEADS IN BUBBLY COALESCED FLUIDIZATION REGIME

Experimental Setup.

The setup used in the bubbly coalesced regime for volume fraction, velocity and viscosity measurement experiments consisted of four major parts: fluidization equipment, densitometers assembly, a high resolution micro-imaging / measuring system or a video-digital camera unit, and a Brookfield viscometer. A schematic diagram of the fluidized bed and video-digital camera unit for velocity measurements is shown in Figure 4. The schematic diagram for source-detector-recorder assembly for x-ray and γ -ray densitometers for volume fraction measurements is shown schematically in Figure 5.

a. Fluidization Equipment. A two-dimensional bed was constructed from transparent acrylic (Plexiglas) sheets to facilitate visual observation and video recording of the bed operations such as gas bubbling and coalescence, and the mixing and segregation of solids. The bed height was 213.36 cm and cross-section was 30.48 cm by 5.08 cm. A centrifugal pump was connected to the bottom of the bed by a 1.0 inch (2.54 cm) diameter stainless steel pipe. Gas injection nozzles from an air compressor were connected to the sides of the bed. Liquid was stored in and recycled back to a fifty five gallon storage tank.

The liquid and gas distributors were located at the bottom of the bed. The liquid was distributed by two perforated Plexiglas plates with many 0.28 cm diameter holes. They were placed at 35.6 cm and 50.8 cm above the bottom of the bed, with 0.25 cm size glass bead particles filled inside. The gas distributor consisted of six staggered porous tubes of 15.24 cm length and 0.28 cm diameter. The fine pores of porous tubes had mean diameter of 42 μ m. The porous tubes were placed at the bottom of the bed just below the top liquid distributor plate.

b. Densitometer Assembly. Two densitometers were used alternatively for measuring the time-averaged volume fractions of three phases at a designated location by means of the x-ray and γ -ray adsorption techniques. The assembly consisted of radioactive sources

as well as detecting and recording devices and a positioning table. A schematic diagram of the source, detector and recording devices assembly is shown in Figure 5.

(1) Radioactive Source. The source is a 200-mCi Cu-244 source having 17.8-year half-life. It emitted x-rays with a photon energy between 12 and 23 keV. The source was contained in a ceramic enamel, recessed into a stainless steel support with a tungsten alloy packing, and sealed in welded Monel Capsule. The device had brazed Beryllium window. For the γ -ray densitometer, a 20-mCi Cs-137 source having a single γ -ray of 667 keV and a half-life of 30 years was used. The source was sealed in a welded, stainless steel capsule. The source holder was welded, filled with lead, and provided with a shutter to turn off the source. This is the same unit used previously by Gidaspow, et al. (1983).

(2) Detecting and Recording Devices. The intensity of the x-ray beam was measured by using a NaI crystal scintillation detector (Teledyne, ST-82-1/B). It consisted of a 2-mm thick, 5.08 cm diameter tube with 0.13-mm thick Beryllium window. For γ -ray densitometer, the intensity of the γ -ray beam was detected by another NaI crystal detector (Teledyne, S-44-I/2). The dimension of the crystal were as follows: 5.08 cm thick and 5.08 cm in diameter. The two detectors could be switched for use with different sources. The photomultiplier of the detector was connected sequentially to a preamplifier, an amplifier and a single-channel analyzer, a rate meter, and a 186 IBM compatible personal computer. The rate meter has a selector and a 0-100 mV scale range.

(3) Positioning Table. Both the source holder and detector were affixed to either side of the bed on a movable frame and could be moved anywhere up-or-down or to-and-fro by means of an electric motor.

c. High Resolution Micro-Imaging / Measuring System. The digital camera technique used to measure particle velocities as shown on Figure 4 comprised of the following units:

(1) Image Recording and Displaying Devices. A high resolution color video camera equipped with electronic shutter speed settings ranging from OFF to 1/10000 sec and super fine pitch color monitor were used to record and display solid velocities.

(2) Data Recording Device. A 486 / 33 MHz IBM compatible personal computer with a micro-imaging board inside and a micro-imaging software, Image-Pro Plus were used to record and store raw solid velocities data at any given location inside the fluidized bed.

d. Brookfield Viscometer. Brookfield digital viscometer (model LVDV-II+) with spring torque of 673.7 dyne-cm was used to measure the effective bed viscosities. This viscometer can produce twenty different rotational speeds ranging from 0 to 100 revolutions per minute (rpm) at four different modes, namely, LV, RV, HA and HBDVII+. The viscometer readings were recorded with a Hewlett-Packard (HP) LaserJet series II printer.

Experimental Procedure and Interpretation.

a. Fluidization Experiments. The liquid from the storage tank was fed to the bed from the bottom of the bed using the centrifugal pump. The gas was fed to the bed through a compressor. Both gas and liquid from the top of the bed were directed through three openings of 1.0 inch (2.54 cm) diameter back to the storage tank, where the gas was separated from the liquid.

In order to achieve a uniform fluidization, the liquid distributor section was designed in such a way that the pressure drop through the distributor section was 10 - 20 % of the total bed pressure drop. The gas was distributed in the fluidized bed through the six staggered porous tubes.

Air and water were used as the gas and liquid, respectively, in this experiment. Ballotini (leaded glass beads) with an average diameter of 0.8 cm and a density of 2.94 g/cm^3 were used as the solids. The experimental operating conditions are shown in the Table 4 (Bahary, 1994).

The experimental volume fractions measurements were made at 240 different locations at every 1.27 cm in both x and y -directions on the left portion of the bed. The experimental operating conditions are shown in the Table 4.

TABLE 4. Operating Conditions for Bubbly Coalesced Regime Experiments

Temperature ($^{\circ}\text{C}$)	23.5
Particle Mean Diameter (cm)	0.8
Particle Density (g/cm^3)	2.94
Initial Bed Height (cm)	22 / 24
Minimum Fluidization Velocity (cm/s)	0.76

b. Volume Fractions Calibration. x-ray and γ -ray densitometers have been used to measure porosities of fluidized beds (Miller and Gidaspow, 1992; Seo and Gidaspow, 1987; Gidaspow, et al., 1983) and solids concentrations in nonaqueous suspensions (Jayaswal, et al., 1990). These techniques are based on the fact that the liquid, gas and solid phases under consideration have different absorptivities for x-ray and γ -ray. The same concept was adopted to measure concentration profiles inside our three phase fluidization systems.

The intensity of the transmitted x-rays or γ -rays can be described as a function of the volume fractions of liquid, gas and the solid phases. The amount of radiation that is absorbed by a material can be given by the Beer-Bougert-Lambert Law:

$$\underline{I = I_o \exp(-\kappa \rho l)} \quad (1)$$

where I is the intensity of transmitted radiation, I_o is the intensity of incident radiation, κ is the attenuation coefficient, ρ is the density of material, and l is the path length. The attenuation coefficient is calculated from a calibration curve. The logarithmic form of equation (1) is

$$\underline{\ln\left(\frac{I_o}{I}\right) = A} \quad (2)$$

where $A = \kappa \rho l$.

For three phase (gas-liquid-solid) fluidized beds, the intensity of the transmitted x-ray or γ -ray could be described as a linear function of the volume fractions of the phases as:

$$\underline{\ln\left(\frac{I_x}{I_{o,x}}\right) = A_{g,x} \epsilon_g + A_{l,x} \epsilon_l + A_{s,x} \epsilon_s} \quad (3)$$

$$\underline{\ln\left(\frac{I_g}{I_{o,g}}\right) = A_{g,g} \epsilon_g + A_{l,g} \epsilon_l + A_{s,g} \epsilon_s} \quad (4)$$

where I_x and I_g are the intensity readings of the x-ray and γ -ray densitometers; and ϵ_g , ϵ_l , ϵ_s are the volume fractions of gas, liquid and solid phases, respectively. The relation for volume fractions is:

$$\underline{\epsilon_g + \epsilon_l + \epsilon_s = 1} \quad (5)$$

The coefficients in equations (3) and (4) were calculated using the least square error technique from the calibration measurements of the intensity readings of x-ray and γ -ray densitometers at known concentrations of gas, liquid and solids in three phase mixtures. However, these coefficients were found to have values with 20% of error for x-ray and 2% of error for γ -ray.

To obtain the time averaged volume fractions at a designated position inside the three phase fluidized bed, an integration time of 40 seconds was used. The volume fraction measurements were obtained after a set of linear calibration was completed for x-ray and γ -ray densitometers as shown in Figure 6. From calibration curves, the time average values of volume fraction for liquid, gas and solid phases were calculated.

c. Velocity Measurements. In order to get a good visualization of microscopic movement of particles, a fiber-optic light was reflected on the field of view in the front and the back of the bed. The field of view in most experiments was a $2\text{ cm} \times 2\text{ cm}$ area. As the particles were fluidized inside the bed, the camera with a zoom lens 18-108 mm and close up focus transferred its field of view to the monitor with streak lines. These streak lines represented the space traveled by the particles in a given time interval specified on the camera. The images were then captured and digitized by a micro-imaging board and analyzed using Image-Pro Plus software. Radial and axial velocity measurements were conducted at different locations inside the bed. The velocity vector was calculated as,

$$\underline{v_x = \frac{\Delta L}{\Delta t} \cos(\alpha)} \quad (6)$$

$$\underline{v_y = \frac{\Delta L}{\Delta t} \sin(\alpha)} \quad (7)$$

where, ΔL is the distance traveled, α is the angle from radial axis, Δt is the inverse of shutter speed, and v_x and v_y are the axial and radial velocity components, respectively.

d. Viscosity Measurements using Brookfield Viscometer. The viscometer was placed at the top of the fluidized bed and secured over the centerline of the bed. A cylindrical spindle (#1 LV) of 0.9421 cm diameter, 7.493 cm effective length and overall height of 11.50 cm was used. The cylindrical spindle was attached to the bottom of the viscometer without the guard and was lowered inside the fluidized bed by an extension wire until it was completely immersed in the mixture during measurements.

The measurements in this experiment were made under LV mode at different speeds between 2 and 20 rpm. At each rotational speed, between 10 and 30 readings were taken. The calibration of the viscometer-spindle apparatus was done using a Newtonian liquid, namely, water, using the procedure of Hetzler and Williams (1969).

The solids viscosity was calculated from measured ("apparent" or effective) homogeneous bed viscosity in fluidized bed defined as,

$$\underline{m_{bed} = e_g m_g + e_l m_l + e_s m_s} \quad (8)$$

However, the effect of liquid and gas viscosities is negligible. In liquid-solid fluidized beds, gas volume fraction (ϵ_g) is zero.

e. Instantaneous Velocity Fluctuation and Granular Temperature. For Maxwellian distribution of velocity, mean axial and radial velocity components can be calculated as the

arithmetic averages. The variances of axial and radial particle velocities (following Maxwellian distribution) can be calculated from their mean values using

$$\langle C^2 \rangle = \frac{1}{N-1} \sum_{i=1}^N (v_i - v_m)^2 \quad (9)$$

where, v_i and v_m are the i -th instantaneous and mean particle velocities, respectively.

The two-dimensional fluidized bed used in the experiment allows flows predominantly in two directions, namely axial (y-) and radial (x-). Hence, the instantaneous velocities measurements were made in axial-radial (y-x) plane only. However, the depth (z-) direction also has a non-zero component of particles fluctuations because of a finite bed

depth. It is reasonable to assume that the $\langle C_z^2 \rangle = \langle C_x^2 \rangle$, because both z- and x- directions have zero mean gas and liquid velocities. Thus, the velocity fluctuations can be written as:

$$\langle C^2 \rangle = \langle C_x^2 \rangle + \langle C_y^2 \rangle + \langle C_z^2 \rangle = 2\langle C_x^2 \rangle + \langle C_y^2 \rangle \quad (10)$$

where $\langle C_x^2 \rangle$ and $\langle C_y^2 \rangle$ are the measured mean square velocity fluctuations in -x and -y directions, respectively. The granular temperature Θ_s , is related to the square of mean fluctuating velocity of particles $\langle C^2 \rangle$ as.

$$\Theta_s = \frac{1}{3} \langle C^2 \rangle = \frac{2}{3} \langle C_x^2 \rangle + \frac{1}{3} \langle C_y^2 \rangle \quad (11)$$

f. "Apparent" Bed Viscosity from Granular Temperature. In two and three phase fluidized beds, the rheological behavior of the bed predominantly reflects the granular viscosity of the solids. Lun, et al. (1984) derived an expression for the viscosity. Gidaspow's (1994) similar expression is used here.

$$m_s = \frac{5r_s d_p (p\Theta_s)^{\frac{1}{2}}}{48(1+e)g_o} \left[1 + \frac{4}{5}(1+e)g_o e_s \right]^2 + \frac{4}{5} e_s^2 r_s d_p (1+e)g_o \left(\frac{\Theta_s}{p} \right)^{\frac{1}{2}} \quad (12)$$

The radial distribution function, g_o , is given in section (4A) in Table 1. The granular temperature Θ_s , is either obtained from the kinetic oscillation energy balance, or by velocity measurement experiments.

Experiments. Results For Bubbly Coalesced Regime.

Phase Hold-Up. Figures 7(a), 7(b) and 7(c) show the experimental results in our two dimensional bed for the time-averaged volume fractions of the liquid, gas and solid, respectively. Figures 7(b) and 7(c) show that there exists a region of a maximum value of volume fraction of gas, slightly shifted away from the center line, and has a value of approximately 0.6. This region can be interpreted as a region through which most of the coalesced bubbles pass. Figures 7(a) and 7(c) show that there are few solids close to the wall. This is due to the downward flow of the gas and the liquid near the wall, causing solids to entrain and move down in that region.

Flow Pattern. The flow patterns inside the gas-liquid-solid fluidized bed were observed visually and by video recording. Figure 8(a) shows a typical photograph of flow pattern in the bubbly coalesced regime. There is downward flow at the wall, upward flow close but not quite at the center and bubble coalescence. The small bubbles estimated to be about 1 mm coalesce together to form the large bubbles of a 4 cm effective diameter. The correlation by Fan (1989) gives diameters of 2 to 4 cm. The flow pattern and also positions of two coalesced large bubbles are not symmetric with respect to the vertical center line of the bed. Figure 8(b) shows that the computed particle volume fractions, at least roughly, agree with visual observations.

Instantaneous Velocity Distribution. The measured velocity data were analyzed using frequency distribution plots. The frequency distribution plots for particle axial and radial velocities are shown in Figures 9(a) and 9(b) for three phase fluidized bed. Figures 10(a) and 10(b) show axial and radial velocities fluctuation distribution in a two phase fluidized bed. These figures clearly demonstrate that the velocity fluctuations in two and three phase fluidized beds follow approximately Maxwellian distribution. Hence, the basic assumption used to derive the kinetic theory of granular flows applies to fluidized beds.

Granular Temperature. Figures 11 shows granular temperature, calculated using particle velocity measurements, as a function of horizontal distance from centerline of the bed at two different heights. Granular temperatures shows a maxima near the center at the bottom of the bed.

The temperatures were calculated to be in the range of 100 to 1000 (cm/sec^2). The fluctuating velocity is in the range of 17 to 39 cm/sec (0.17 to 0.39 m/s). Typical values of the fluctuating velocities for gas-solid fluidized beds were computed by Ding and Gidaspow (1990) to be in the range of 0.17 to 1.7 m/s . Also, based on solids discharge rates from mass flow hoppers, Gidaspow et al. (1986) obtained critical granular velocities in the range of 56.39 to 113.49 cm/sec (0.5639 to 1.1349 m/s) for 86 to 1550 μm size glass beads and 105.19 cm/sec (1.0519 m/s) for 603 μm sized sand particles.

The mean fluctuating velocities obtained from bed viscosity measurements using the Brookfield viscometer are very close to those calculated based on the direct velocity

measurement experiments. Figure 12 shows a comparison of the measured and the calculated bed viscosities in fluidized beds with a uniform distributor. The figures show that there is reasonable agreement between the solids viscosity measured using the Brookfield viscometer and those calculated from granular temperature using kinetic theory and direct measurement of solids velocity using the high resolution micro image / measuring system technique.

Computational Results For Bubbly Coalesced Regime.

The three phase hydrodynamics model shown in Table 1 was used in the computations. As an initial condition, the gas-liquid-solid bed was assumed to be at the minimum fluidization state. The computer simulations were carried out in two different modes: symmetric and asymmetric. In the symmetric mode, the fluidized bed behavior was assumed to be symmetric across the centerline parallel to the axial direction, and the gas at the inlet was distributed uniformly. In this mode only half of the bed was simulated. In the asymmetric mode, it was assumed that the gas at the inlet entering the two sides of the bed had different volume fractions. This assumption was supported by visual observation of the experiment shown in Figure 7(a).

In the symmetric mode, the computations were carried out using a mesh of 1040 finite difference computational cells with $0.635 \text{ cm} \times 2 \text{ cm}$ cell sizes. In the asymmetric mode, the complete bed was simulated. A total of 1504 computational cells with $1.016 \text{ cm} \times 2 \text{ cm}$ cell sizes were used. The inlet and initial conditions for both the cases are shown in Figure 13. In both the modes, simulations were carried out for 20 seconds with time increment of 5×10^{-5} seconds. A no-slip condition was used at the walls. The computations were conducted on a Hewlett-Packard 730 workstation.

Figures 14(a) and 14(b) show contours for instantaneous volume fractions and flow patterns simulated using symmetric and asymmetric modes, respectively. Computed flow pattern in asymmetric mode correctly shows upflow in the center region as seen in the experiments (see Figure 8(a)). However, the symmetric mode simulation incorrectly shows downflow in the center region. For asymmetric mode, the computed time-average volume fraction contours inside the bed for liquid, gas and solids are shown in Figures 15(a), 15(b) and 15(c), respectively.

For both symmetric and asymmetric modes, gas bubbles have a tendency to coalesce midway between the center of the bed and the walls. In the asymmetric mode computation the computed gas bubble moves in a snake-like fashion as observed in the experiment. Also in the asymmetric mode the two large bubbles coalesce at the center of the bed while in the symmetric mode the two large voids do not coalesce.

For asymmetric mode, the computed velocity vectors inside the bed for all three phases are shown in Figures 16. The computed velocity is very high in the region of the large bubbles. Figures 8(a) and 16 show that all three phases have downward movement near

the wall and upward movement at the center, the same flow pattern also reported by Chen, Reese, and Fan (1994).

This downflow produces a rotation or particle vorticity, given by inviscid equation below,

$$\frac{\partial \epsilon_z}{\partial t} + v_x \frac{\partial \epsilon_z}{\partial x} + v_y \frac{\partial \epsilon_z}{\partial y} = - \left(\frac{g}{1 - e_{mf}} \right) \frac{\partial e_g}{\partial y} \quad (14)$$

The equation shows that the vorticity produces a change in gas volume fraction ϵ_g . Then although we supply gas at a uniform rate, the gas is no longer uniformly distributed. Furthermore, Bouillard and Gidaspow (1991) have shown that when the gas at the bottom moves faster than in the rest of the bed, there is a catch-up effect and large gas voids may form, as depicted by Figure 8(a). It is the packing effect of the bubbles that produces this regime. When the injected bubbles are far apart, for low gas velocities, the bubbles move up at constant velocities. In this regime the drag is independent of the gas volume fraction. It is given by the corrected Stoke's law. At high gas velocities, the gas volume fraction is high and we use the Ergun equation to compute the drag in our model. Here the paths of the small injected bubbles intersect and bubbles coalesce. The situation is identical to that described in chapter 6 for gas-solid fluidized beds by Gidaspow (1994).

Comparison between Experimental and Computed Results in Bubbly Coalesced Regime

Phase Hold-up. Computed time average solid volume fraction contours inside the bed are shown in Figure 8(b). A photograph of the experiment in Figure 8(a) shows that the solid is concentrated in the lower 25 cm portion of the bed. There is a murky interface between the solid and the liquid-gas in the upper portion of the bed. This is in part reality and in part caused by inadequate time averaging. Time averaging of simulated values was done over about 20 seconds. Averaging over a longer time period could not be used due to a small loss of particles observed both in the experiment and more so in the simulation. The computation has higher particles loss because walls effects were neglected in two dimensional formulation. To correct this deficiency a three dimensional code is under development. Figure 15(b) shows that there is more gas in the lower portion of the bed (in the presence of solids) than in the upper portion where only gas and liquid are present.

Figures 17 and 18 show comparison between the experimentally measured and the simulated time-average volume fractions for gas and solids phases at different radial positions inside the bed. The figures show that there is a good agreement between the experimental and the computational results near the center and the wall regions.

Flow Pattern. Figure 19 shows a comparison between experimental and computed time-averaged axial solids velocity profiles at a height of 13.0 cm from the bottom of the bed for asymmetric mode simulation. The figure shows good comparison between measured

and asymmetric mode computed velocity profiles. However, at a height of 2.54 cm, the residual effects of liquid inlets can be seen.

Particulate Viscosity. The variance obtained from data such as depicted in Figure 15 gives the granular temperature (Gidaspow, 1994). The "apparent" bed viscosity was calculated from granular temperature using kinetic theory model shown in part (4A) of Table 1. A comparison of the estimated bed viscosity and those measured using a Brookfield viscometer (Bahary, 1994) is shown in Table 5.

"Apparent" Bed Viscosity and Granular Temperature. The "apparent" bed viscosities are shown in Table 5. In this table, the liquid volume fractions are estimated using correlation (Kim, et al., 1972) shown in equations (1) and (2) and solid volume fractions are calculated from visually measured expanded bed heights under fluidizing conditions. The reported volume fractions are averaged values. The agreement is excellent.

Bubble Coalescence Criterion. In a slurry bubble column three basic regimes can be observed (Shah, et al., 1982; Fan, 1986). For a large column diameter at low gas velocities, which means at low inlet gas volume fractions in the proposed model, the bubbles are so far apart that their velocities, called C below and in Gidaspow's book (1994) in chapter 6, can be given approximately by a Stokes' type equation (15), shown below. Table 1, Eq. (5) shows the more general case.

$$C = \frac{\Delta r g d_{bubble}^2}{18m} \quad (15)$$

In this dispersed bubble regime the small bubbles move up the column without coalescing. As the velocity increases a packing effect makes itself felt. Then as a special case of the relations given in Table 1, C can be given by the first term of the Ergun equation for a packed column, shown in Equation (16).

$$C = \frac{\Delta r g d_{bubble}^2}{150m_{mixture}} e^2 = \left(\Delta r g \right)^{\frac{1}{3}} \frac{\left(6sD_{orifice} \right)^{\frac{2}{3}}}{150m_{mixture}} e^2 \quad (16)$$

In the second part of equation (16), the bubble diameter has been replaced by its expression obtained from its formation at an orifice at the distributor. This formula shows the effect of surface tension. A different way to compute the bubble diameter is to use a hydrodynamic stability analysis. In this study a constant bubble diameter was used. Hence surface tension enters the analysis only indirectly through bubble diameter.

TABLE 5. Three-Phase Fluidized Bed Solids Viscosity Comparison.

Sup. Gas Velocity (cm/s)	Sup. Liq. Velocity (cm/s)	Solid Vol. Fraction	Granular Temperature (cm/s) ²	Viscosity from Velocity Measurements	Viscosity from Brookfield Viscometer
3.364	2.037	0.346	845	4.26	4.36
3.364	4.027	0.272	435	2.95	3.13

The square dependence on porosity in Equation (16) gives the mechanism for bubble coalescence. At the inlet the porosity is larger than in the upper portion of the bed, hence the bubbles entering the bed move faster than those in the upper portion of the bed. There is a catch-up effect and hence bubbles coalesce. This is a possible explanation for the presence of small and large bubbles in the bubble coalesced regime. When the column diameter is small these large bubbles coalesce into a slug.

PART III: GRANULAR TEMPERATURE AND REYNOLDS STRESS FOR METHANOL CATALYST

Slurry Bubble Column Reactor

Slurry bubble column reactors have recently (Parkinson, 1997) become competitive with traditional tubular fixed-bed reactors for converting syn-gas into liquid fuels. In the U.S. a plant is being built by Air Products and Eastman Chemical (DOE, 1997) to produce methanol from syn-gas in a slurry bubble column reactor.

The advantage of a fluidized bed reactor over that of a fixed bed reactor is better heat and mass transfer due to constant agitation of the catalyst and the ability to introduce and remove the catalyst into the reactor. Such an operation requires an understanding of the flow of the catalyst.

Except for proprietary work of EXXON and other companies, the design of slurry bubble column reactors for indirect liquefaction is being done by the use of one-dimensional models. All hydrodynamic input is through empirical holdup correlations. The state of the art of the design of the slurry bubble column reactors is illustrated by the Viking Systems International (1993) report to PETC, now reorganized as the Federal Energy Technology Center (FETC).

The model presented in this paper permits the computation of three phase hydrodynamics. The only empirical input needed is an effective restitution coefficient of the particles (Gidaspow, et al., 1995; Wu, 1996; Pape, et al., 1996).

A 2-D THREE-PHASE BED WITH MULTIPLE JETS

Bed structure

To simulate a slice of the Air Products methanol reactor (Air Products, 1991) with jets a thin rectangular three phase fluidized bed was designed and constructed.

In order to have a symmetric system seven identical jets (7/8×7/8×7/8 inches) are installed at the bottom of the bed. See Figure 20. Each of these jets is connected to a valve to control the gas flow rates. The reason for using square jets is to eliminate the 3D effects caused by circular jets. At the bottom of each jet a cloth type material (with a pressure drop of 2 psi at the maximum gas flow rate) is used to prevent the 50 µm catalyst particles from going inside the gas pipe. The bed is constructed of 1/2 inch thickness Plexiglas. An opening at the top of the bed lets the air go out of the bed to the atmosphere.

The air flow rate can be varied up to 190 cf/hr at a pressure of 40 psi in order to achieve a superficial gas velocity of 12 cm/sec. In a typical Air Products experiment the weight ratio of solid to liquid was about 2:3. Figure 21 shows bed size and measurement location.

Granular Temperature and Reynolds Stress Measurements

The influence of the solid concentration on the granular temperature has been studied. For each run the solid-liquid ratio has been changed by loading more solids in the bed. Due to the small particle size a uniform dispersion is assumed to exist in the experiment. With this assumption the average bed expansion has been calculated and in this manner the solid volume fractions were obtained. In all of the experiments the superficial gas velocity was kept constant and all of the measurements were conducted at the same location of the bed so that the only variable is the solid concentration.

The granular temperatures and Reynolds Stresses have been calculated from instantaneous particle velocity measurements. These instantaneous particle velocities have been measured using a series of processes utilizing different tools. A CCD camera and built-in hardware were used to capture the trace of particles moving inside the bed. At this stage the illumination technique and also the camera speed play a significant role to get a sharp image. The captured particle traces were digitized with the aid of an advanced image processing software (IPPLUS®). Necessary operations such as background correction and filtering were performed. The final image was used to measure the length and horizontal angle of the streak lines in order to obtain vertical and horizontal velocities. The histograms were drawn and the variance of the velocities have been calculated. See Fig 22 for a sample of a histogram. In part II of this study the granular temperature was calculated using the assumption that the velocity distributions were Maxwellian. Since such an assumption is too rough an approximation, in this section the granular temperatures were calculated using the method of Gidaspow and Huilin (1996) applied to FCC particles in a riser. The granular temperature was calculated using the equation for variance of velocity in the i direction :

$$\underline{s_i^2 = \frac{1}{N} \sum_{i=1}^N (v_i - v_m)^2} \quad (17)$$

and the assumption of equality of the variances in the non-flow (z and x) directions:

$$\underline{q = \frac{1}{3}(\mathbf{s}_y^2 + \mathbf{s}_z^2) = \frac{2}{3}\mathbf{s}_x^2 + \frac{1}{3}\mathbf{s}_y^2} \quad (18)$$

The Reynolds stress has been calculated using the following formula:

$$\underline{\overline{u'v'} = \frac{1}{N} \sum (v - \bar{v})(u - \bar{u})} \quad (19)$$

Figure 23 shows the results of these experiments. As can be seen the granular temperature passes through a maximum value at low solids loading around $\epsilon_s=0.01$. In the dilute limit as shown by Gidaspow(1994), the equation for the granular temperature, that is the balance of random kinetic energy, shows that the granular temperature θ is proportional to the volume fraction of solids, ϵ_s raised to the 2/3 power. This is analogous to the increase of thermal temperature of ideal gases with density upon compression, where the 2/3 corresponds to the ratio of the specific heats. Classical kinetic theory of granular flow gives an infinite granular temperature at zero solid volume fraction for shear flow. For high volume fractions of solids, Figure 23 shows the classical decrease of the granular temperature with volume fraction. This is known to be due to the decrease of the mean free path. For packed beds there will be no particle oscillations. Hence the behavior of the granular temperature in Figure 23 is general and is not restricted to the flow of 75 μm FCC catalyst in the IIT CFB or to Air Products catalyst in our unit. Operationally this means it may not be desirable to operate at very high catalyst concentrations due to reduced stirring at the high catalyst concentrations. This behavior is very similar to that observed by Gidaspow and Huillin (1996) in a circulating fluidized bed of 75 μm FCC particles.

We have observed much higher granular temperatures with gas flow than was the case for liquid flow with Air Products catalyst. This means there is much better stirring caused by the high gas flow; clearly a desirable feature in a reactor. There the highest granular temperature was only one $(\text{cm/sec})^2$, one hundred times lower. Hence the high gas flow produces the desirable stirring.

A Link Between the Granular Temperature and the Particle Reynolds Stress

For steady, developed shear flow (Gidaspow, 1994; Cao and Ahmadi, 1995) with a negligible interaction energy supply, i.e. equal particle and fluid oscillations, the production of oscillations by particle collisions equals the dissipation due to inelastic collisions. With these approximations the fluctuating kinetic energy equation (Eq. (4A) in Table 1) reduces itself to the balance:

$$\begin{array}{c}
- P_{xy} \cdot \frac{\mathcal{I}u_s}{\mathcal{I}y} = 12 \mathbf{e}_s^2 r_s g_o (1 - e^2) \left(\frac{\mathbf{q}}{d_p} \right) \left(\frac{\mathbf{q}}{p} \right)^{\frac{1}{2}} \\
\hline
\begin{array}{cc}
\text{production of} & \text{dissipation due to} \\
\text{particle oscillations} & \text{particle collisions with an} \\
\text{by shear } P_{xy} & \text{effective restitution coefficient, } e
\end{array}
\end{array} \quad (20)$$

where $\mathcal{I}u_s$ is the particle velocity in the x direction, the basic flow direction, and $\mathcal{I}y$ is the perpendicular direction.

Gidaspow (1994) used such an equation to estimate the restitution coefficient in a CFB

where the shear rate, $\left(\frac{\mathcal{I}u_s}{\mathcal{I}y} \right)$ was known. Here the shear, P_{xy} was directly measured.

From its definition,

$$P_{xy} = r_s \mathbf{e}_s \left\langle C_x C_y \right\rangle \quad (21)$$

where C_i is the instantaneous minus the average particle velocity in the i direction and $\langle \rangle$ means averaging over the velocity space. In terms of the conventional turbulence theories, Equation (19) gives the particle Reynolds stress

$$P_{xy} = r_s \mathbf{e}_s \overline{u'_s v'_s} \quad (22)$$

where the bar over the velocities has the same meaning as the bracket averaging.

Equations (20) and (22) provide a link between the Reynolds stress and the granular temperature. This relation involves the as yet unknown shear rate. The shear rate can be eliminated using a second expression for shear stress.

$$- P_{xy} = m_s \frac{\mathcal{I}u_s}{\mathcal{I}y} \quad (23)$$

where m_s is the viscosity of the solid.

For the dense flow, this viscosity is given by

$$\underline{\underline{m_s = \frac{4}{5} e_s^2 r_s d_p g_o (1+e) \left(\frac{q}{p} \right)^{\frac{1}{2}}}} \quad (24)$$

As a limiting value the balance between production of oscillations and their dissipation, as given by Equation (20), was previously (Gidaspow, 1994) shown to be

$$\underline{\underline{\left(\frac{1}{15} \right)^{\frac{1}{2}} \frac{\eta u_s}{\eta y} d_p = (1-e)^{\frac{1}{2}} q^{\frac{1}{2}}}} \quad (25)$$

This equation permits the elimination of the shear rate in Equation (20). Division of Equation (20) by (25) and use of (22) gives the link between the Reynolds stress and the granular temperature in terms of inelastic dissipation.

$$\underline{\underline{\frac{\overline{u'_s v'_s}}{3q} \equiv \frac{u'_s v'_s}{u_s'^2 + v_s'^2 + w_s'^2} = \left(\frac{16}{15p} \right)^{\frac{1}{2}} e_s g_o \frac{(1-e^2)}{(1-e)^{\frac{1}{2}}}}} \quad (26)$$

For nearly elastic particles , Eq. (26) gives

$$\underline{\underline{\frac{\overline{u'_s v'_s}}{3q} = 1.1954 e_s g_o (1-e)^{\frac{1}{2}}}} \quad (27)$$

which is valid for the dense regime.

The dilute limit yields an expression that is independent of particle concentration, as

$$\underline{\underline{\frac{\text{Reynolds Stress}}{\text{Granular Temperature}} = \left| \frac{\overline{u'_s v'_s}}{q} = \left(\frac{5}{8} \right)^{\frac{1}{2}} (1-e^2)^{\frac{1}{2}} \right|_{\text{dilute limit}}} \quad (28)$$

For isotropic turbulence Eq. (28) gives no real solution for the restitution coefficient.

Particle Attrition

Air Products methanol catalyst particles that have been used as the solid phase in our three phase fluidization have been examined to find the breakage. The fresh catalyst was analyzed by a sieve method. The distribution of particle size is given in Figure 24.

After one year usage of the catalyst in the bed in which the air was always flowing at a velocity of at least 0.2 cm/sec through seven jets, the particles have been analyzed by a Reflected Light Microscope. The pictures from microscope were transferred to our image processing software (IPPLUS[®]) where the particles size were measured. Two pictures

that have been captured are shown in Figure 25. The distribution of particle size is given in Figure 26. As can be seen the used catalyst is mostly fines and much smaller than the original fresh catalyst. The distribution has a double peak. It shows that there was a lot of fine particles production due to jets and particle-particle and particle-wall collisions.

TABLE 6 - Restitution Coefficient for 50 μm Catalyst in G-L-S Bed

e_s	$\frac{\overline{u'v'}}{q}$	$1 - e$
0.13	0.2873	0.06837
0.07	-0.4127	0.14707
0.02	-0.4069	0.14263
0.0075	-0.0716	0.00411
0.0004	0.2461	0.04969

Cluster Formation

As shown in Figure 27, some clusters are formed. These clusters are a group of particles and may be considered as one moving object. Indeed the viscosity of the Air Products catalyst slurry measured with a Brookfield viscometer was ten times that estimated using kinetic theory, based on 50 μm catalyst particle size.

Optimum Catalyst Design

The measurements reported here permit us to speculate concerning optimum Fischer-Tropsch catalyst design. The diffusional resistance inside the catalyst leads one to make the catalyst as small as possible, since the resistance is proportional to particle diameter. However, this study shows that small particle diameters lead to small particle oscillations and to agglomeration. This gives a large particle resistance to mass transfer. Hence there exists an optimum particle size. Furthermore as seen from Figure 23 and theoretical speculations as the particle concentration increases, the particle oscillations decrease, stopping completely in the packed bed state. Hence there is also some optimum catalyst concentration.

The particle oscillations in Fig. 23 are much larger than for the liquid-catalyst system (Gidaspow and Huillin, 1997). They are caused by the flow of the gas. Although much information in this area proprietary, obtained by expensive trial and error of slurry reactor design, it appears that gas flow rates used in this technology are substantially above those needed for reaction and are used to promote stirring. This is another area needing modeling. The proposed CFD model was developed to answer such questions. Wu (1996) and Gidaspow, et al., (ASME, 1996) have developed a reaction model.

CONCLUSIONS

1. Discussion at various National Science Foundation-Department of Energy (NSF-DOE) workshops in the late eighties and early nineties produced a general agreement between the participants that for validation of time averaged multiphase flow equations it is necessary to compare the computed phase velocities and concentrations, sometimes called hold-ups, to well defined experiments. In this study we measured the particle velocities with a new technique and hold-ups with a combination of an x-ray and a γ -ray densitometers. There is a fair agreement between the model and the experiments. The differences are principally due to non-uniformities in our distributor.

For 800 μm glass beads, computed and measured time average velocities agree in the sense that :

- a. There exists down flow at the walls.
 - b. The velocities peak in the region of most frequent bubble motion.
 - c. In the center of the bed there is a small negative down flow.
2. Computations have shown the need for knowing phase viscosities. Kinetic theory shows that the viscosities can be obtained from granular temperatures. In this study we have developed a new technique for measuring the granular temperature of particles using a digital video camera. We have obtained an excellent agreement between the viscosities of a three phase and a two phase slurry obtained by measuring the granular temperature and by measuring the viscosity with a Brookfield viscometer.
3. The large value of the slurry viscosity, several poises for large particles, compared with the one centipoise viscosity for water clearly shows the dominant effect of particle collisions. In modeling this system we can ignore the liquid and the gas viscosities.
4. A link between the particle Reynolds stress and the granular temperature was developed for shear flow. It was demonstrated experimentally for Air Products Methanol catalysts.
5. From the measurement of the Reynolds stress and the granular temperature of a methanol catalyst in a three phase bubble coalesced fluidized bed with multiple jets the effective restitution coefficient was obtained to be about 0.9. This parameter is the only unknown in the kinetic theory model. Its knowledge permits the simulation of methanol reactor hydrodynamics.
6. The present data are consistent with the Radiation Particle Tracking turbulence intensity and particle velocity measurements of Larachi, et al. (1996). In their fluidized bed they used 3 mm glass beads, had a higher expanded bed height and used higher flow rates than in the present study. Due to these factors they had upflow in the center and downflow at the walls. In this study we also have downflow. We can achieve upflow in the center by increasing the flow rates and particle inventory as demonstrated for a bubbling gas-solid fluidized bed (Gidaspow, 1994). The granular temperature measured and computed in this study is essentially the sum of the radial and axial turbulence intensities reported by Larachi, et al. The model in its present state does not compute the individual turbulence intensities.

Reynolds stresses were measured in L.S. Fan's laboratory at Ohio State University (Reese, 1996) using a PIV technique, similar to that used here. The ratio of the absolute value of

the shear Reynolds stresses to the granular temperature, computed from reported axial and radial normal stresses, have the same trend, as predicted by equation (28).

ACKNOWLEDGMENT

This work was partially supported by the National Science Foundation, grant No. CTS-9305850 and by the Department of Energy UCR grant No. DE-FG-22-94PC94208.

NOMENCLATURE

Abbreviation	Term
A	absorbance (equals κl)
C, c	fluctuating velocity of a particle
C_D	drag coefficient
d_k	characteristic diameter of particulate phase k
e	coefficient of restitution
G	solid compressive stress modulus
g	gravity
g_o	radial distribution function
I	intensity of transmitted radiation
[I]	unit tensor
L	length traveled
l	path length
N	number of particle velocity measurements
p	pressure
q	flux vector of fluctuating energy
Re_k	Reynolds number of phase k
t	time
u	velocity in the basic direction of flow
v	velocity in the perpendicular direction
v	velocity vector
X_k	reduced volume fraction $\frac{\mathbf{e}_k}{\mathbf{e}_k + \mathbf{e}_m}$
Greek letters	
α	angle of particle movement
β_{km}	coefficient in particle-particle drag coefficient equation
m	interphase momentum transfer between phase k and phase
γ	collision energy dissipation
ϵ_k	volume fraction of phase “k”
ϵ	void fraction
ζ	vorticity
$3/2\Theta_s$	fluctuating energy
κ	conductivity of fluctuating energy

	mass attenuation coefficient
μ	shear viscosity
μ_s	(shear viscosity $\times$ volume fraction) of solids
ξ	bulk viscosity
ξ_s	(bulk viscosity $\times$ volume fraction) of solids
ρ	density
τ	stress
Φ_s	viscous energy dissipation
Ψ_s	particle sphericity

Subscripts

0	incident
bed	effective bed
dil	dilute phase
g	gas phase
k	phase k
i	for i-th instantaneous measurement
l	liquid phase
m	phase m
	mean
max	maximum
mf	minimum fluidization
s	solid phase
sup	superficial
t	terminal
x	x-ray
x	x- axial component
y	y- radial component
γ	γ -ray

Superscripts

T	transpose
---	-----------

BIBLIOGRAPHY

- Ahmadi, G. and D. Ma (1990). "A Thermodynamical Formulation for Dispersed Multiphase Turbulent Flows—I," *Int. J. Mutiphase Flow*, Vol. 16, No. 2, pp. 323-340.
- Air Products and Chemicals, Inc. (1991). "Liquid Phase Methanol LaPorte Process Development Unit: Modification, Operation and Support Studies," *Draft Report to DOE for Contract No. DE-AC22-87PC90005* .
- Arastoopour H. and Y.Yang (1992). "Experimental Studies on Dilute Gas and Cohesive Particles Flow Behavior using Laser Doppler Anemometer," *Fluidization VII*, pp. 723-730.

- Bahary, M. (1994). *Experimental and Computational Studies of Hydrodynamics of Three Phase and Two-Phase Fluidized Beds*, Ph.D. Thesis, Illinois Institute of Technology, Chicago, Illinois.
- Bouillard, J.X. and D. Gidaspow (1991). "On the Origin of the Bubbles and Geldart's Classification," *Powder Technology*, 68, 13-22.
- Bouillard, J.X., Lyczkowski R.W. and D. Gidaspow (1989). "Porosity Distribution in a Fluidized Bed with an Immersed Obstacle," *AIChE J.*, 35, no.6, 908-922.
- Bowen, R.M. (1976). "Theory of Mixtures," in *Continuum Physics, Vol. III*, editor A.C. Eringen, 1-117, Academic Press, New York.
- Cao, J. and G. Ahmadi (1995). "Gas-Particle Two Phase Turbulent Flow in a Vertical Duct" *Int. J. Multiphase Flow*, Vol. 21, No.6, pp.1203-1228.
- Carlos, C.R. and R.F. Richardson (1968). "Solid Movement in Liquid Fluidised Beds - I. Particle Velocity Distribution," *Chem. Eng. Sci.* 23, 813-824.
- Chen, R.C., J. Reese and L.-S. Fan (1994). "Flow Structure in a Three-Dimensional Bubble Column and Three Phase Fluidized Bed," *AIChE J.*, 40, no.7, 1093-1104.
- Cody G.D., Goldfarb G.V., Storch G.V. and A.N. Norris (1996). "Particle Granular Temperature in Gas Fluidized Beds," *Powder Tech.*, 87, pp. 211-232.
- Cody, G.D. and D.J. Goldfarb (1997), "Discontinuity in Particle Granular Temperature Across the Geldart B/A Boundary," To be published in *1997 AIChE Symposium Series on Fluidization and Fluid-Particle Systems*.
- Courant, R., E. Isaacson and M. Rees (1952). "On the Solution of Nonlinear Hyperbolic Differential Equations by Finite Differences," *Communication in Pure and Applied Mathematics*, 5, 243.
- Ding, J. and D. Gidaspow (1990). "A Bubbling Fluidization Model Using Kinetic Theory of Granular Flow," *AIChE J.*, 36, 523-528.
- Drew, D., L. Cheng and R.T. Lahey (1979). "The Analysis of Virtual Mass Effects in Two-Phase Flow." *Int. J Multiphase Flows*, 5, 223-242.
- Fan, L.-S. (1989). *Gas-Liquid-Solid Fluidization Engineering*, Butterworths, Boston, Massachusetts.
- Gidaspow, D. and L. Huillin (1996). "Collisional Viscosity of FCC Particles in a CFB," *AIChE J.*, Vol. 42, 2503-2510.
- Gidaspow, D., Bahary, M. and Y. Wu (1995). "Hydrodynamic Models for Slurry Bubble Column Reactors," *Coal Liquefaction and Gas Conversion Contractors Review Conference Preprints*, Pittsburgh, PA.
- Gidaspow, D.(1994). *Multiphase Flow and Fluidization. Continuum and Kinetic Theory Descriptions*. Academic Press, Boston, Massachusetts.
- Gidaspow, D., U.K. Jayaswal and J. Ding (1991). "Navier-Stokes Equation Model for Liquid-Solid Flows Using Kinetic Theory," *Liquid Solid Flows*, FED - Vol. 118, ASME, New York, 165-172.
- Gidaspow, D.(1986). "Hydrodynamics of Fluidization and Heat Transfer: Supercomputer Modeling," *Appl. Mech. Rev.*, 39, no.1, 1-23
- Gidaspow, D., C. Lin and Y.C. Seo (1983). "Fluidization in Two-Dimensional Beds with a Jet, Part 1: Experimental Porosity Distributions," *I&EC Fundam*, 22, 187-193.
- Hetzler and Williams, (1969). "Fluidized Bed Viscosity and Expansion, Correlated With Glass Forming liquid Model," *I&EC Fund.*, 666-677.

- Jackson, R. (1985) "Hydrodynamic Stability of Fluid-Particle Systems," in *Fluidization*, edited by J.F. Davidson, R. Clift and D. Harrison, Academic Press, 47-72.
- Jayaswal, U.K. (1991) *Hydrodynamics of Multiphase Flows: Separation, Dissemination and Fluidization*, Ph.D. Thesis, Illinois Institute of Technology, Chicago, Illinois.
- Jayaswal, U.K., D. Gidaspow and D.T. Wasan (1990). "Continuous Separation of Fine Particles in Nonaqueous Media in a Lamella Electrosettler," *Separations Technology*, 1, 3-17.
- Kim, S.D., Baker, C.G.J. and M.A. Bergougnou (1972). "Hold-up and Axial Mixing Characteristics of Two and Three Phases Fluidized Beds," *Can. J. Chem Engng.*, 50, 695.
- Larachi, F., Cassanello, M., Chaouki, J. and C. Guy (1996). "Flow Structures of the Solids in a 3-D Gas-Liquid-Solid Fluidized Bed," *AIChE J.*, 42, no.9, 2439-2452.
- Lyczkowski, R.W., D. Gidaspow, C.W. Solbrig and E.C. Hughes (1978). "Characteristics and Stability Analysis of Transient One-dimensional Two-Phase Flow equations and their Finite Difference Approximations," *Nuclear Science and Engineering*, 66, 378-396.
- Lun, C.K.K., S.B. Savage, D.J. Jeffrey and N. Chepurniy (1984). "Kinetic Theories for Granular Flow : Inelastic Particles in Couette Flow and Singly Inelastic Particles in a General Flow Field," *J. Fluid Mech.*, 140, 233-256.
- Miller, A. and D. Gidaspow (1992). "Dense, Vertical Gas-Solid Flow in a Pipe," *AIChE J.*, 38, 1801-1815.
- Mohammadi, B. and O. Pironneau (1994). "*Analysis of the K-Epsilon Turbulence Model*" Wiley Publisher.
- Pape R., Gidaspow D. and S. Wu (1996). "Multiphase Flow in Slurry Bubble Column Reactors and Solid Propellant Rockets," Presented at the 2nd *International Symposium on Numerical Methods for Multiphase Flows*, ASME Fluids Engineering Division, San Diego, CA.
- Parkinson G. (1997). "Fischer-Tropsch Comes Back," *Chem. Eng.*, pp. 39-41.
- Prosperetti, A. (1982). "Numerical Aspects of the Simmer-11 Code," in *Multiphase Process in LMFB Safety Analysis*, Ispra, Italy, April, 197-224.
- Reese, J.R. (1996), *Investigation of the Intrinsic Flow Phenomena in Bubble Columns Utilizing a Particle Image Velocimetry Technique*. Ph.D. Thesis, Ohio State University.
- Rivard, W.C. and M.D. Torrey (1977). "K-FIX: A Computer Program for Transient, Two-Dimensional, Two-Fluid Flow," *LA-NUREG-6623*, Los Alamos.
- Saffman, P.G. (1965). "The Lift on a Small Sphere in a Slow Shear Flow," *J. Fluid Mech.*, 22, 385-400.
- Samuelsberg, A. and B. H. Hjertager (1996a). "Computational Modeling of Gas/Particle Flow in a Riser," *AIChE J.*, v. 42, n. 6, pp. 1536-1546.
- Samuelsberg, A. and B. H. Hjertager (1996b). "Experimental and Numerical Study of Flow Patterns in a Circulating Fluidized Bed," *Int. J. Multiphase Flow*, v. 22, n. 3, pp. 575-591.
- Savage, S.B. (1983). "Granular Flows at High Shear Rates," in *Theory of Dispersed Multiphase Flow*, editor R.E. Meyer, Academic Press, New York.
- Seo, Y.-C. and D. Gidaspow (1987). "An x-ray-, γ -ray Method of Measurement of Binary

- Solids Concentrations and Voids in Fluidized beds," *I&EC Research*, 26, 1622-1628.
- Shah, Y.T., Kelkar B.G. and S.P. Godbole (1982). "Design Parameters Estimations for Bubble Column Reactors," *AIChE J.*, 28, 353-379.
- Soo, S.L. (1967). *Fluid Dynamics of Multiphase System*, Blaisdell Publishing, Waltham, Massachusetts.
- Song, G.H. and L.-S. Fan (1986). "Rheological Behavior of a Gas-Liquid-Solid Fluidized Bed," in *Proceedings of the World Congress III of Chemical Engineering*, 504-507, Tokyo.
- Stewart, H.B. and B. Wendroff (1984). "Two-Phase Flow: Models and Methods," *J. Comput. Phys.*, 56, 363-409.
- Tarmy, B.L. and C.A. Coualoglou (1992). "Alpha-Omega and Beyond Industrial View of Gas/Liquid/Solid Reactor Development," *Chem. Eng. Sci.*, 47, no. 13-14, 3231-3246.
- Viking Systems International Report to DOE/PETC (1993). "Design of Slurry Reactor for Indirect Liquefaction Applications".
- Wu Y. (1996). *Simulation of Methanol Synthesis in Slurry Bubble Column Reactors*. Ph.D. Thesis, Illinois Institute of Technology, Chicago, IL.

FIGURE 1. Three-Phase Fluidization System for Simulation of Dispersed Bubble Regime.

FIGURE 2. Computed Granular Temperature and Solid Shear Viscosity for Case 1 in Dispersed Bubble Regime.

FIGURE 3. Computed Velocity Patterns for Dispersed Bubble Regime.

FIGURE 4. Schematic Diagram for Three-Phase Fluidization Apparatus and Video-Digital Camera Unit for Bubbly Coalesced Regime Experiments.

FIGURE 5. Schematic Diagram for Source-Detector-Recorder Assembly for X-Ray and γ -Ray Densitometers.

(a) X-Ray

(b) γ-Ray

FIGURE 6. (a) X-Ray, and (b) γ-Ray Calibration Curves for Lead Glass Beads in a Three-Phase Fluidized Bed.

FIGURE 7. Experimental Time Average Volume Fraction Contours for Bubbly Coalesced Regime.

FIGURE 8. (a) Experimental, and (b) Simulated Bubble Coalescence in Three-Phase Fluidized Bed at Superficial Gas Velocity of 3.7 cm/s and Superficial Liquid Velocity of 2.03 cm/s.

FIGURE 9. Frequency Distribution of (a) Axial, and (b) Radial Velocity Components of Particles at $X = 4.0$ cm and $Y = 4.5$ cm for Liquid-Gas-Solid Fluidized Bed at Sup. Liquid Velocity of 4.0 cm/sec and Sup. Gas Velocity of 3.36 cm/sec.

FIGURE 10. Frequency Distribution of (a) Axial, and (b) Radial Velocity Components of Particles at $X = 4.0$ cm and $Y = 4.5$ cm for Liquid-Solid Fluidized Bed at Sup. Liquid Velocity of 4.0 cm/sec.

FIGURE 11. Granular Temperature vs. Radial Distance at Different Bed Heights in Gas-Liquid-Solid Fluidized Bed at Sup. Liquid Velocity of 4.04 cm/sec and Sup. Gas Velocity of 3.36 cm/sec.

FIGURE 12. Comparison of Measured and Calculated Solids Viscosity in Fluidized Bed with Uniform Distributor.

Outlet Conditions:

$V_g = V_s = 0$ cm/s
 $V_i = 0.7$ cm/s
 $p = 0.1013E07$ dynes/cm²

(a) Symmetric Mode

Outlet Conditions:

$V_g = V_s = 0$ cm/s
 $V_i = 5.4$ cm/s
 $p = 0.1013E07$ dynes/cm²

(b) Asymmetric Mode

FIGURE 13. Three-Phase Fluidization System for the Simulation of Bubbly Coalesced Regime in (a) Symmetric, and (b) Asymmetric Modes.

(a) Symmetric Mode

(b) Asymmetric Mode

FIGURE 14. Computed Bubble Formation in Three-Phase Fluidized Bed in (a) Symmetric, and (b) Asymmetric Modes at Superficial Gas Velocity of 3.7 cm/s and Superficial Liquid Velocity of 2.03 cm/s.

FIGURE 15. Computed Time Average Volume Fraction Contours for Bubbly Coalesced Regime in Asymmetric Mode Simulation.

FIGURE 16. Computed Velocity Patterns for Bubbly Coalesced Regime in Asymmetric Mode Simulation.

FIGURE 17. Comparison of Computational and Experimental Time Average Volume Fractions at Radial Position of 4.0 cm (Center Region) in Bubbly Coalesced Regime for Asymmetric Mode Simulation.

FIGURE 18. Comparison of Computational and Experimental Time Average Volume Fractions at Radial Position of 13.0 cm (Wall Region) in Bubbly Coalesced Regime for Asymmetric Mode Simulation.

FIGURE 19. Comparison of Computational and Experimental Solids Velocity Profiles at Axial Position of 13.0 cm in Bubbly Coalesced Regime for Asymmetric Mode Simulation.

Figure 20 - Jet Details

Figure 21- Sketch of Three-Phase Fluidized Bed for Measurement of Granular Temperature (Turbulence) Approaching Air Products Methanol Synthesis Reactor with no Liquid Flow

Fig 22 - Particles Speed, Radial and Axial Velocity Distribution at $\epsilon_s=0.07$
(m = mean , σ = standard deviation)

$$-P_{xy} \cdot \frac{u_s}{u_y} = 1 - 2e^2 r_s g_o (1 - e^2) \left(\frac{q}{d_p} \right) \left(\frac{q}{p} \right)^{\frac{1}{2}}$$

production of
particle oscillations
by shear P_{xy}

dissipation due to
particle oscillations with an
effective restitution coefficient, e

$$\frac{\text{Reynolds Stress}}{\text{Granular Temperature}} = \frac{\overline{u'_s v'_s}}{q} = \left(\frac{5}{8} \right)^{\frac{1}{2}} (1 - e^2)^{\frac{1}{2}} \quad (\text{for dilute limit})$$

Reynolds Stress and Granular Temperature Comparison

**Figure 23 - Granular Temperature and Particle Reynolds Stress
for a Three-Phase Bed with $U_g = 2.8$ cm/s**

Figure 24 - Fresh Catalyst Size Distribution

Figure 25 - Used Catalyst Particles Pictures Captured by Microscope

Figure 26 - Size Distribution of Used Catalyst

Figure 27 - Cluster Formation from Small Particles

HYDRODYNAMIC SIMULATION OF METHANOL SYNTHESIS IN GAS-LIQUID SLURRY BUBBLE COLUMN REACTORS

By

Yuanxiang Wu and Dimitri Gidaspow

Department of Chemical and Environmental Engineering

Illinois Institute of Technology

Chicago, IL 60616

ABSTRACT

A transient, two-dimensional hydrodynamic model for production of methanol from syn-gas in an Air Products/DOE LaPorte slurry bubble column reactor was developed. The model predicts downflow of catalyst at the walls and oscillatory particle and gas flow at the center, with a frequency of about 0.7 Hertz. The computed temperature variation in the reactor with heat exchangers was only about 5 °K, indicating good thermal management.

The computed slurry height, the gas holdup and the rate of methanol production agree with LaPorte's reported data.

Unlike the previous models in the literature, this model computes the gas and the particle holdups and the particle rheology. The only adjustable parameter in the model is the effective particle restitution coefficient.

INTRODUCTION

Slurry bubble column reactors have recently (Parkinson, 1997) become competitive with traditional tubular fixed-bed reactors for converting syn-gas into liquid fuels. In the EXXON process, the syn-gas is generated by partial oxidation and steam reforming of natural gas in a fluidized catalytic reactor. Liquid fuels produced from natural gas become competitive with oil in remote regions where the price of natural gas is low (Parkinson, 1997). In the production of oil, the gas was either re-injected into the well or even flared as a waste-product. In the U.S. a plant is being built by Air Products and Eastman Chemicals (DOE, 1997) to produce methanol from syn-gas in a slurry bubble column reactor.

In the U.S. the source of syn-gas will be coal. There is a long range need to develop efficient processes to make transportation fuels from U.S. abundant coal resources. An increase efficiency of coal utilization will lead to a corresponding, decrease of carbon dioxide emission which is a current world wide concern. Many previously proposed processes for making liquids from coal involved liquid-gas-solid contacting. A three-phase reactor was used in the H-coal, SRC and in the EXXON donor solvent coal liquefaction processes.

The advantage of a fluidized bed reactor over that of a fixed bed reactor is better heat and mass transfer due to constant agitation of the catalyst and the ability to introduce and remove the catalyst into the reactor. Such an operation requires an understanding of the flow of the catalyst. Yet as recently as five years ago Tarmy and Coualaloglou (1992) of EXXON have shown that there existed no hydrodynamic models for three phase fluidization in the literature. EXXON (Heard, 1996) is now developing such models which are very similar to that reported in this paper. Fan(1989) has reviewed the early literature. Except for proprietary work of EXXON and other companies, the design of slurry bubble column reactors for indirect liquefaction is being done by the use of one-dimensional models. All hydrodynamic input is through empirical holdup correlations. The state of the art of the design of the slurry bubble column reactors is illustrated by the Viking Systems International (1993) report to PETC, now reorganized as the Federal Energy Technology Center (FETC). The model presented in this paper is an extension of this work to include three-phase hydrodynamics.

The model uses the principles of conservation of mass, chemical species, momentum and energy for each phase. The recently developed kinetic theory of granular flow(e.g. Savage 1983, Lun et al, 1984), as reviewed by Gidaspow (1994), treats the catalyst phase as another fluid with its own temperature, called the granular temperature, its own pressure due to particle collision and its own viscosity. The granular temperature is the random kinetic energy of the particles per unit mass. This particle oscillation can be measured with CCD camera (Gidaspow and Huilin, 1996), with a vibration meter (Cody, et al, 1997) or with a laser doppler anemometer (Zhang, et al, 1996). The granular temperature can be computed, as done in this study, from a balance of the random kinetic energy which is similar to the well-known $k-\epsilon$ model (Mohammadi and Pironneau, 1994) used in single phase flow and extended to multiphase systems by Ahmadi and Ma (1990) and Cao and Ahmadi (1995). The most important input into this model is an effective restitution coefficient. Laboratory measurements conducted at IIT(Gidaspow, et al 1997) using an Air Products methanol catalyst in a bubble column reactor in churn-turbulent flow gave us an estimate of this effective restitution coefficient. It was computed from a measurement of the Reynolds stress and the granular temperature for the catalyst.

To simulate the slurry bubble column reactors, the IIT's computer code (Wu, 1996) has been modified. Modules for chemical reactions, particularly for the synthesis of methanol, phase changes and heat exchangers were added to the code. The kinetic theory was used to compute the viscosity of the catalyst. We had previously shown that this viscosity agrees with that measured with a Brookfield viscometer for glass beads.

Air Products' (1991) RUN E-8 series for methanol production were simulated. The kinetic theory has been used to compute the catalyst viscosities and the energy equations have been solved to predict the temperature profiles. The slurry height, the methanol production and the gas-liquid-solid volume fraction profiles agreed well with those obtained at the Air Products' LaPorte pilot plant (1991). A simulation with a finer grid was carried out to investigate the effect of grid on the accuracy and convergence of the numerical computation.

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 (Gidaspow, 1994).

Conservation of Mass for each phase:

Gas Phase:

$$\frac{\partial}{\partial t}(\epsilon_g \rho_g) + \nabla \cdot (\epsilon_g \rho_g \mathbf{v}_g) = \dot{m}_g$$

Liquid and Solid Phase: ($k = \ell, s$)

$$\frac{\partial}{\partial t}(\epsilon_k \rho_k) + \nabla \cdot (\epsilon_k \rho_k \mathbf{v}_k) = \dot{m}_k$$

where $\dot{m}_\ell = \epsilon_\ell \sum_j^N M^j R_j$ $\dot{m}_g = -\dot{m}_\ell$ $\dot{m}_s = 0$

R_j is the rate of mass transfer between gas and liquid phases.

Conservation of Phases:

$$\epsilon_g + \epsilon_\ell + \epsilon_s = 1$$

Momentum Equations

Gas Phase:

$$\frac{\partial}{\partial t}(\epsilon_g \rho_g \mathbf{v}_g) + \nabla \cdot (\epsilon_g \rho_g \mathbf{v}_g \mathbf{v}_g) = \epsilon_g \rho_g F_g + \sum_{m=\ell, s} \beta_{gm} (\mathbf{v}_m - \mathbf{v}_g) + \nabla \cdot [\boldsymbol{\tau}_g] + \dot{m}_g \mathbf{v}_g$$

accumulation net outflow external drag shear production due
forces to phase change

Liquid and Solid Phase: ($k = \ell, s$)

$$\frac{\partial}{\partial t}(\epsilon_k \rho_k \mathbf{v}_k) + \nabla \cdot (\epsilon_k \rho_k \mathbf{v}_k \mathbf{v}_k) = \epsilon_k \rho_k F_k + \sum_{m=g, \ell, s} \beta_{km} (\mathbf{v}_m - \mathbf{v}_k) + \nabla \cdot [\boldsymbol{\tau}_k] + \dot{m}_k \mathbf{v}_k$$

Energy Equations To treat non-isothermal multiphase flow systems, the energy equations are needed to compute the heat transfer primarily due to heat exchangers.

Gas Phase:

$$\begin{aligned} \frac{\partial}{\partial t}(\varepsilon_g \rho_g H_g) + \nabla \cdot (\varepsilon_g \rho_g H_g \mathbf{v}_g) = & \left(\frac{\partial \mathcal{P}_g}{\partial t} + P_g \nabla \cdot \mathbf{v}_g \right) + \nabla \cdot (k_g \nabla T_g) + \sum_i r_{ig} \Delta H_{ig} \\ & \text{accumulation} \quad \text{net outflow} \quad \text{work} \quad \text{conductivity} \quad \text{reactions} \\ & + \sum_{m=\ell, s} \left\{ h_{vm}(T_m - T_g) + \beta_{gm}(v_m - v_g)^2 - \dot{m}_m H_g \right\} \\ & \text{heat transfer} \quad \text{due to friction} \quad \text{due to} \\ & \text{between phases} \quad \text{between phases} \quad \text{phase change} \end{aligned}$$

Liquid and Solid Phase: ($k = \ell, s$)

$$\begin{aligned} \frac{\partial}{\partial t}(\varepsilon_k \rho_k H_k) + \nabla \cdot (\varepsilon_k \rho_k H_k \mathbf{v}_k) = & h_{vk}(T_g - T_k) + \sum_{m=g, \ell, s} \beta_{km}(v_m - v_k)^2 + \dot{m}_k H_g \\ & + \nabla \cdot (k_k \nabla T_k) + \sum_i r_{ik} \Delta H_{ik} \end{aligned}$$

Fluctuating Energy Equation for the Particles: ($k = s$) In the approach of Ahmadi and Ma (1990) and Cao and Ahmadi (1995), a fluctuating kinetic energy balance is written for each phase. For the gas-solid system they find the reasonable result that the fluctuating velocity of particles is the same as that of the fluid. This assumption is made in this study. Hence only the equation for the granular temperature of the particles is needed.

$$\begin{aligned} \frac{3}{2} \left[\frac{\partial}{\partial t}(\varepsilon_k \rho_k \Theta_k) + \nabla \cdot (\varepsilon_k \rho_k \Theta_k \mathbf{v}_k) \right] = & \nabla \cdot (\kappa_k \nabla \Theta_k) - \gamma_k + \Phi_k \\ & \text{accumulation} \quad \text{net outflow} \quad \text{conductivity} \quad \text{dissipation} \quad \text{production} \\ & \text{due to collision} \quad \text{due to shear} \end{aligned}$$

Constitutive Equations (Ding and Gidaspow, 1990; Gidaspow 1994) Particulate solids pressure and viscosity are function of granular temperature: ($k = s$)

Equation of state for particles:

$$P_k = \rho_k \varepsilon_k \Theta_k \left\{ 1 + 2(1 + e_k) g_{0k} \varepsilon_k \right\}$$

Bulk viscosity:

$$\xi_k = \frac{4}{3} \varepsilon_k^2 \rho_k d_k g_{0k} (1 + e_k) \sqrt{\frac{\Theta_k}{\pi}}$$

Particulate viscosity:

$$\mu_k = \frac{2\mu_{k_{dil}}}{(1 + e_k) g_{0k}} \left\{ 1 + \frac{4}{5} (1 + e_k) g_{0k} \varepsilon_s \right\}^2 + \frac{4}{5} \varepsilon_k^2 \rho_k d_k g_{0k} (1 + e_k) \sqrt{\frac{\Theta_k}{\pi}}$$

Dissipation due to inelastic collisions:

$$\gamma_k = 3(1 - e_k^2) \varepsilon_k^2 \rho_k g_{0k} \Theta_k \left\{ \frac{4\sqrt{\Theta_k}}{d_k \sqrt{\pi}} - \nabla \cdot \mathbf{v}_k \right\}$$

Conductivity:

$$\kappa_k = \frac{2\kappa_{k,dil}}{(1 + e_k) g_{0k}} \left\{ 1 + \frac{6}{5} (1 + e_k) g_{0k} \varepsilon_k \right\}^2 + 2\varepsilon_k^2 \rho_k d_k g_{0k} (1 + e_k) \sqrt{\frac{\Theta_k}{\pi}}$$

Where

$$g_{0k} = \left\{ 1 - \left(\frac{\varepsilon_k}{\varepsilon_{k,max}} \right)^{1/3} \right\}^{-1}$$

Dilute phase viscosity and conductivity:

$$\mu_{k,dil} = \frac{5}{96} \rho_k d_k \sqrt{\pi \Theta_k} \quad \kappa_{k,dil} = \frac{75}{384} \rho_k d_k \sqrt{\pi \Theta_k}$$

Production due to shear:

$$\Phi_k = [\tau_k] : \nabla \mathbf{v}$$

Shear Stresses:

$$\begin{aligned} [\tau_g] &= \left\{ -P_g - \frac{2}{3} \mu_g \varepsilon_g \nabla \cdot \mathbf{v}_g \right\} [I] + \mu_g \varepsilon_g [\nabla \mathbf{v}_g + (\nabla \mathbf{v}_g)^T] \\ [\tau_k] &= \left\{ -P_k + (\varepsilon_k - \frac{2}{3} \mu_k) \nabla \cdot \mathbf{v}_k \right\} [I] + \mu_k [\nabla \mathbf{v}_k + (\nabla \mathbf{v}_k)^T] \end{aligned} \quad k = \ell, s$$

Equation of State for gas:

$$\rho_g = \frac{\bar{M}_g P_g}{z R T_g}$$

Drag Coefficients: ($k = \ell, s$) (Based on Ergun Equation)

$$\beta_{gk} = \beta_{kg} = \frac{3}{4} C_D \frac{\rho_g \varepsilon_k |\mathbf{v}_g - \mathbf{v}_k|}{d_k \psi_k} \varepsilon_g^{-2.65} \quad \varepsilon_g < 0.8$$

(based on single sphere)

$$\beta_{gk} = \beta_{kg} = 150 \frac{(1 - \varepsilon_g) \varepsilon_k \mu_g}{(\varepsilon_g d_k \psi_k)^2} + 1.75 \frac{\rho_g \varepsilon_k |\mathbf{v}_g - \mathbf{v}_k|}{\varepsilon_g d_k \psi_k} \quad \varepsilon_g > 0.8$$

$$\beta_{ts} = \beta_{st} = \frac{3}{2} (1 + e) \frac{\rho_s \rho_t \varepsilon_s \varepsilon_t |\mathbf{v}_t - \mathbf{v}_s|}{\rho_s d_s^3 + \rho_t d_t^3} (d_s + d_t)^2$$

where $C_D = \frac{24}{\text{Re}_k} (1 + 0.15 \text{Re}_k^{0.687})$

$$\text{Re}_k = \frac{\rho_g \varepsilon_g |v_g - v_k| d_k \psi_k}{\mu_g} \quad \text{Re}_k = 1000 \quad \text{if} \quad \text{Re}_k > 1000$$

External Forces Acting on Each Phase

$$F_g = \frac{g}{\varepsilon_g}$$

$$F_k = \frac{g}{\varepsilon_g} \left(1 - \frac{1}{\rho_k} \sum_{m=g,\ell,s} \varepsilon_m \rho_m \right) \quad k = \ell, s$$

Enthalpy:

$$H_g = C_{p_g} (T_g - T_g^0)$$

$$H_k = C_{p_k} (T_k - T_k^0)$$

Gas-Solid Heat Transfer: (Gunn's Model)

$$Nu_k = \left\{ (2 + 5\varepsilon_k^2)(1 + 0.7 \text{Re}_k^{0.2} \text{Pr}^{1/3}) + \left(\frac{2}{15} + 1.2\varepsilon_k^2 \right) \text{Re}_k^{0.7} \text{Pr}^{1/3} \right\} Sp_k$$

$$Nu_k = \frac{h_{vk} d_k}{k_g^0} \quad \text{Pr} = \frac{C_{p_g} \mu_g}{k_g^0} \quad Sp_k = \frac{6\varepsilon_k}{d_k}$$

Gas Phase Heat Transfer:

$$k_g^0 = 8.65 \times 10^5 \left(\frac{T_g}{1400} \right)^{1.786}$$

$$k_g = (1 - \sqrt{1 - \varepsilon_g}) k_g^0$$

Particulate Phase Heat Transfer:

$$\frac{k_k}{k_g^0} = \frac{\sqrt{\varepsilon_s}}{(1 - \varepsilon_g)} \left\{ \varphi \frac{k_k^*}{k_g^0} + (1 - \varphi) \frac{k_k^0}{k_g^0} \right\}$$

$$\frac{k_k^0}{k_g^0} = \frac{2}{A_k} \left\{ \frac{B_k \left\{ (k_k^*/k_g^0) - 1 \right\}}{A_k^2 (k_k^*/k_g^0)} \cdot \ln \frac{(k_k^*/k_g^0)}{B_k} - \frac{B_k - 1}{A_k} - \frac{B_k + 1}{2} \right\}$$

where $A_k = 1 - \frac{B_k}{(k_k^*/k_g^0)}$

$$B_k = 1.25 \left(\frac{\varepsilon_k}{\varepsilon_g} \right)^{10/9} (1 + 3\chi)$$

$$\chi = \sqrt{\frac{(\sum \varepsilon_k \rho_k)(\sum \varepsilon_k \rho_k / d_k^2)}{(\sum \varepsilon_k \rho_k / d_k)^2}} - 1 \quad k = l, s$$

$$k_k^* = 0.3289 \quad \varphi = 7.26 \times 10^{-3}$$

REACTIONS, KINETICS AND MASS TRANSFER

Reactions and Kinetics. In the synthesis of methanol from syn-gas the following chemical reactions are considered:

Several researchers had investigated the kinetic rate for methanol synthesis. There were two kinds of models, a power law rate expression model and a mechanistic model.

A mechanistic model was developed by Lee (1990):

$$r_{MeOH} = A \exp\left(-\frac{E}{RT}\right) \left(C_{H_2} - C_{H_2, eq}\right)$$

$$A = 3380 \text{ cm}^3 / \text{kg} \cdot \text{s} \quad E = 18,800 \text{ kcal} / \text{kmol}$$

This model does not account for partial pressure of carbon monoxide,

Wedel et al. (1982) developed a power law rate expression based on a review of various literature models:

$$r = \varepsilon_s \rho_s \left\{ 1.98 \times 10^7 \exp(-56343 / RT) P_{H_2}^{0.4} P_{CO}^{0.18} - 2.15 \times 10^{10} \exp(-85930 / RT) P_{CH_3OH}^{0.13} \right\}$$

To predict a more accurate methanol production rate, a power law rate expression, discussed in Air Products' (1992) report, is used in this computational run. The model was based on the rate expressions for methanol synthesis (Weimer et al. 1987) and model the parameters were determined from experimental research.

$$r = \varepsilon_s \rho_s K_r f_{co}^{1/3} f_{H_2}^{2/3} \left(1 - \frac{f_{MeOH}}{K_{eq} f_{co} f_{H_2}^2}\right)$$

Mass Transfers Between Gas and Liquid. The mass transfer rate can be expressed as:

$$R_j = \varepsilon_t K_{j\ell} a (C_j^{g-\ell} - C_j^\ell)$$

Where C_j^l is bulk concentration of species j and C_j^{g-l} is concentration of species j at gas-liquid interface which can be defined by Henry law:

$$C_{j\ell}^{g-\ell} = \frac{f_j}{H_j}$$

Graff et al. (1988) measured solubilities of syn-gas in the temperature of 210 to 260°C in a high molecular weight solvent. Their temperature depended Henry constants were used for LaPorte's operating conditions.

$$\begin{aligned}
H_{CO} &= 0.175 \exp(638 / RT) \\
H_{CO_2} &= 0.402 \exp(-6947 / RT) \\
H_{H_2} &= 0.0782 \exp(4875 / RT) \\
H_{CH_3OH} &= 1.49 \exp(-17235 / RT)
\end{aligned}$$

Species Balances:

Gas Phase:

$$\frac{\partial}{\partial t} (\varepsilon_g \rho_g y_g^j) + \nabla \cdot (\varepsilon_g \rho_g y_g^j v_g) = \frac{\alpha^j \varepsilon_s \rho_s M^j r}{3.6 \times 10^6} - \varepsilon_\ell M^j R_j$$

Liquid Phases:

$$\frac{\partial}{\partial t} (\varepsilon_k \rho_k y_k^j) + \nabla \cdot (\varepsilon_k \rho_k y_k^j v_k) = \varepsilon_\ell M^j R_j$$

$$\begin{aligned}
\sum_j^N y_k^j &= 1 & k &= g, \ell \\
j &= CO \quad CO_2 \quad H_2 \quad CH_4 \quad CH_3OH \quad wax \\
\alpha^j &= -1 \quad 0 \quad -2 \quad 0 \quad 1 \quad 0
\end{aligned}$$

The rate of phase change consists of mass transfer of species between gas and liquid:

$$\dot{m}_\ell = \varepsilon_\ell \sum_j^N M^j R_j \quad \dot{m}_g = -\dot{m}_\ell \quad \dot{m}_s = 0$$

OPERATING CONDITIONS

The operating conditions are same as those of LaPorte's RUN E-8.1 (Air Products 1991). Figure 1 shows the reactor grid employed in this simulation. Bubbles go through the bed and the slurry stays in the reactor. Early operation of the LaPorte methanol reactor involved recirculation of the catalyst slurry.

Diameter of the reactor	57cm
Height of the reactor	813cm
Superficial gas velocity	15.24 cm/s
Superficial liquid velocity	0 cm/s
Superficial solid velocity	0 cm/s
Temperature	250.3 °C
Pressure	753.2 psig
Catalyst diameter	50 μm
Liquid	wax
Density of liquid	0.70025 g/cm ³
Grid size (dx & dy)	168cm x 20.3 cm

Number of cells in the grid	34x40
Restitution coefficient	0.999999
Time interval	10^{-4} sec.

NUMERICAL CONSIDERATIONS

Initial Conditions A constant pressure, 753.2 psig, is kept at the top of the reactor. The initial conditions are summarized as follows:

<i>height(cm)</i>	<i>gas</i>	<i>liquid</i>	<i>solid</i>
0 – 183	$\varepsilon_g = 0.050$ $v_g = 4.8$ $u_g = 0$	$\varepsilon_\ell = 0.426$ $v_\ell = 0$ $u_\ell = 0$	$\varepsilon_s = 0.524$ $v_s = 0$ $u_s = 0$
183 – 427	$\varepsilon_g = 0.050$ $v_g = 4.8$ $u_g = 0$	$\varepsilon_\ell = 0.950$ $v_\ell = 0$ $u_\ell = 0$	$\varepsilon_s = 0.000$ $v_s = 0$ $u_s = 0$
427 – 813	$\varepsilon_g = 1.000$ $v_g = 0.24$ $u_g = 0$	$\varepsilon_\ell = 0.000$ $v_\ell = 0$ $u_\ell = 0$	$\varepsilon_s = 0.000$ $v_s = 0$ $u_s = 0$

Syn-gas composition (CO-rich):

	<i>CO</i>	<i>CO₂</i>	<i>H₂</i>	<i>N₂</i>	<i>CH₃OH</i>
%mol	51	13	35	1	0
y_g^j %wt	68.07	27.26	3.34	1.33	0

Boundary Conditions. The thermal boundary conditions around the computing mesh and a heat block are summarized as follows.

$$\text{Boundaries:} \quad \frac{\partial T_k}{\partial x} = 0 \quad \frac{\partial T_k}{\partial y} = 0 \quad k = g, \ell, k$$

Around heat block:

$$\text{Case 1. constant heat flux} \quad \frac{\partial T_k}{\partial x} = C_{fx} \cdot \varepsilon_k \quad \frac{\partial T_k}{\partial y} = C_{fy} \cdot \varepsilon_k \quad k = g, \ell, k$$

$$\text{Case 2. constant block temperature } T_b \quad \frac{\partial T_k}{\partial x} = K_x \cdot \varepsilon_k (T_b - T_k) \quad \frac{\partial T_k}{\partial y} = K_y \cdot \varepsilon_k (T_b - T_k) \quad k = g, \ell, k$$

The inflow conditions, including gas velocity and composition, and the top pressure are prescribed. An assumption of non-slip at the walls is made for both the gas and the liquid phases. The boundary conditions around the computing mesh, shown as Figure 1, are summarized as follows.

	<i>gas</i>	<i>liquid</i>	<i>solid</i>
<i>bottom</i>	$\varepsilon_g = 1$	$\varepsilon_\ell = 0$	$\varepsilon_s = 0$
<i>orifice</i>	$v_g = 81.3 \text{ cm / s}$	$v_\ell = 0$	$v_s = 0$
	$u_g = 0$	$u_\ell = 0$	$u_s = 0$
	$y_g^j = y_g^{j0}$	$y_\ell^j = 0$	$y_s^j = 0$
<i>left / right</i>	$v_g = 0$	$v_\ell = 0$	$v_s = 0$
	$u_g = 0$	$u_\ell = 0$	$u_s = 0$
<i>top</i>	$\frac{\partial \varepsilon_g}{\partial y} = 0$	$\frac{\partial \varepsilon_\ell}{\partial y} = 0$	$\frac{\partial \varepsilon_s}{\partial y} = 0$
	$\frac{\partial v_g}{\partial y} = 0$	$\frac{\partial v_\ell}{\partial y} = 0$	$\frac{\partial v_s}{\partial y} = 0$
	$u_g = 0$	$u_\ell = 0$	$u_s = 0$
	$\frac{\partial y_g^j}{\partial y} = 0$	$\frac{\partial y_\ell^j}{\partial y} = 0$	$\frac{\partial y_s^j}{\partial y} = 0$

Computation A finite volume method is used to solve these partial differential equations simultaneously. The dependent variables are as follows.

$$\varepsilon_g, \varepsilon_\ell, \varepsilon_s, v_g, v_\ell, v_s, P_g, y_g^j, y_\ell^j, y_s^j$$

$$j = \text{CO}, \text{CO}_2, \text{H}_2, \text{N}_2, \text{CH}_3\text{OH}, \text{wax}$$

COMPUTATIONAL RESULTS AND DISCUSSION

The initial state of the reactor is shown in Figure 1. The obstacles shown represent heat exchangers. At time zero, the syn-gas is injected into reactor through six orifices and the gas velocity is increased gradually to the final value during the first computing second. The total computing time was 80 seconds. All values in the Figures and Tables are time and cross section area averaged over the last 40 seconds.

Table 1 lists the material balance of the simulations and Table 2 lists the comparison of simulation and LaPorte's RUN E-8.1. They show very close CO conversion and rate of methanol production.

Figures 2 and 3 show the time response of gas mass flowrate at reactor top. There are strong oscillations occurring during the first 4 seconds after start-up (syn-gas injection). After that, oscillations are mild.

Figure 4 shows the time average gas-liquid-solid volume fraction profiles. Table 2 and Figure 4 show that the height of the slurry and the gas holdup roughly agree with RUN E-8.1.

Table 1 Material Balance: (CO:H₂=1.5:1)

	Inlet		Outlet	
	% mol	kgmol/hr	% mol	kgmol/hr
CO	51	87.9	51.18	74.8
CO ₂	13	22.4	15.39	22.4
H ₂	35	60.3	23.03	33.6
CH ₃ OH	0	0.0	9.20	13.4
N ₂	1	1.7	1.18	1.7
$\bar{M}$ (kg/kgmol)	20.98		24.84	
Flowrate (kgmol/hr)		172.3		145.9
Flowrate (kg/hr)		3614		3625

Table 2 Comparison of Simulation and Air Products' (1991) RUN E-8.wazzu 1:

	CO conv. (%)	gas holdup (%)	slurry height (inches)	total catalyst (kg)	CH ₃ OH (gmol/hr /kg)	net CH ₃ OH (TPD)
Simulation	14.24	26.9	215	740	16.93	9.62
RUN E-8.1	13.50	29.5	200	567	.50	10.03

Figure 5 shows the comparison of methanol profile computed by Vikings' (1993), one-dimensional steady state model and the two-dimensional hydrodynamic model. The one-dimensional model predicts a high methanol production because of the assumption of uniform catalyst concentration. The hydrodynamic model, however, predicts much closer methanol production (Table 2) since it accounts for the effect of the distribution of gas, catalyst, temperature and the flow patterns inside the reactor. The values of the granular temperature are close to those measured for the Air Products catalyst in a laboratory apparatus at IIT in a three phase fluidized bed with multiple jet inlets (Gidaspow, et al, 1997). Such a measurement is needed for the Air Products pilot plant to understand the mixing process. It can probably be made using the vibration technique of Cody, et al (1997). The computed viscosity in Figure 7 is that due to collision of particles only. Break-ups of catalyst particles and subsequent agglomeration of fines was not considered in the model.

Figure 6 shows a transient distribution of the rate of methanol reaction.

Figure 7 shows instant catalysts concentration, gas holdup, thermal temperature, granular temperature and solid viscosity profiles in the slurry bubble column reactor.

Figures 8a,b and 9a,b show transient gas flow patterns. There exist vortices inside the reactor. They imply good mixing in the slurry bubble column reactor. The IIT experiment

(Bahary, 1994, Gidaspow, et al, 1995 and 1997) with no reaction shows similar circulation patterns.

Typical results of the computed variables are shown in Figure 7. Since a steady state is never reached, all the variables undergo constant oscillation. Figure 7 shows that there is dense Phases particle region at the bottom. The thermal temperature is higher at the center, as expected. However, the variation is of the order of 5 degrees. The blocks representing heat exchangers are about 400 °K. There is a distribution of granular temperature and the computed particulate viscosity in the reactor. Wu (1996) presents a computer program for this problem and shows more results printed from a video of the simulation.

CONVERGENCE CHECK

To demonstrate an independence of the solution on the grid size, a simulation run, based on the previous run for Air Products' reactor (Wu et al. 1995 and Pape et al. 1996), with a fine grid was done. The conditions of this run are exactly same as the previous run except for the grid size, in which the dy of this run is one third less than that of the previous one.

Figure 4 shows the comparison of the time-averaged g-l-s volume fraction profiles for both runs. They have the same slurry height, 530 cm. The curves are nearly identical.

Figures 2 and 3 show the frequency responses of the gas flowrate at the outlet. Both runs have approximately the same frequency of 0.7 Hertz.

Figures 8a,b and 9a,b demonstrate the similar flow patterns for both runs. They display down-flows at the walls, up-flow at the center and vortices near the bottom.

CONCLUSIONS

In summary, the computed slurry height, the gas holdup and the rate of methanol production agree well with LaPorte's RUN E-8.1. The two-dimensional hydrodynamic model is better than the one-dimensional, steady state model in predicting the methanol production and the hydrodynamics of the slurry bubble column reactors.

NOMENCLATURES

A	coefficient matrix
a	interfacial area per unit volume (cm^2/cm^3)
B	coefficient matrix
C_D	drag coefficient
C_j^l	concentration of j in bulk liquid phase
C_j^{g-l}	concentration of j in g-l interface
C_k	fluctuating velocity of particle
C_{pg}	specific heat of gas
C_{pk}	specific heat of phase k

d_k	diameter of solid particle or liquid droplet
e_k	restitution coefficient of phase k
F_g	forces acting on gas phase
F_k	forces acting on phase k
E	strength of electric field
f_j	fugacity of j
H_j	Henry's constant of j
H_g	enthalpy of gas
H_k	enthalpy of phase k
h_{vk}	gas-phase k heat transfer coefficient
$G()$	solid compressive stress modules
g	gravity acceleration
g_{0k}	radial distribution of phase k
$[I]$	unit tensor
K_{eq}	reaction equilibrium constant
K_r	reaction kinetic coefficient
K_{je}	mass transfer coefficient of j in liquid phase
k_g	thermal conductivity of gas
k_k	thermal conductivity of phase k
k_g^0	mean thermal conductivity of gas
k_k^0	mean thermal conductivity of phase k
k_k^*	effective thermal conductivity of phase k
M^j	molecular weight of j
$\overline{M}_g$	average gas molecular weight
M_k	number of reactions in phase k
$\dot{m}_k$	rate of generation of phase k
N	total number species
Nu_k	Nusselt number
P_g	gas pressure
P_k	pressure of phase k

Pr	Prandtl number
q_k	surface charge of phase k
r_{ik}	rate of ith reaction in phase k
R	gas constant
R_k^j	rate of mass transfer, j specie in phase k
Re_k	Reynolds number
T	temperature
T_g	gas temperature
T_k	temperature of phase k
T_g^0	reference gas temperature
T_k^0	reference temperature of phase k
u	velocity in x direction
v	velocity in y direction
y_k^j	weight fraction of i in phase k
z	compressible factor

Greek letters:

α_{ik}^j	stoichiometric coefficient of ith reaction in k phase ξ_k
β_{kl}	frictional coefficient between phase k and l
γ_k	collisional energy dissipation
ΔH_{ik}	reaction heat of ith reaction in phase k
ε_k	volume fraction of phase k
Θ	granular temperature
κ_k	conductivity of fluctuating energy
μ_k	viscosity of phase k
ξ_k	bulk viscosity
ρ_k	density of phase k
τ_{ck}	cohesive force
τ_k	shear stress of phase k
Φ_k	energy dissipation
ψ_k	sphericity of particle or droplet

Subscripts:

g, l, s	gas, liquid, solid respectively
i	ith reaction
k	solid or liquid phase

Superscripts

j	species
---	---------

ACKNOWLEDGMENT:

This work was supported by DOE University Coal Research Grant No. DE-FG22-94PC94028.

REFERENCES:

- Ahmadi, G. and Ma, D., "A Thermodynamical Formulation for Dispersed Multiphase Turbulent Flows--I." Int. J. Multiphase Flow, Vol. 16, No. 2, pp.323-340, 1990.
- Air Products and Chemicals, Inc., "Liquid Phase Methanol LaPorte Process Development Unit: Modification, Operation, and Support Studies," Draft Report to DOE for Contract No. DE-AC22-87PC90005, 1991.
- Air Products and Chemicals, Inc. "Synthesis of Dimethyl Ether and Alternative fuels in the Liquid Phase from Coal-Derived Synthesis Gas," Topical Report to DOE for Contract No. DE-AC22-90PC89865, 1992.
- Bahary, M., "Experimental and Computational Studies of Hydrodynamics in Three-Phase and Two-Phase Fluidized Beds," Ph.D. Thesis, Illinois Institute of Technology, Chicago, Illinois, 1994.
- Cao, J. and Ahmadi, G., "Gas-Particle Two-Phase Turbulent Flow in a Vertical Duct." Int. J. Multiphase Flow, Vol. 21, No. 6, pp. 1203-1228, 1995.
- Cody, G.D. and Goldfarb, D.J., "Discontinuity in Particle Granular Temperature Across the Geldart B/A." To be published in 1997 AIChE Symposium Series on Fluidization and Fluid-Particle Systems, 1997.
- Ding, J. and Gidaspow, D., "A Bubbling Fluidization Model Using Kinetic Theory of Granular Flow," AIChE J., Vol. 36, pp. 523-538, 1990.
- DOE Newsletter, June, 1997.
- Fan, L.S., "Gas-Liquid-Solid Fluidization Engineering." Butterworth Publishers, 1989.
- Heard, W.B. "CFD of Multicomponent, Multiphase Mixtures," Presented at Computational Fluid Dynamics in Chemical Reaction Engineering, Engineering Foundation Conferences, San Diego, CA, October, 1996.
- Gidaspow, D., "Multiphase Flow and Fluidization--Continuum and Kinetic Theory Descriptions," Academic Press, Inc., 1994.
- Gidaspow, D. Bahary, M. and Wu, Y., "Hydrodynamic Models for Slurry Bubble Column Reactors," Coal Liquefaction and Gas Conversion Contractors Review Conference, Pittsburgh, PA, August, 1995.

- Gidaspow, D. and Huilin, L., "Collisional Viscosity of FCC Particles in a CFB." AICHE J., Vol. 42, 2503-2510, 1996
- Gidaspow, D., Bahary, M., Mostofi, R. and Wu, Y., "Hydrodynamic Models for Slurry Bubble Column Reactors." US Department of Energy Grant DE-FG22-94PC94028, Final Technical Report to DOE and FETC, June, 1997.
- Graff, G.H., Winkelman, J.G.M., Stamhuis, E.J. and Beenackers, A.A.C.M., "Kinetics of the Three-Phase Methanol Synthesis," Chem. Eng. Sci., Vol. 43, No. 8, pp.2161-2168, 1988.
- Lee, S., "Methanol Synthesis Technology," CRC Press Inc., 1990.
- Lun, C.K., Savage, S.B., Jeffrey, D.J. and Chepurniy, N., "Kinetic Theory for Granular Flow: Inelastic Particles in Couette Flow and Slightly Inelastic Particles in a General Flowfield." J. Fluid Mech., 140, pp. 223-256, 1984.
- Mohammadi, B. and Pironneau, O., "Analysis of the K-Epsilon Turbulence Model." Wiley Publisher, 1994
- Pape, R., Gidaspow, D. and Wu, S., "Multiphase Flow in Slurry Bubble Column Reactors and Solid Propellant Rockets," Presented at the 2nd International symposium on Numerical Methods for Multiphase Flows, ASME Fluids Engineering Division, San Diego, CA, July, 1996.
- Parkinson, G., "Fischer-Tropsch Comes Back," Chem. Eng., pp. 39-41, April, 1997
- Savage, S.B., "Granular Flows at High Shear Rates," Theory of Dispersed Multiphase Flow, edited by Meyer, R. E., Academic Press, pp. 339-358, 1983.
- Tarmy, B.L. and Coualaloglou, C.A., "Alpha - Omega and Beyond Industrial View of Gas/Liquid/Solid Reactor Development," Chem. Eng. Sci., Vol. 47, No. 13/14, pp. 3231-3246, 1992
- Vikings Systems International, "Design of Slurry Reactor for Indirect Liquefaction Applications," Report to DOE/PETC, 1993.
- Wedel, W.V., Ledakowicz, S. and Deckwer, W.D., "Kinetics of Methanol Synthesis in the Slurry Phase," Chem. Eng. Sci., Vol.43, No. 8, pp. 2169-2174, 1988.
- Weimer, R. F., Terry, D. M., and Stepanoff, P. R., "Laboratory Kinetics and Mass Transfer in the Liquid Phase Methanol Process," AICHE National Meeting, New York, 1987.
- Wu, Y., "Simulation of Methanol Synthesis in Slurry Bubble Column Reactors," Ph.D. Thesis, Illinois Institute of Technology, Chicago, Illinois, 1996
- Wu, Y. and Gidaspow, D., "Hydrodynamic Models for Slurry Bubble Column Reactors," 3rd Technical Progress Report to DOE for Contract No. DE-FG22-94PC94208, April., 1995.
- Zhang, Y.F., Yang, Y. and Arastoopour, H., "Electrostatic Effect on the Flow Behavior of a Dilute Gas/Cohesive Particle Flow System." AICHE J., Vol. 42, No. 6, pp. 1590-1599, 1996.

Figure 1 Reactor Operation Condition and Simulation Grid.

Figure 2 Gas Flowrate at Reactor Top and Frequency Response (Fine Grid).

Figure 3 Gas Flowrate at Reactor Top and Frequency Response (Coarse Grid).

Figure 4 Time Averaged G-L-S Volume Fraction Profiles.

Figure 5 Methanol Concentration Profiles for IIT's Hydrodynamic, One-dimensional and Vikings' (1993) Models.

Figure 6 Instant Rate of Reaction for Methanol Production (gmol/s/cm^3).

Figure 7 Simulation of Air Products Slurry Bubble Column Reactor (RUN E8.1) at 12 seconds from Start-up.

Figure 8a Gas Flow Patterns (Fine Grid).

Figure 8b Gas Flow Patterns (Fine Grid).

Figure 9a Gas Flow Patterns (Coarse Grid).

Figure 9b Gas Flow Patterns (Coarse Grid).