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ON

HYDRODYNAMIC MODELS FOR SLURRY BUBBLE COLUMN REACTORS

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ABSTRACT

The objective of this investigation is to convert our "learning gas-solid-liquid" fluidization model into a predictive design model. The IIT hydrodynamic model computes the phase velocities and the volume fractions of gas, liquid and particulate phases. Model verification involves a comparison of these computed velocities and volume fractions to experimental values.

After a discussion of our research with the DOE-Air Products team in January, we decided to concentrate on the slurry configuration of interest to DOE-Air Products which has no recirculation of liquid. In such a system the gas is the continuous phase, rather than the liquid that we had used in our model in the past. We have built such a cold flow two dimensional plastic model. We have also changed our computer code. At the request of Air Products and DOE we have started a simulation of LaPorte RUN E-8.1 (1991) for production of methanol as described in the Air Products report sent to us. For isothermal operation, there is good mixing, and the preliminary results shown in this report indicate that we should obtain an agreement between the experiment and the simulations. A final report will be prepared upon completion of the simulation.

Diana Matonis, a Ph.D. candidate supported by an IITRI fellowship, has developed a three dimensional version of our G-L-S code which will be used in the present study.

DISCLAIMER

SIMULATION OF SYNTHESIS OF METHANOL IN AIR PRODUCTS AND CHEMICALS' SLURRY REACTOR
WITHOUT CIRCULATION OF SLURRY

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INTRODUCTION:

Air Products and Chemicals, Inc. produced methanol from syn-gas, a mixture of H_2 and CO, in the LaPorte pilot unit (1987, 1991, 1992). We are simulating this process using our multiphase code with the reaction of methanol. In our pervious report (1994a), the case of LaPorte RUN E-2-B(1987) was simulated. A good agreement with LaPorte's NDG concentrations of catalyst and the production of methanol was obtained. In the present report, RUN E-8.1(1991) is used. The major difference of this simulation from the pervious one is the absence of slurry circulation. Also upon request of Air Products and Chemical, Inc., we added the heat exchangers to the reactor.

The following difficulties in our simulation need to be mentioned:

1. Our multiphase code with reaction is only 2 dimensional. If the tube of the heat exchanger is put into the 2-D reactor, it must partition the 2-D reactor into 2 parts without connection. Therefore, a discontinuous heat exchanger is used in the simulation. A 3-D multiphase code with reaction needs to be developed. Diana Matonis, a Ph.D candidate, is developing a 3-D code.

2. In order to track the propagation of methanol formation inside the reactor, it is best to choose an initial state without any syn-gas (inert only such as N_2). Then the syn-gas is injected at zero time. We did this, but it takes a long computing time to reach product's steady state at the top outlet. This report only shows the results of the partial steady state.

3. A non-isothermal simulation was conducted first. But an extreme hot area was formed in the entrance (below the heat exchanger) in the very early computing time because of the accumulation of reaction heat. So, an isothermal simulation was conducted. The parameters of the heat generation and the temperature of the inlet gas need to be adjusted in a future run.

REACTION:

According to the report of Air Products and Chemical, Inc.(1991), RUN E-8.1 produced methanol only. The methanol dehydration and water shift reaction were very small. Therefore only methanol synthesis is considered here:

$$CO + 2\,H_2 = CH_3OH$$

The methanol kinetic expression is chosen from DME report(1992):

$$r = kf_{co}^{1/3} f_{H_2}^{2/3} \left(1 - \frac{f_{MEOH}}{K_{eq} f_{co} f_{H_2}^2}\right)$$

MASS TRANSFER BETWEEN GAS AND LIQUID PHASE:

$$R_i = K_{Lia} a (C_i^{g-L} - C_i^L)$$

From Viking Systems International's report and Ledakowicz et al(1984):
K_{Lia}=0.3--1.3(1/s). By using Henry's Law:

$$C_{Li}^{g-L} = \frac{f_i}{H_i}$$

Followings are expressions of Henry's constants from Graaf, G.H.(1988) for T=210-260 ^oC.

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

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

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

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

$$H_{H_2O} = 0.33 \exp(-8633/RT)$$

HYDRODYNAMIC MODEL for multiphase flow with reaction and interfacial mass transports(D. Gidaspow 1994b).

Continuity equations:

$$\frac{\partial}{\partial t}(\varepsilon_g \rho_g) + \nabla\cdot(\varepsilon_g \rho_g V_g) = \dot{m}_g$$

$$\frac{\partial}{\partial t}(\varepsilon_1 \rho_1) + \nabla\cdot(\varepsilon_1 \rho_1 V_1) = \dot{m}_1$$

$$\frac{\partial}{\partial t}(\varepsilon_s \rho_s) + \nabla\cdot(\varepsilon_s \rho_s V_s) = \dot{m}_s$$

$$\varepsilon_g + \varepsilon_1 + \varepsilon_s = 1$$

Momentum equations:

$$\frac{\partial}{\partial t}(\varepsilon_g \rho_g V_g) + \nabla\cdot(\varepsilon_g \rho_g V_g V_g) = -\nabla P_g - \varepsilon_g \rho_g g + \nabla\tau_g + \beta_{sg}(V_s - V_g) + \beta_{1g}(V_1 - V_g) + \dot{m}_g V_g$$

$$\frac{\partial}{\partial t}(\varepsilon_1 \rho_1 V_1) + \nabla\cdot(\varepsilon_1 \rho_1 V_1 V_1) = -\nabla P - \varepsilon_1 \rho_1 g + \nabla\cdot\tau_1 + \beta_{1g}(V_g - V_1) + \beta_{1s}(V_s - V_1) + \dot{m}_1 V_1$$

$$\frac{\partial}{\partial t}(\varepsilon_s \rho_s V_s) + \nabla\cdot(\varepsilon_s \rho_s V_s V_s) = -\nabla P_s - \varepsilon_s \rho_s g + \nabla\cdot\tau_s + \beta_{sg}(V_g - V_s) + \beta_{1s}(V_1 - V_s) - \dot{m}_s V_s$$

$$\dot{m}_s = 0 \qquad \dot{m}_1 = -\dot{m}_g = \varepsilon_1 \sum_{i=1}^{N} R_i M_i \qquad i = H_2,\ CO,\ CO_2,\ CH_4,\ CH_3OH,\ H_2O$$

Shear stresses:

$$\nabla P_k = G(\varepsilon_k)\nabla\varepsilon_k$$

$$\tau_1 = \varepsilon_1 \mu_1 \left([\nabla V_1 + (\nabla V_1)^T] - \frac{2}{3}\nabla\cdot V_1 I \right)$$

$$\tau_k = \mu_k(\nabla V_k + (\nabla V_k)^T) + \left(\xi_k - \frac{2}{3}\mu_k\right)\nabla\cdot V_k I$$

where

$$G(\varepsilon_k) = 10^{8.76\varepsilon_k - 0.27} \quad (dynes/cm^2)$$

$$\xi_k = \frac{4}{3}\varepsilon_k^2 \rho_k d_k g_0 (1-e)\sqrt{\theta_k/\pi}$$

$$g_0 = (1 - (\varepsilon_k/\varepsilon_{k,max})^{1/3})^{-1}$$

$$\mu_k = 5\varepsilon_k$$

Drag coefficients:

$$\beta_{1k}=\beta_{k1}=150\cdot\frac{\varepsilon_k^2\mu_1}{\varepsilon_1(d_k\psi_k)^2}+1.75\cdot\frac{\rho_1\varepsilon_k|V_1-V_k|}{d_k\psi_k} \qquad \varepsilon_1<0.8$$

$$\beta_{1k}=\beta_{k1}=0.75C_D\frac{\varepsilon_k\varepsilon_1\rho_1|V_1-V_k|}{d_k\psi_k}\varepsilon_1^{-2.65} \qquad \varepsilon_1\geq 0.8$$

$$\beta_{gs}=\beta_{sg}=\frac{3}{2}\alpha_{gs}(1+e)\frac{\rho_s\rho_g\varepsilon_s\varepsilon_g(d_s+d_g)^2}{\rho_s d_s^3+\rho_g d_g^3}|V_s-V_g|$$

where

$$C_D=\frac{24}{Re_k}(1+0.15Re_k^{0.687}) \qquad Re_k<1000$$

$$C_D=0.44 \qquad Re_k\geq 1000$$

$$Re_k=\frac{\varepsilon_1\rho_1|V_1-V_k|d_k\psi_k}{\mu_1} \qquad k=g,s \qquad \alpha_{gs}=0.5$$

SPECIES BALANCE: FOR GAS AND LIQUID PHASE:

$$\frac{\partial}{\partial t}(\varepsilon_g\rho_g y_i)+\nabla\cdot(\varepsilon_g\rho_g V_g y_i)=\frac{\hat{a}_i\varepsilon_s\rho_s M_i r}{3.6\times10^6}-\varepsilon_1 M_i R_i$$

$$\frac{\partial}{\partial t}(\varepsilon_1\rho_1 x_i)+\nabla\cdot(\varepsilon_1\rho_1 V_1 x_i)=\varepsilon_1 M_i R_i$$

$$\sum y_i=1 \qquad \sum x_i=1$$

$$CO + 2H_2 = CH_3OH + 0CH_4 + 0N_2 + 0CO_2$$

a_i =	-1	-2	1	0	0	0

By solving above equations simultaneously, we can obtain the following variables changing with time and position in a 2-D reactor:

$$\varepsilon_g,\varepsilon_l,\varepsilon_s,u_g,u_l,u_s,v_g,v_l,v_s,x_i,y_i$$

REACTOR'S OPERATING CONDITIONS: (see Fig 1 and Table 1 and 2)

2-D reactor	22.5"x320"
pressure	753.2 psig
temperature	250.3 ^{o}C
gas velocity	15.24 cm/s
catalyst density	3.011 g/cm^3
catalyst diameter	50 micrometer
liquid density	0.70025 g/cm^3
gas type	CO-rich.

SIMULATION:

The initial state of the reactor is shown in Fig 1 and Table 1. The gas phase consists of the inert N_2 only. At time zero, the syn-gas is injected to reactor through six orifices and the gas velocity is increased gradually to the final value during the first computing second. The values of all variables for each cell are stored every 0.05 seconds. After two weeks the program stopped at computing time of 35s because of the capacity limit of the hard disk. Then we continued the run by using a restart technique. This report is based on the results of the first 35 seconds.

ANALYSIS AND DISCUSSION:

Fig 2 shows the system output (or gas flowrate at the outlet) varying with time and the frequency response. There are strong oscillations occurring during the first 2.5 seconds. After that. a hydrodynamic steady state could be assumed. The two frequency peaks represent the system's oscillating frequency. To check the hydrodynamic model it is better to compare the frequency with the histogram of the LaPorte's RUN E-8.1.

The PCSHOW movie shows the volume fractions of gas, liquid and solid changing with time and the fast propagation of methanol concentration in the very early time. In Fig 3 we can see the mixing of the three phases when gas is injected at 0.5s. Fig 5 shows the shapes of the three phases at 5s. These shapes stay constant to 35s without a significant change. This phenomena matches with Fig 2 and supports the above steady state assumption. Fig 6a shows the propagation with the injection of syn-gas and Fig 6(b), 6(c) show the methanol concentration profiles at time 2.5s and 5.0s. The yellow area of Fig 6(c) keeps expanding very slowly with time. Since the N_2 fills the whole reactor before the injection of syn-gas, a very long time is needed to fill the reactor with syn-gas and methanol.

Fig 7, 8 and 9 show that the transient flow patterns of the gas phase do not change significantly during hydrodynamic steady state period. There is circulation inside the reactor, particularly in the lower area due to the non-uniform distribution of the orifices and wall effectiveness.

Fig 10 shows the time average volume fractions of gas, liquid and solid along the reactor's height. The slurry level and catalyst concentration are pretty close to LaPorte's measurements (see Table 1).

Fig 11 shows the composition profiles in gas phase for the lower area in which the distribution of methanol, in view of the PCSHOW movie, looks like it has reached steady state in chemical reaction sense . The rate of methanol production in Table 2 is estimated based on Fig 10 and average velocity in y-direction.

The final results will be submitted upon completion of the simulation.

Table 1. The reactor's compositions of initial setting, steady state and RUN E-8.1

	range 1	range 2	range 3
initial	0-72"	72"-168"	168"-320"
gas(%)	0.050	0.050	1.000
liquid(%)	0.426	0.950	0.000
solid(%)	0.524	0.000	0.000

	range 1	range 2
steady state	0-184"	184"-320"
gas(%)	0.170	1.000
liquid(%)	0.670	0.000
solid(%)	0.160	0.000

	range 1	range 2
Run E-8.1	0-196"	196"-300"
gas(%)	0.295	1.000
liquid(%)	0.555	0.000
solid(%)	0.150	0.000

Table 2 Gas compositions and methanol production

vol %	CO	CO_2	H_2	N_2	CH_3OH
inlet	51	13	35	1	0
lower area	51	14	25.5	1.5	8

	CO conv. (%)	Total Catalyst (kg)	MeOH(gmol/h/kg)	Net MeOH(TPD)
lower area*	13.53	740	14.59	8.267
RUN E-8.1	13.50	567	20.50	10.03

* Estimation based on the results of the lower area (height = 0--120")

NOTATION

a ----interfacial aera per unit volume(cm^2/cm^3)

C_i^L ----concentration of i in bulk liquid phase ($mole/cm^3$-L)

C_i^{g-L}----concentration of i in G-L interface($mole/cm^3$-L)
C_D ----drag coefficient

d_i ----diameter of solid/gas bubble

e ----restitution coefficient
g_0 ----radial distribution function

H_i ----Henry's constant of i (bar m^3/mole)
K_{Li}----mass transfer coefficient of i in L-phase(cm/s)

$\dot{m}_k$ ----rate of generation of phase k($g/cm^3/s$)
M_i ----molecular weight of component i($g/mole$)

P ----pressure

r ----rate of reaction(mole/kg-cat./hr)
R_i ----rate of mass transfer($mole/cm^3/s$)

Re_k----Reynolds number
T ----temperature(K)
u, v----velocity in x,y-direction(cm/s)

V ----velocity vector(cm/s)

x_i ----weight fraction of i in liquid phase
y_i ----weight fraction of i in gas phase

Greek letters:

α_i ----stoichiometric coefficient of i

β ----frictional coefficient
ε ----volume fraction

ρ ----density(g/cm^3)

μ ----viscosity
θ ----granular temperature

τ ----shear stress

ψ ----sphericity of solid/gas bubble
ξ ----bulk viscosity

Subscripts:

g, l, s----gas, liquid, solid respectively

i ----species

k ----solid or gas

REFERENCE:

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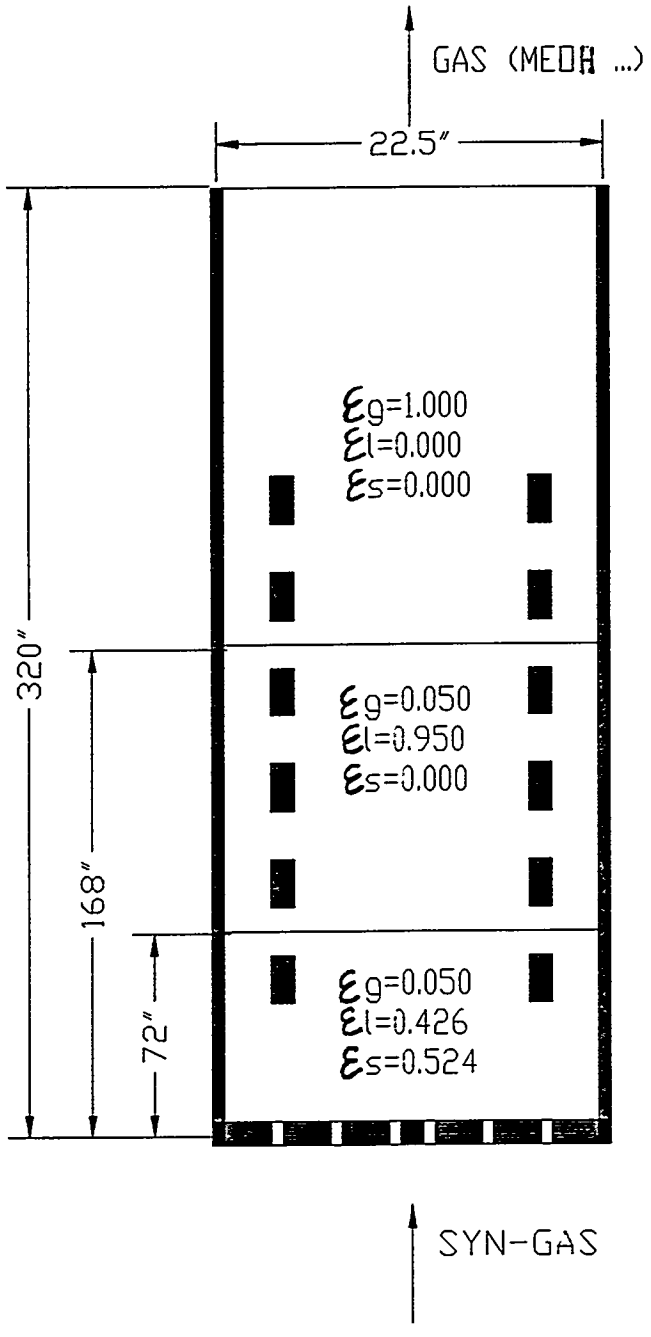
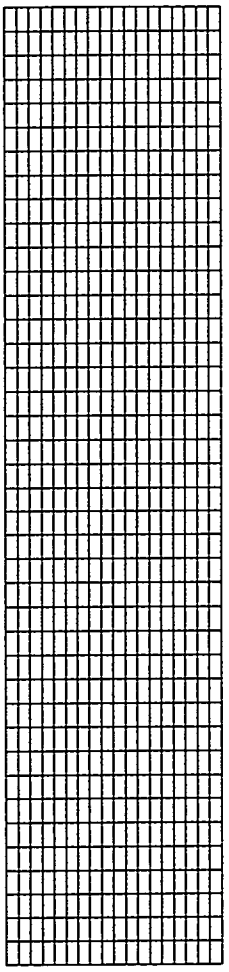
Fig. 1 Reactor and grid



The grid is the right half of the reactor.



grid 18x40

dx=0.7″
dy=8″

Fig2 System output and frequency response

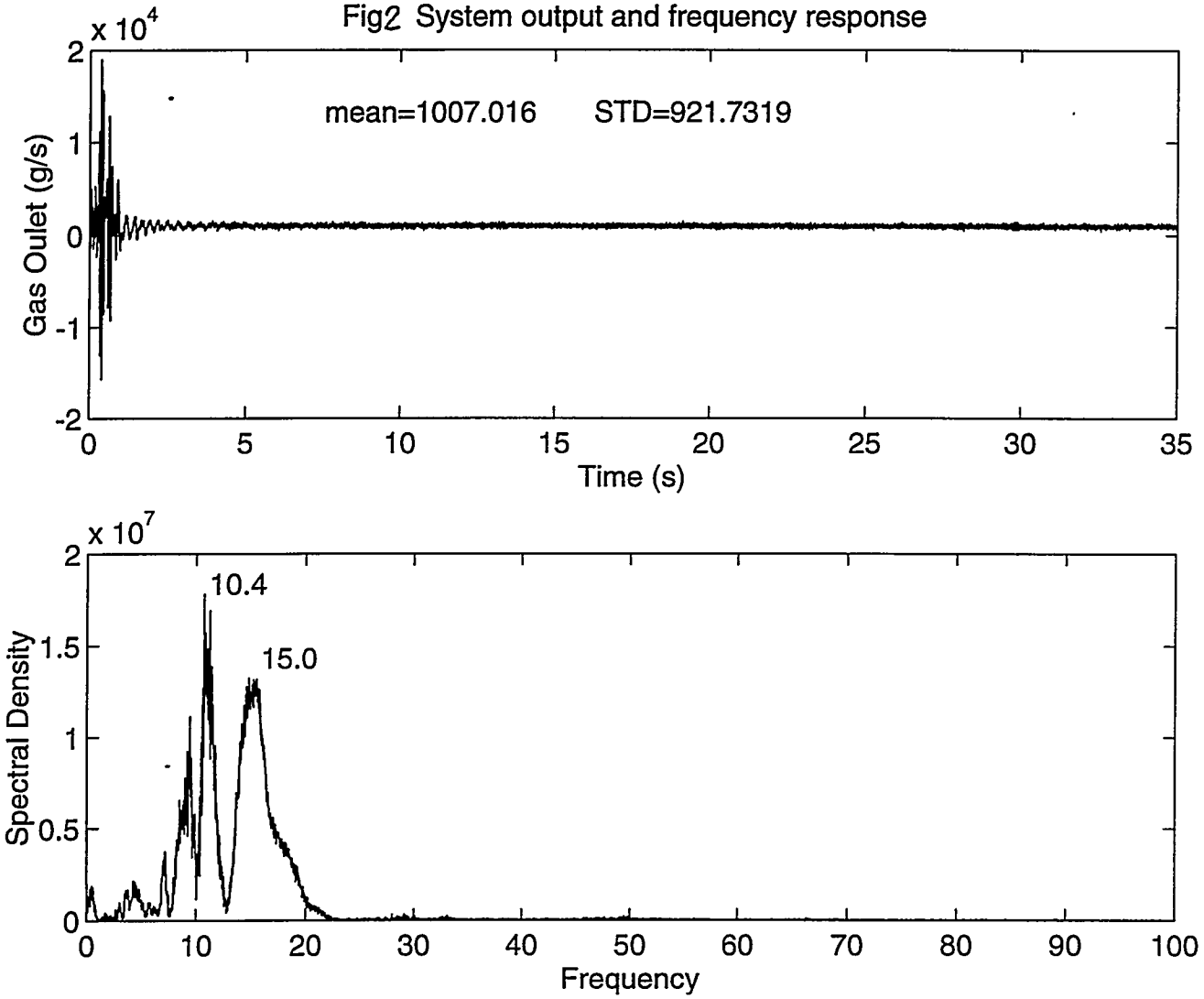
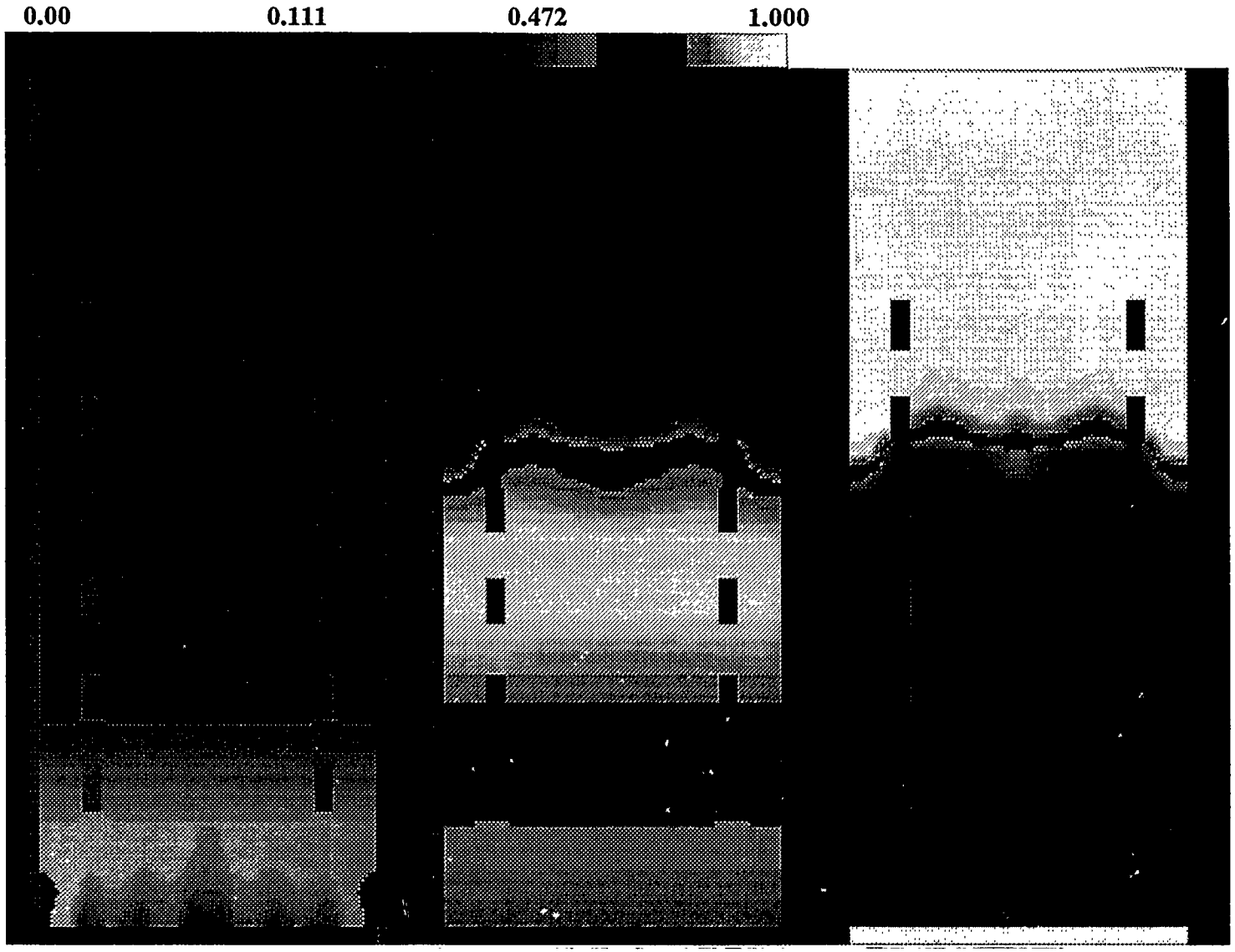


Fig. 3 The volume fraction profiles of gas, liquid and solid at time = 0.5s.



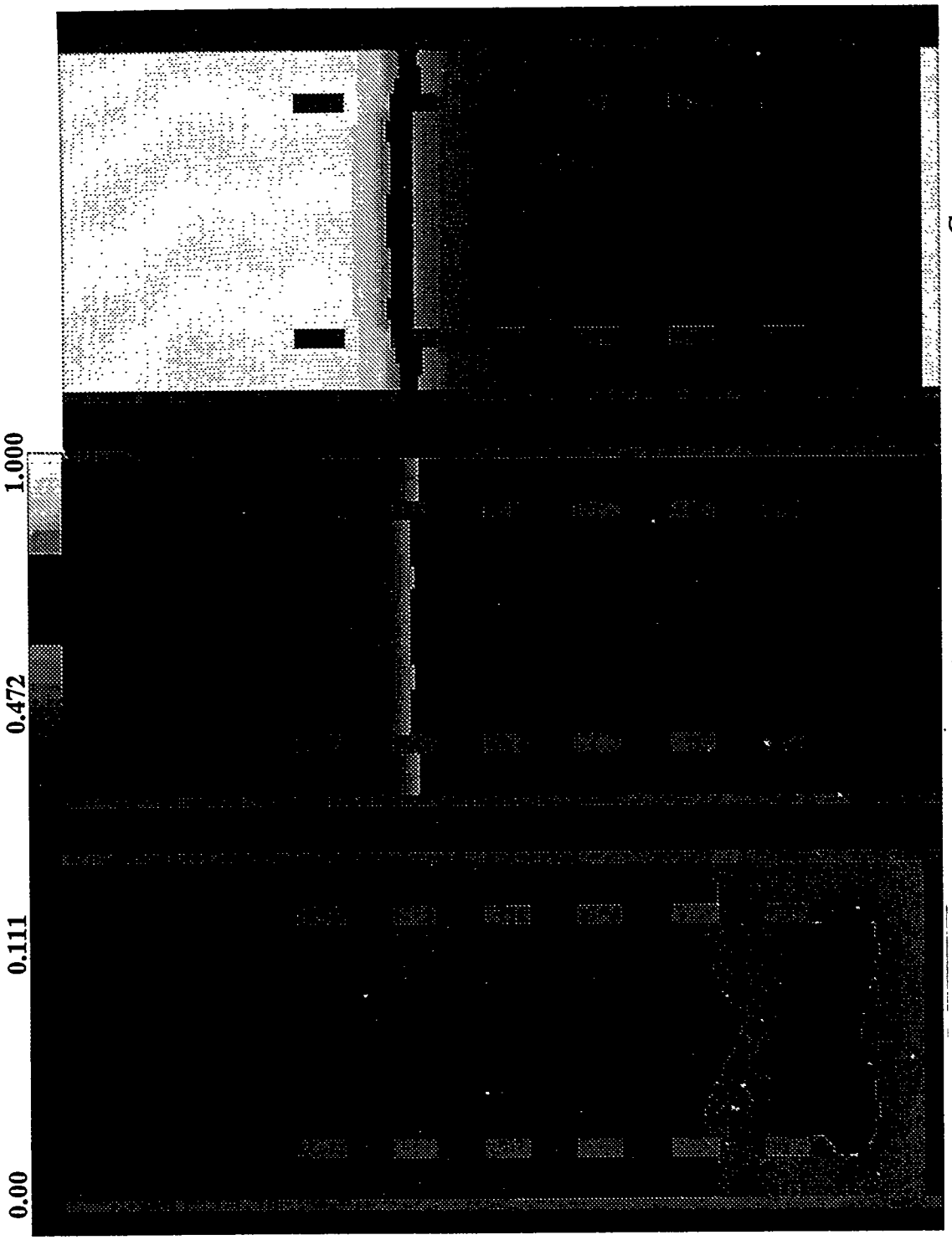


Fig. 4 The volume fraction profiles of gas, liquid and solid at time = 2.5s.

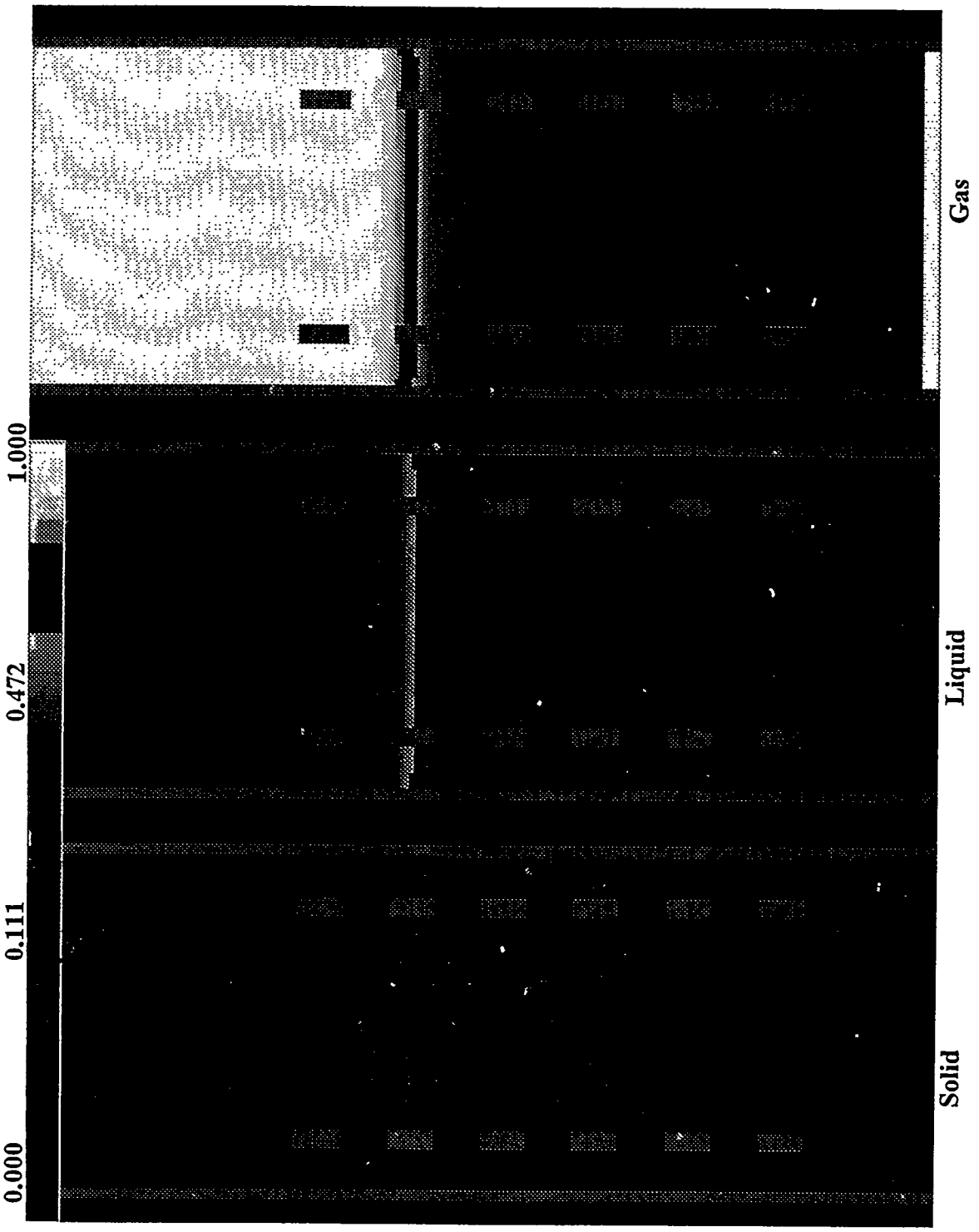
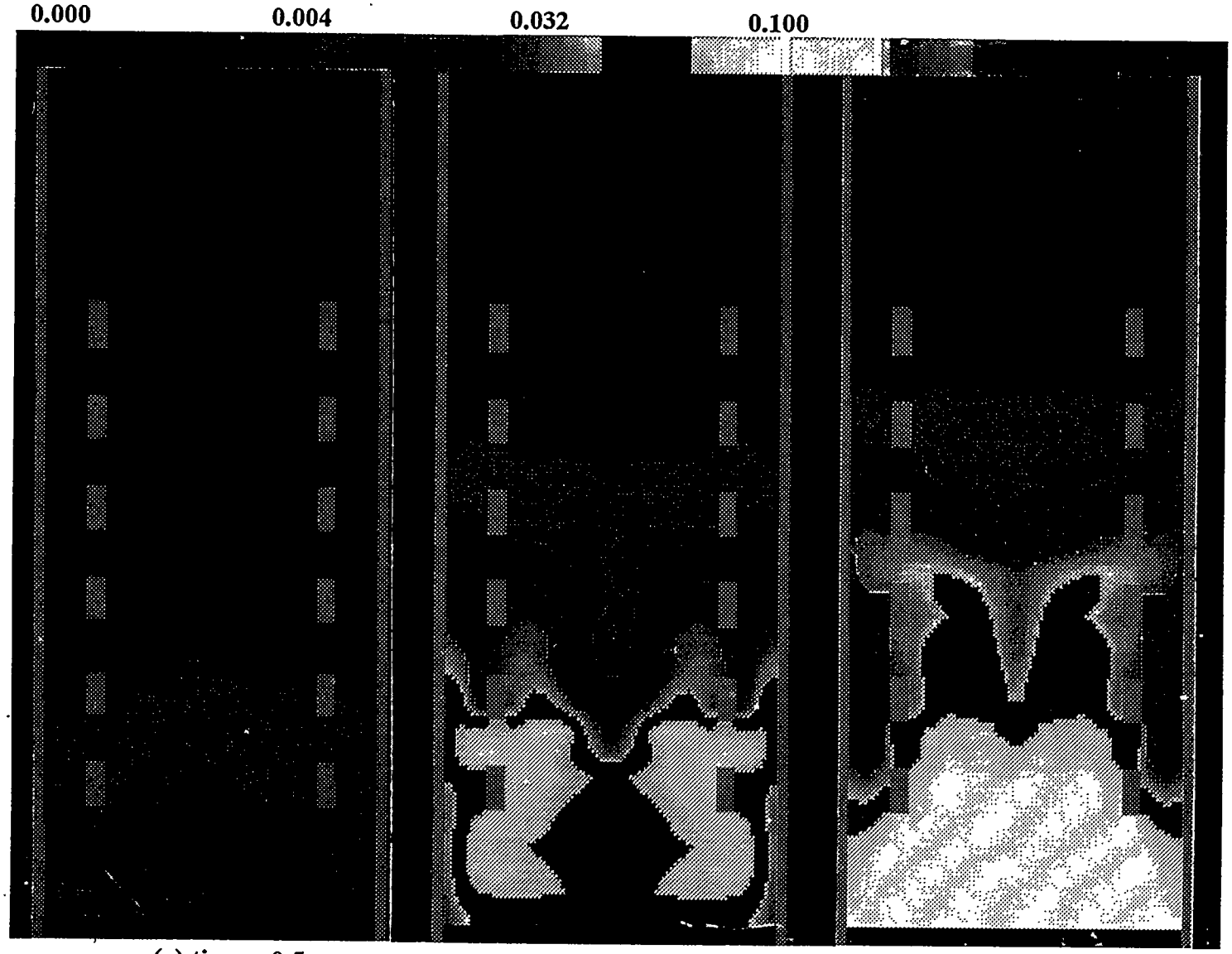


Fig. 5 The volume fraction profiles of gas, liquid and solid at time = 5s.

Fig. 6 The methanol concentration profiles in gas phase (mole fraction).
(a) time = 0.5s, (b) time = 2.5s, (c) time = 5.0s.



(a) time = 0.5s (b) time = 2.5s (c) time = 5.0s.

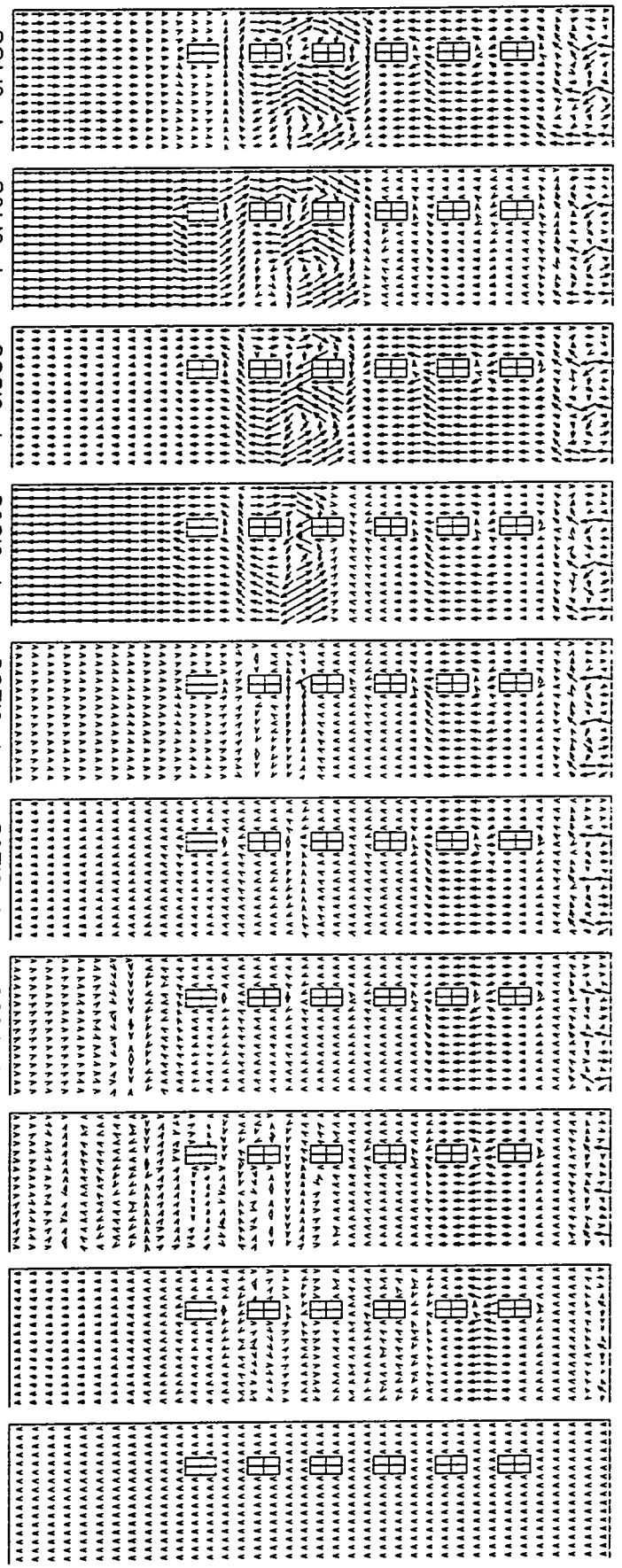


Fig. 7 The transient gas flow pattern as a function of time.

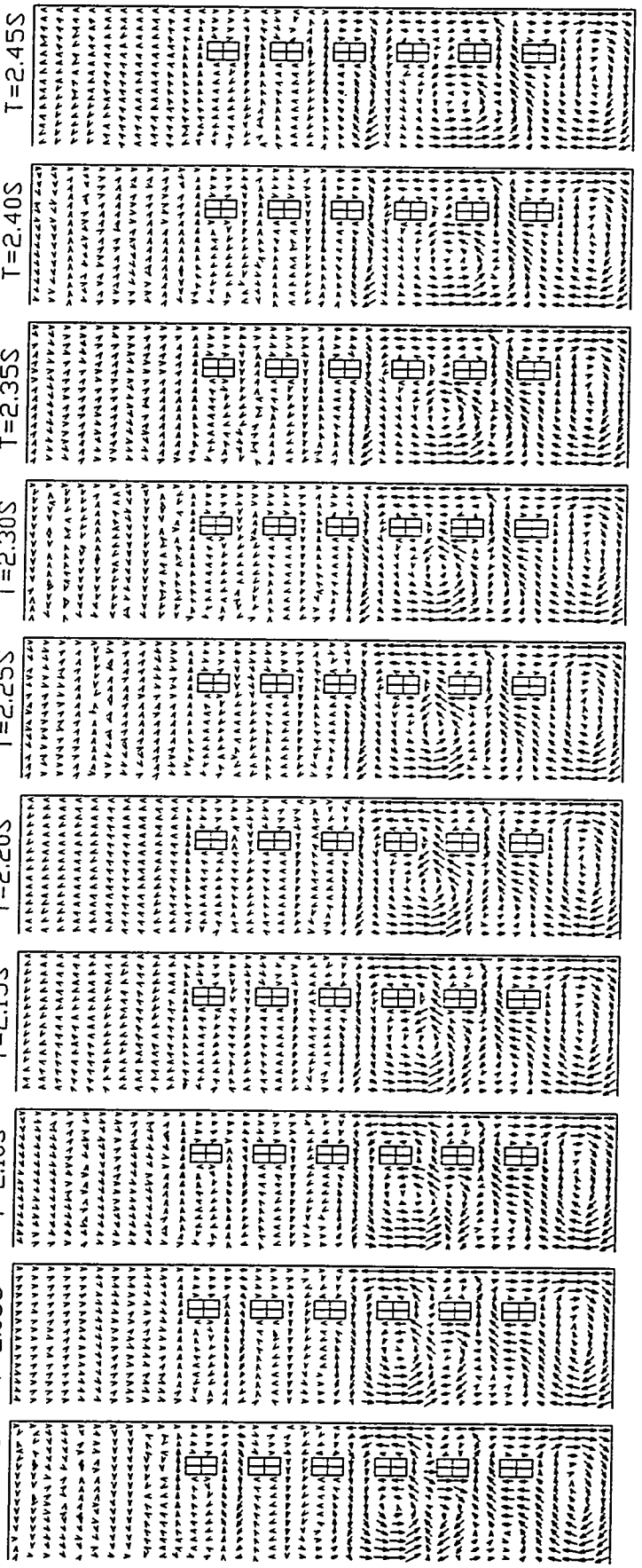


Fig. 8 The transient gas flow pattern as a function of time.

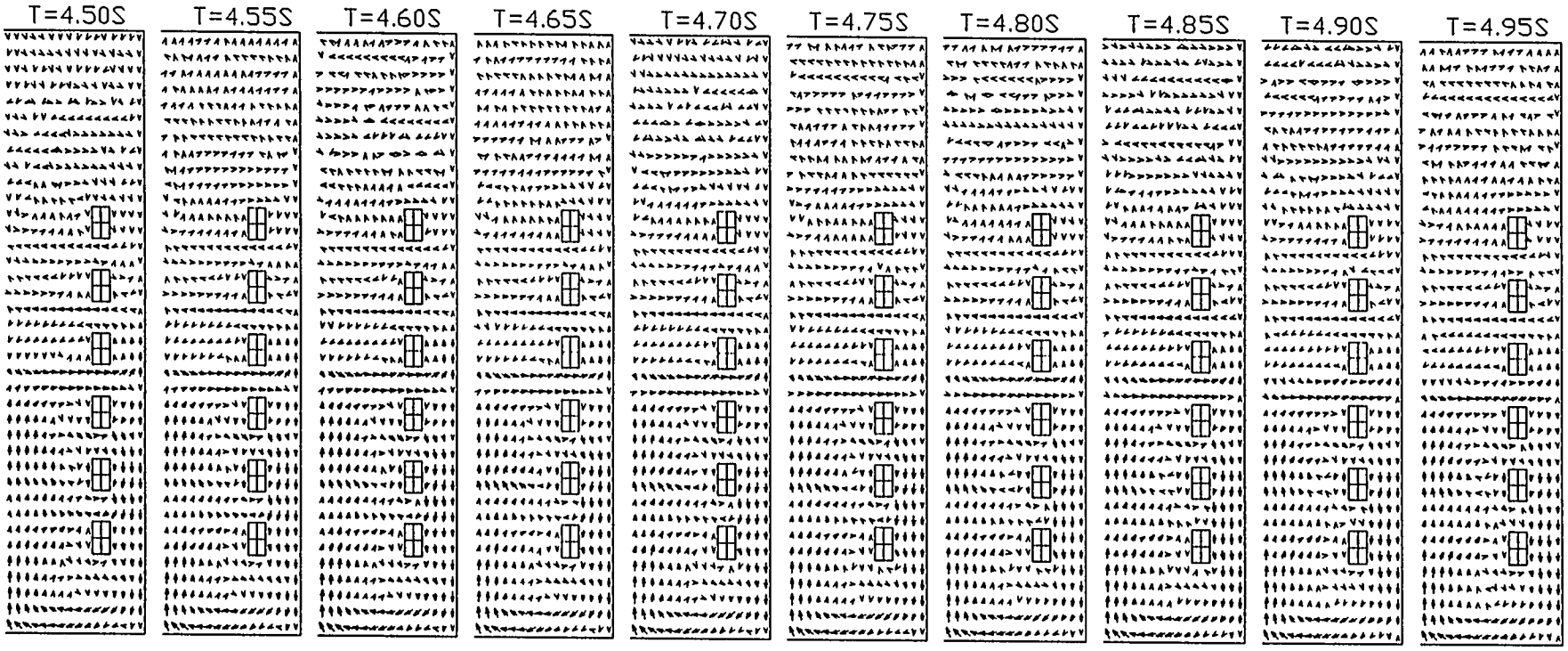
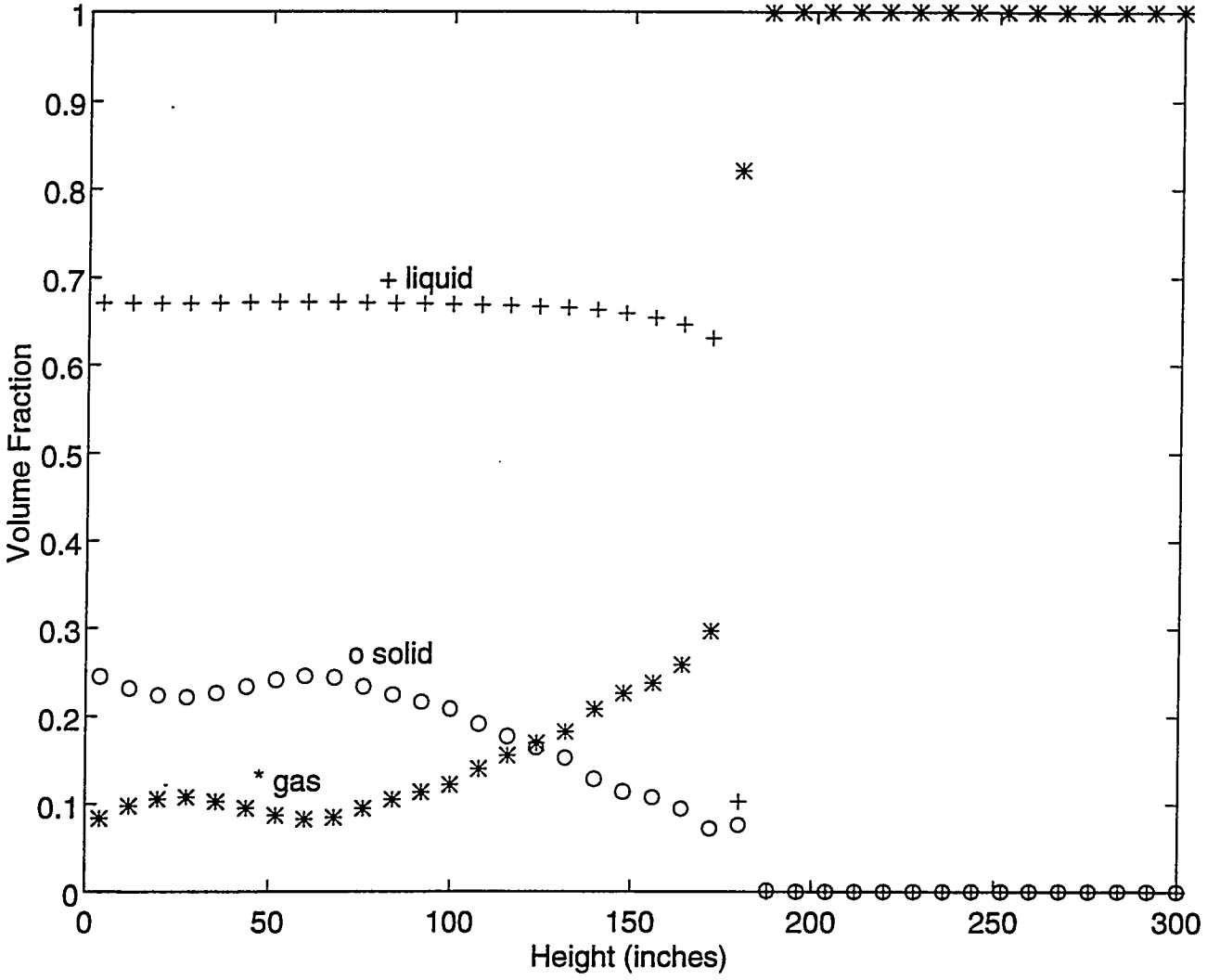


Fig. 9 The transient gas flow pattern as a function of time.

Fig10 Volume fraction profile (time average from 10s to 18s)



Figll Gas composition profiles (time average from 10s to 18s)