

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

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**ABSTRACT**

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 °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 Coualoglou (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.



**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:

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

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

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

**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.

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

**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:

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

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:

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

Equation of State for gas:

$$\rho_g = \frac{\bar{M}_g P_g}{zRT_g}$$

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)

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

$$\beta_{ls} = \beta_{sl} = \frac{3}{2} (1 + e) \frac{\rho_s \rho_\ell \varepsilon_s \varepsilon_\ell |\mathbf{v}_\ell - \mathbf{v}_s|}{\rho_s d_s^3 + \rho_\ell d_\ell^3} (d_s + d_\ell)^2$$

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

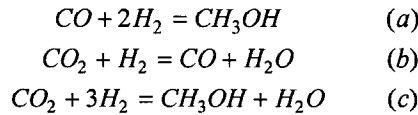
$$B_k = 1.25 \left(\frac{\varepsilon_k}{\varepsilon_g}\right)^{10/9} (1 + 3\chi)$$

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

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

## 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:

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

Where  $C_j^l$  is bulk concentration of species j and  $C_j^{g-\ell}$  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.

$$H_{CO} = 0.175 \exp(638 / RT)$$

$$H_{CO_2} = 0.402 \exp(-6947 / RT)$$

$$H_{H_2} = 0.0782 \exp(4875 / RT)$$

$$H_{CH_3OH} = 1.49 \exp(-17235 / RT)$$

### 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:

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

$$\sum_j^N y_k^j = 1 \quad k = g, \ell$$

$$j = \begin{matrix} CO & CO_2 & H_2 & CH_4 & CH_3OH & wax \end{matrix}$$

$$\alpha^j = \begin{matrix} -1 & 0 & -2 & 0 & 1 & 0 \end{matrix}$$

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 <sup>3</sup> |
| 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           | $\varepsilon_g = 0.050$<br>$v_g = 4.8$<br>$u_g = 0$  | $\varepsilon_\ell = 0.426$<br>$v_\ell = 0$<br>$u_\ell = 0$ | $\varepsilon_s = 0.524$<br>$v_s = 0$<br>$u_s = 0$ |
| 183 – 427         | $\varepsilon_g = 0.050$<br>$v_g = 4.8$<br>$u_g = 0$  | $\varepsilon_\ell = 0.950$<br>$v_\ell = 0$<br>$u_\ell = 0$ | $\varepsilon_s = 0.000$<br>$v_s = 0$<br>$u_s = 0$ |
| 427 – 813         | $\varepsilon_g = 1.000$<br>$v_g = 0.24$<br>$u_g = 0$ | $\varepsilon_\ell = 0.000$<br>$v_\ell = 0$<br>$u_\ell = 0$ | $\varepsilon_s = 0.000$<br>$v_s = 0$<br>$u_s = 0$ |

Syn-gas composition (CO-rich):

|                     | <i>CO</i> | <i>CO<sub>2</sub></i> | <i>H<sub>2</sub></i> | <i>N<sub>2</sub></i> | <i>CH<sub>3</sub>OH</i> |
|---------------------|-----------|-----------------------|----------------------|----------------------|-------------------------|
| <i>%mol</i>         | 51        | 13                    | 35                   | 1                    | 0                       |
| $y_g^j$ <i>%wt.</i> | 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.

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

*Around heat block:*

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

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

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:H<sub>2</sub>=1.5:1)

|                      | Inlet |          | Outlet |          |
|----------------------|-------|----------|--------|----------|
|                      | % mol | kgmol/hr | % mol  | kgmol/hr |
| CO                   | 51    | 87.9     | 51.18  | 74.8     |
| CO <sub>2</sub>      | 13    | 22.4     | 15.39  | 22.4     |
| H <sub>2</sub>       | 35    | 60.3     | 23.03  | 33.6     |
| CH <sub>3</sub> OH   | 0     | 0.0      | 9.20   | 13.4     |
| N <sub>2</sub>       | 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<br>conv.<br>(%) | gas<br>holdup<br>(%) | slurry<br>height<br>(inches) | total<br>catalyst<br>(kg) | CH <sub>3</sub> OH<br>(gmol/hr<br>/kg) | net<br>CH <sub>3</sub> OH<br>(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 ( $\text{cm}^2/\text{cm}^3$ ) |
| 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                   |
| $K_{j\ell}$ | 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                          |
| $\bar{M}_g$ | 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:

|                 |                                                               |
|-----------------|---------------------------------------------------------------|
| $\alpha_{ik}^j$ | stoichiometric coefficient of ith reaction in k phase $\xi_k$ |
| $\beta_{kl}$    | frictional coefficient between phase k and l                  |
| $\gamma_k$      | collisional energy dissipation                                |
| $\Delta H_{ik}$ | reaction heat of ith reaction in phase k                      |
| $\varepsilon_k$ | volume fraction of phase k                                    |
| $\Theta$        | granular temperature                                          |
| $\kappa_k$      | conductivity of fluctuating energy                            |
| $\mu_k$         | viscosity of phase k                                          |
| $\xi_k$         | bulk viscosity                                                |
| $\rho_k$        | density of phase k                                            |
| $\tau_{ck}$     | cohesive force                                                |
| $\tau_k$        | shear stress of phase k                                       |
| $\Phi_k$        | energy dissipation                                            |
| $\psi_k$        | sphericity of particle or droplet                             |

Subscripts:

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

Superscripts

|   |         |
|---|---------|
| j | species |
|---|---------|

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