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**Engineering Development of Slurry Bubble Column
Reactor (SBCR) Technology**

**Quarterly Report
January 1 - March 31, 1996**

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ENGINEERING DEVELOPMENT OF SLURRY BUBBLE COLUMN REACTOR (SBCR) TECHNOLOGY

Quarterly Technical Progress Report No. 4 for the Period 1 January - 31 March 1996

Contract Objectives

The major technical objectives of this program are threefold: 1) to develop the design tools and a fundamental understanding of the fluid dynamics of a slurry bubble column reactor to maximize reactor productivity, 2) to develop the mathematical reactor design models and gain an understanding of the hydrodynamic fundamentals under industrially relevant process conditions, and 3) to develop an understanding of the hydrodynamics and their interaction with the chemistries occurring in the bubble column reactor. Successful completion of these objectives will permit more efficient usage of the reactor column and tighter design criteria, increase overall reactor efficiency, and ensure a design that leads to stable reactor behavior when scaling up to large diameter reactors.

Summary of Progress

- *Technique Development*

The high-temperature, high-pressure bubble column was improved by adding differential pressure transducers with a computer data acquisition system, calibrating the high-temperature, high-pressure liquid flow meter and fabricating several distributor plates that can be easily interchanged.

(The Ohio State University)

- *Data Acquisition*

Measurements of density at high temperature and pressure were made. Fundamental physical property data for two- and three-phase systems are not well understood, but are vital to understanding the fluid mechanics of such systems. Thus, a program of measuring properties such as interfacial tension and density has been undertaken. Liquid density increased by about 5% when pressure was increased from 15 to 3000 psig at room temperature, while the increase was 6% at 250°F.

(The Ohio State University)

The study of two-dimensional flow sometimes simplifies flow problems and facilitates the understanding of the actual 3-D case. Thus, the effect of increasing scale on instantaneous flow structures in 2-D bubble columns was studied under a variety of flow rates using Particle Image Velocimetry (PIV). In columns larger than 8 inches, the 4-region flow structure (discussed in the last quarterly report) was found in the transition region, but only a 3-region flow structure was found in smaller columns. Gas holdup distribution also differed with increasing length. These detailed results will form the basis for validation of computational fluid dynamic codes for two-phase flow.

(The Ohio State University)

- *Model Development/Data Processing*

Analysis of the tracer data from the hydrodynamic trial showed that:

- ◆ The standard axial dispersion model generally fits the tracer data well. Although one can calculate values for the coefficients in the axial dispersion model, the model itself is physically unreasonable. New models are needed to increase the accuracy of scaleup.
- ◆ Liquid dispersion coefficients can only be calculated reliably when the detector is far away from the injector. (This conclusion was made previously by inspection of the data. It was incorporated in the planning for the trial.)
- ◆ Gas phase dispersion coefficients are strongly dependent on gas holdup. Gas holdup depends upon the extent of conversion at any point in the reactor, which in turn depends upon the flow characteristics of the reactor (CSTR or PFR).
- ◆ The calculated dispersion coefficients are about 150% greater than predicted by the standard correlations (with data measured at atmospheric pressure).
- ◆ Gas phase dispersion coefficients are from 1-3.5 times lower than predicted by standard correlations (atmospheric pressure).
- ◆ Both liquid and gas axial dispersion coefficients increase with increasing gas velocity.
- ◆ Additional work to develop a suitable data base is needed in order to characterize flow patterns in bubble column reactors at high temperatures and pressures.

(Washington University in St. Louis)
(Air Products and Chemicals)

The Ohio State University Research

The following report from Ohio State University for the period January - March 1996 contains the following brief chapters:

1. Measurement of liquid density (Tasks 2-5)
2. Bubble effects on the transient flow pattern in bubble columns (Task 3)
3. High-pressure and -temperature slurry column shakedown (Task 2)
4. Work to be performed next quarter (Task 7)
5. References

WORK PERFORMED

1. *Measurement of liquid density*

An area of high pressure and high temperature operation of slurry bubble column systems which is not fully understood is the effect of the physical property (densities, viscosity, surface tension, etc.) of the gas and liquid phases on the transport phenomena as the pressure and temperature increase. It may be possible to characterize the transport phenomena of slurry bubble column systems operated at high pressure and high temperature based on the physical properties of the phases rather than the operating pressure and temperature

The liquid density changes with pressure and temperature due to its compressibility and gas absorption. The hydrostatic weighing method was adopted to measure the effective liquid density, i.e., the density of a mixture of liquid and absorbed gas. The experimental setup is shown in Fig. 1. The submerged volume of a floating body in the liquid changes with the density of the liquid based on the Archimedes principle. Thus, the liquid density can be determined from the submerged float volume change. The densities of Paratherm NF heat transfer fluid were measured at a various temperatures and various pressures, and the experimental results are shown in Fig. 2. In general, the liquid compressibility can be negligible for a small variation of pressures. However, for a large variation of pressures, the intermolecular distance significantly decreases causing the density to increase. This is specially true for organic liquids. As shown in Fig. 2, the liquid density increases by about 5% when the pressure increases from atmospheric pressure to 3000 psig at a room temperature. An increase in temperatures results in an increase in the free energy, thereby enhancing intermolecular movement and yielding a reduction in the density. An increase in temperature from 68 to 250 F causes the liquid density to increase by about 6% for the entire pressure range tested.

2. *Bubble effects on the transient flow pattern in bubble columns*

The instantaneous flow structure in bubble columns was examined this quarter with emphasis on the scale-up effects. The experiments were carried out in 2-D bubble columns. The column width

was varied from 4" to 24".

As reported in the last quarterly report, the transient flow structure in a bubble column can be characterized by a 4-region or a 3-region flow patterns. Columns operated in the 4-region flow condition are comprised of the descending flow region, the vortical flow region, the fast bubble flow region and the central plume region. The fast bubble flow region is observed to move in a wave-like manner, and thus, the flow in the vicinity of this region can be characterized macroscopically in terms of wave properties. In small columns, the central plume region becomes indistinguishable from the fast bubble flow region yielding a 3-region flow. Based on flow visualization and the description of the flow regimes given above, the approximate dependency of the flow regimes on gas velocity and column width can be determined. Figure 3 shows that in columns less than 8" in width, by increasing the gas velocity, the flow regime will change directly from the dispersed bubble flow regime to 3-region flow. However, in larger columns, the flow regime will change from dispersed bubble flow, to 4-region flow, and then to 3-region flow. In large columns when the gas velocity reaches 1 cm/s the vortex size does not increase. Therefore, by continuously increasing the gas velocity the fast bubble flow regions will gradually grow and merge together to form a central fast bubble region in which the bubbles coalesce and break-up violently. However, in small columns, the bubbles merge together quickly to form a central bubble flow region which occupies the central plume region directly. Figure 3 shows that 1 cm/s and 3 cm/s are the demarcations between the dispersed bubble flow regime to the 4-region flow, and 4 to 3-region flow, respectively. Figure 3 was compared with the regime classification for 3-D systems reported by Shah et al. (1982), the two figures (Figure 3 and Figure 2.2 of Shah et al., 1982) bear considerable resemblance for dispersed bubble regime and coalesced bubble regime. Thus, it is apparent that the 2-D column results obtained in this study reveal that the coalesced bubble regime (or churn-turbulent flow) can be subdivided into 4-region flow and 3-region flow. In a 3-D system the flow will change from the dispersed bubble flow regime at lower gas velocities, to the coalesced bubble regime which has been found to consist of the vortical-spiral and turbulent flow conditions at high gas velocities (Chen et al., 1994). Here, the 3-region flow in a 2-D system, which exhibits coherent flow structures, will transform to the turbulent flow condition in the 3-D system when the gas velocity continues to increase. Even though the flow

field in a 2-D column deviates to some extent from that in a 3-D column, the present results provide the qualitative and quantitative similarities of dynamic flow structure between 2-D and 3-D bubble columns.

The flow regime transition and subsequently the gas holdup distribution, in small columns differs from that in large columns. In small columns, the bubbles coalesce at the bottom of the column right above the bubble injectors and, therefore, the flow structure develops quickly in the axial direction. Thus, the gas holdup distribution remains constant through the entire region above injector. Figure 4 shows the effect of the gas velocity on the radial distribution of the gas holdup measured at $L_m = 31.5"$ ($L_m / L_s = 0.5$, where L_m is the height above the bubble injectors) in a 6" wide bubble column. The figure illustrates that the shape of the radial gas holdup distribution shifts from a uniform bubbly distribution at low gas velocity to a central bubble distribution at higher gas velocities. This result asserts that in small columns the flow regime transforms directly from the dispersed bubble flow regime to the 3-region flow condition.

In large columns, as noted, the flow structure changes with gas velocities from the dispersed bubble flow to 4-region flow, and from 4-region flow to 3-region flow. Figure 5 shows the radial gas holdup distribution in the entire 19" cm column for a gas velocity of 1.54 cm/s; the figure reveals the radial symmetric behavior of the gas holdup.

3. High pressure and temperature slurry column shakedown

Two differential pressure transducers were mounted on the high pressure and temperature column. The differential pressure transducers were calibrated against liquid hydrostatic pressure in the column with liquid only. The zero points of the pressure transducers were found to shift with increasing pressure. A correlation was developed for the zero point shift of these two transducers. The calibration curve obtained the high pressure system is shown in Fig. 6. A computer data acquisition system was also connected to the transducers for the on-line measurements of differential pressures.

Liquid flow meter used in the high pressure and high temperature system was calibrated this quarter. The liquid flow rate is measured by a pneumatic flow meter installed before the column.

In the high pressure and temperature system, liquid in the supply tank is initially preheated to a desired operating temperature, and is then pumped into the column through a flow control valve and a flow meter. The gas enters at the bottom of the column via a sparger, mixes with the liquid in the plenum section; then the mixture is introduced into the column through a distributor. The gas and liquid streams from the column pass through a back pressure regulator and flow into the exhaust reservoir where gas-liquid separation is achieved. The system can be operated in either non-circulation or liquid-continuous mode of operation. In the non-circulation mode of operation, the liquid accumulates in the exhaust reservoir; in the liquid-continuous mode of operation the liquid is recirculated back into the supply tank. The flow meter's readings vary with operating conditions and physical properties of liquid. The readings were correlated with the flow rates obtained by measuring the liquid volume changes in the liquid supply tank in a given time interval in the non-circulation mode of operation.

In a non-coalescence bubble column, the ultimate bubble size distribution depends primarily on the initial bubble size distribution. Initial bubble sizes are function of distributor geometry and operating parameters. To study the distributor effects on the initial bubble size, a porous plate distributor and a perforated plate distributor were made this quarter for the high pressure and temperature bubble column. In the high pressure system, a flanged closure is used for the connection between the plenum section and the test section. It is also use for facilitating distributor exchange. A groove is made on the flanged closure to house an exchangeable distributor plate.

WORK TO BE PERFORMED NEXT QUARTER

1. Quantitative analysis of the transient flow pattern in bubble columns will be continued next quarter with emphasis on the Reynold stress.
2. Gas holdup in the high pressure and temperature bubble column will be studied next quarter.

REFERENCES

Chen, R.C., J. Reese, and L.-S. Fan, "Flow Structure in a Three-Dimensional Bubble Column and Three-Phase Fluidized Bed," *AIChE J.*, **40**, 1093 (1994).

Shah, Y.T., B.G. Kelkar, S.P. Godbole, and W.D. Deckwer, "Design Parameters Estimations for Bubble Column Reactors," *AIChE J.*, **28**, 353 (1982).

Force Balance Equation

$$S[\rho_l L_1 + \rho_l (L - L_1)] g = (W_1 + W_2) + \rho_g L_2 S g$$

W_1 : weight of metal A

W_2 : weight of tube B

Figure 1. Experimental setup for the measurements of liquid density in the high pressure and high temperature system

Figure 2. Variation in the density of Paratherm NF heat transfer fluid with pressures and temperatures.

Figure 3 Operating regimes of two-dimensional bubble columns

Figure 4 Radial gas holdup distribution in 15.24 cm column for $L_m/L_s = 0.5$ and $U_g = 0.81, 1.63, 2.4 \text{ cm/sec}$

Figure 5 Radial gas holdup distribution in 48.3 cm column, demonstrating that the holdup behavior in the column is symmetric

$$DV = 0.00249 - 1.999E-5 \cdot P - 1.764E-7 \cdot P^2$$

Figure 6. The calibration curve for zero point shift of a pressure transducer obtained in the high pressure column.

Washington University Research

The following report (which has been submitted as a topical report) from Washington University for the period January -March 1996 contains the following chapters:

Abstract

Executive Summary

Table of Contents

1. Introduction
2. Objectives
3. Tracer Experiments
4. Modeling
5. Parameter Estimation by Fitting the Model to Data
6. Gas-Liquid Mixing and Scaleup Issues in Bubble Columns
7. Conclusions
8. Nomenclature
9. References

Slurry Bubble Column Hydrodynamics

Tracer Studies of the LaPorte AFDU Reactor During Methanol Synthesis

Fourth Quarterly Report for
Contract DOE-FC 2295 PC 95051
January - March, 1996

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Abstract

The radioactive tracer studies, using impulse injections of Mn^{56} 50 μm particles in the slurry phase and Ar^{41} in the gas, conducted at three process rates during the methanol synthesis runs at the AFDU slurry bubble column reactor at LaPorte, Texas, were interpreted based on the axial dispersion model (ADM). Both liquid and gas axial dispersion coefficients showed an increase with superficial gas velocity. Responses of detectors located at various column heights point to the inadequacy of the ADM to interpret properly the gas and liquid flow pattern and mixing in the column. An alternative model is proposed.

Executive Summary

Radioactive tracer experiments were executed at the AFDU slurry bubble column reactor at LaPorte, Texas, at three different process rates (superficial gas velocities ranging from 14 to 36 cm/s, reactor temperature of 250 °C, reactor pressures of 3.6 MPa and 5.2 MPa, and a catalyst loading of approximately 45 wt %) to determine the flow pattern and backmixing of the liquid and gas during methanol synthesis. Impulse injections of radioactive Mn^{56} particles were used at different positions along the column to monitor the mixing of the liquid (batch) phase. Impulse injection of Ar^{41} were made at the syngas inlet to map the flow pattern of the gas. Responses to these tracer impulse injections were monitored at various column heights with four scintillation detectors located at 90° angles at each height. The axial dispersion model (ADM) was employed to interpret the tracer response data, since this model was used in the past for analysis of reactor performance.

The objectives of the study were : (a) to obtain flow pattern and backmixing information and backmixing data from actual pilot plant high pressure, high temperature reactors under operating conditions, (b) to examine the dependence of the obtained parameters on gas velocity and operating pressure, (c) to assess the ability of the available correlations to predict the measured axial dispersion coefficients and (d) to assess the suitability of the axial dispersion model for describing backmixing in reactors of this type and to determine the suitability of parameters used in reactor performance equations.

The findings, described and discussed in this report, can be summarized as follows:

1. The axial dispersion model (ADM) results in good fits with experimental tracer response data for the liquid phase. However, there is a wide scatter in the fitted axial dispersion coefficient, which points to the inadequacy of the model. An alternative phenomenological model is suggested.
2. The ADM is only fitted to the detector responses that showed no overshoots. The so-determined axial liquid dispersion coefficients typically exhibit a standard deviation of up to $\pm 35\%$.
3. Fitting of the ADM for the gas tracer response at detectors far removed from the inlet requires a good knowledge of both the gas holdup profile in the column and of the local gas velocity. Hence, tracer response is intimately tied to reactor performance which dictates the level of reduction in syngas flow rate depending on the level of conversion.

4. Questions can be raised about the accuracy of the measured holdup profile along the column height since differential pressure measurements are in considerable disagreement with nuclear density gauge measurements, and there is no independent evidence for the uniformity of slurry concentration along column height.
5. Fitting of the ADM to the gas phase response curves measured at a distance from the inlet, based on argon solubility calculated from thermodynamics, measured gas holdup profiles and assumed linear decay in gas velocity, yields the gas axial dispersion coefficients with a standard deviation typically within ± 22 %. The overall volumetric mass transfer coefficient, which is the other parameter from such a curve fitting, exhibits a standard deviation of up to ± 100 %.
6. The average value of the estimated parameters is shown in the table below:

Run	P	$\bar{\epsilon}_G$	U_{Gin}	X_{CO}	$D_L \pm \sigma_L$	$D_G \pm \sigma_G$	$K_L a \pm \sigma_k$
No.	MPa		cm/s		cm^2/s	cm^2/s	1/s
14.6	5.2	0.39	25	0.16	4355 ± 1532	5649 ± 1022	0.37 ± 0.37
14.7	5.2	0.33	14	0.18	2713 ± 678	2908 ± 723	0.38 ± 0.06
14.8	3.6	0.37	36	0.33	5143 ± 516	6621 ± 1437	0.35 ± 0.12

Both liquid and gas axial dispersion coefficients increase with increased gas velocity at constant pressure. The volumetric mass transfer coefficient seems unaffected by gas velocity. The effect of pressure is not clear since in run 14.8 while the pressure was reduced the superficial gas velocity was increased.

The available correlations for axial dispersion coefficients (with data base of atmospheric pressure operation) underpredict the observed liquid axial dispersion coefficient within 150 % but overpredict the gas dispersion coefficient by 100 % to 360 %.

Additional work is needed in characterizing the reactors at operating conditions and in developing a suitable data base.

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1 Introduction

This investigation involves the study of the mixing characteristics in a slurry bubble column reactor during liquid phase methanol (LPMEOH) synthesis runs. The experiments were conducted in the AFDU Oxygenates High Pressure Reactor at LaPorte, Texas. Powdered methanol catalyst (~ 45 wt % loading) suspended in inert hydrocarbon oil forms the batch slurry phase. Synthesis gas is bubbled through a sparger placed at the bottom of the reactor. The gas disengages from the oil in the freeboard section of the reactor, and the unreacted feed gas is recycled back to the reactor.

The principal reaction for methanol synthesis is

At the process conditions used the methanol formed is in the vapor phase. The feed gas to the reactor is synthesis gas which is a mixture typically consisting of CO (30 %), H_2 (60 %), CO_2 (5 %) and inerts (N_2). The composition of the feed gas, given above in mole %, may be varied by changing the feed ratio, depending upon process requirements. The presence of CO_2 is usually required, as it serves to start the reaction. A side reaction known to occur is the water gas shift reaction:

Based on the above reaction stoichiometry (Equations 1 and 2), there is a reduction in the volume of the gas. The actual reduction depends on the feed rate, composition, and conversion. For the tracer runs studied, feeds with varying composition were used. The experimental conditions along with the feed compositions, observed conversions and changes in gas volumetric flowrate are reported in Table 1. The conversion of CO for the three runs studied ranges from 16% to 33%. An excess of CO results in lower conversion (runs 14.6 and 14.7 compared to run 14.8). Although CO conversion varies for the three cases, due to a corresponding change in feed composition, the effective overall change in the gas flowrate is about the same for all the runs, around -18 %.

Table 1: Experimental Conditions (Temp : 250° C)

Run No.	P MPa	Gas Holdup	U_G cm/s	Feed Composition mol %			Conv of CO to MeOH	Inlet Vol. Flowrate SCFH	Change in Flowrate %
				H_2	CO	CO ₂			
14.6	5.2	0.39	25	35.4	50.8	12.7	15.9	143121	-17.1
14.7	5.2	0.33	14	35.0	50.9	12.7	17.5	81151	-19.2
14.8	3.6	0.37	36	60.2	24.0	10.3	33.0	141690	-17.7

1.1 Gas Holdup Measurements

Holdup measurements within the reactor were made using two techniques. These are: 1. Differential Pressure measurements (DP) and 2. Nuclear Density Gauge (NDG) measurements.

DP measurements rely on the assumption that liquid (slurry) velocities and shear stresses near the wall are small in comparison with the hydrostatic head. Thereby

$$\rho g = \frac{\Delta P}{\Delta z} \quad (3)$$

where

$$\rho = \rho_L \epsilon_L + \rho_G \epsilon_G \quad (4)$$

The subscripts 'L' and 'G' refer to the slurry and gas phase, respectively. The density of the gas phase is very small when compared with that of the slurry, and therefore the second term in Equation 4 can be ignored. The slurry density in the column is assumed to be uniform (ρ_L) and is calculated using the information on solids holdup ((catalyst weight/density)/dispersion volume) (Shollenberger, 1995).

Nuclear Densitometry (NDG) is a noninvasive method in which a source emitting a narrow beam of radiation through the column is used with a detector opposite it to scan across the column cross section. This yields a series of chordal measurements. A single line averaged holdup is usually obtained across the centerline, (i.e. diameter) of the column. However, this can result in a higher holdup value than the actual cross-sectional average holdup. A distribution of the void fraction across a given cross-section can be obtained in a series of such scans at different angular orientations (tomography), which on averaging results in the true cross-sectional mean. The difference between the holdup estimates from these two γ ray techniques (i.e., tomography and chordal averaging) is illustrated in Figure A.1.1. of Appendix I. The reasons for the discrepancy have been discussed elsewhere (Kumar et al., 1996).

It was found that the nature of the averaging method in the NDG measurements leads to higher values of gas holdup than the actual cross-sectional average value, especially for cases of steep void fraction profiles in the column. However, when the void fraction profile is more uniform, the discrepancy between DP and NDG determined holdup values is reduced. Due to this factor, for present considerations, the DP measurements will be initially considered for more accurate holdup estimates.

Axial holdup profiles at various process conditions are shown for both measurements in Appendix I (Figure A.1.3.). It is seen that there is an initial decrease in holdup with axial position, up to a height of about 10 column diameters, after which the holdup remains quite uniform up to a height of about 15 column diameters. From this level upward there is a steady increase in gas holdup. Since the reaction results in the decrease of gas volume, it is surmised that this increase in holdup towards the free surface of the liquid is the result of foaming in the system. Such a trend in the axial gas holdup profiles is reported for all process conditions (Figure A.1.3.a).

Unfortunately, even this result of increasing gas holdup with column height in the upper sections of the column cannot be unconditionally accepted at face value. If a catalyst concentration gradient develops along this tall column, then the slurry concentration at the top of the column is smaller than the one at the bottom (or the average), i.e., $\rho_{L,T} < \rho_L$. The pressure drop measurement by the DP method in the top region of the column actually yields

$$\left(\frac{\Delta P}{\Delta z}\right)_{top} = \rho_{L,T} \epsilon_{L,T} g \quad (5)$$

However, if we use the average slurry density (ρ_L) to estimate the slurry holdup, ϵ_L from this measured value, it can be readily seen from Equation 6 that the slurry holdup is underestimated since $\rho_{L,T}/\rho_L < 1$.

$$\epsilon_L = \frac{1}{\rho_L g} \left(\frac{\Delta P}{\Delta z}\right)_{top} = \epsilon_{L,T} \frac{\rho_{L,T}}{\rho_L} < \epsilon_{L,T} \quad (6)$$

Therefore the gas holdup is overestimated, and the rise of gas holdup with height in the upper part of the column may be the artifact of the DP measurement interpretation. It should be noted that if NDG is used, and the attenuation of the slurry varies with catalyst concentration, then a less dense slurry at the top of the column, if the attenuation calculation is based on a more concentrated slurry, will yield an overestimate of gas holdup also.

This indicates that both the DP and NDG techniques can yield, as an artifact of the assumption of uniform catalyst concentration, an increased gas holdup along the

column length if pronounced axial catalyst concentration profiles are present.

2 Objectives

The objective of this work is to study the mixing characteristics of the gas and liquid phase in the slurry bubble column reactor using radioactive tracer experiments. Interpretation of the tracer experiments at this stage is based on the one-dimensional axial dispersion model (ADM). The ADM is chosen because it is almost always used by others, and since the previous runs at LaPorte have utilized this approach as well. This choice is, in addition, dictated by the fact that ADM has also been used in reactor design and performance calculations. Thus, examination of the tracer studies can provide some insight regarding the appropriateness of the backmixing parameters used in reactor performance calculations.

However, our long-term goal is to assess the suitability of the present model (ADM) to describe mixing in the gas and liquid phase in slurry bubble column reactors and suggest alternatives if needed.

3 Tracer Experiments

A schematic of the AFDU slurry bubble column reactor is shown in Figure 1. It has an internal diameter of 0.46 m and a height of 15.24 m, with the liquid - gas - solid dispersion level maintained at 13.25 m (L/D ratio of 28.8) during the runs discussed here. The vapor phase and liquid phase tracer experiments were conducted separately. Radioactive Ar-41, used to study the residence time distribution of the vapor phase, was injected as a pulse at the inlet of the reactor. Radioactive Manganese-56 ($50\text{ }\mu\text{m}$) particles mixed in oil were used for liquid (slurry) phase tracing. Four pulse injections were made at a given process rate: (1) lower nozzle N2 - 4.5" (11.4 cm) from wall, (2) nozzle N2 - at wall, (3) upper nozzle N1 - 4.5" (11.4 cm) from wall, and (4) nozzle N1 - at wall. The axial levels of these injection points are shown in Figure 1. The injections made at 4.5" (11.4 cm) from the wall will be referred to as "center injections," as they are made into the core part of the column where the liquid is known to move upward by convection (Devanathan et al., 1990).

Radiation measurements from the vapor and liquid tracers were made using several 2" by 2" NaI scintillation detectors positioned outside the column, at various axial levels, as shown in Figure 1. Sets of four detectors were placed at 90 degree angles at seven heights. In addition, detectors were placed at the inlet and outlet of the

Figure 1: Schematic of Reactor for Tracer Experiments

reactor. During the liquid tracer study, the inlet detector was placed close to the liquid injection point to monitor the shape of the injected pulse.

The radiation (counts/time) measurements made at the detectors were used to obtain the residence time distribution of the radioactive tracer. To analyze of the tracer data with the one dimensional axial dispersion model (ADM) for both the vapor and liquid phase, the responses from the four detectors at each level were averaged to obtain a cross-sectional averaged response at the corresponding level. This was done since the model is one dimensional and does not have the capability of resolving radial and azimuthal variations.

The total radiation (counts/time) recorded at the detector is an integral of the

contribution of the entire mass (or volume) of tracer, which can be considered to comprise individual point sources within the field of view of the detector. For the tracer experiments considered in this study, the detectors were shielded on their sides. Therefore only the front circular surface of the detectors could see the radiation. With this configuration, the spatial range from which a detector receives most of its signal was assessed. The equations used for this calculation (Tsoulfanidis, 1983) are shown in Appendix II. For a uniform distribution of radioactive tracer in the column, it is concluded that more than 90 percent of the intensity recorded at a detector, shielded on its sides, comes from a small volume (less than 1 percent of the entire reactor volume) closest to the face of the detector. This is shown in Figure A.2.1, where the exponential decay in intensity with distance can be seen.

For gases and liquid, which are no longer point sources, the specific activity, defined as the number of disintegrations/time/volume of the nuclei of the radioisotope, depends on the mass or volume of the radioactive source (Tsoulfanidis, 1983), and thereby on the local concentration of tracer.

Since the ADM, when applied to the liquid and gas phase, can only consider uniform tracer concentration and phase holdups, the intensity (counts/time) recorded at the detector can be assumed to be directly proportional to the concentration of tracer at a given axial location of the detector. The liquid Mn-56 tracer with a half life of 2.58 hr emits γ radiation at 0.85 MeV. This tracer remains only in the liquid (slurry) phase. Hence, the average detector response is directly proportional to the tracer concentration in the liquid phase. However, the gas tracer Ar-41 of half life 1.29 hr, emitting γ rays at 1.29 MeV, is soluble in the liquid. Therefore, for the gas experiments, the total tracer concentration at a given time and axial position, which is assumed to be proportional to the average detector response, is taken to be

$$C_t(t, z) = \epsilon_L C_L(t, z) + \epsilon_G C_G(t, z) \quad (7)$$

4 Modeling

The one dimensional axial dispersion model (ADM) was used to model mixing in the liquid and vapor phase. It was chosen for reasons stated earlier. This model essentially assumes the fluid to be in plug flow with axial dispersion superimposed on it.

4.1 Liquid Phase Tracer

For the case of a batch liquid (slurry) with non-volatile tracer, the one dimensional dispersion model can be written as:

$$\frac{\partial C_L}{\partial t} = D_L \frac{\partial^2 C_L}{\partial z^2} \quad (8)$$

Initial and boundary conditions are:

$$t = 0; \quad C_L = \delta(t)\delta(z - z_i) \quad (9)$$

$$z = 0; \quad z = L; \quad \frac{\partial C_L}{\partial z} = 0 \quad (10)$$

where z_i and L denote the level of injection and liquid dispersion height, respectively. The model has a single parameter, the liquid phase dispersion coefficient, D_L . It can be solved analytically, and the response at a given detector level, z , to an impulse input at z_i is:

$$C_L(t, z) = 1 + 2 \sum_{n=1}^{\infty} \cos\left(\frac{n\pi}{L} z_i\right) \cos\left(\frac{n\pi}{L} z\right) \exp(-D_L n^2 \pi^2 t) \quad (11)$$

The average response of the four detectors at each level was considered. Both experimental data and model predicted responses were normalized with respect to their maximum value before the fitting procedure was performed. Hence the best value of the parameter, D_L , was obtained by minimizing the sum of the square of the errors, given by

$$\min_{D_L} \sum_{i=1}^{N_p} \left(\frac{R(t_i, z)}{R_{max}} - \frac{C_L(t_i, z)}{C_{Lmax}} \right)^2 \quad (12)$$

where $R(t_i, z)$ is the averaged response of the four detectors at z and time t_i , and R_{max} is the maximum value of the detector response at z . $C_L(t_i, z)$ is the model predicted liquid tracer concentration at level z and time t_i , and C_{Lmax} is the maximum liquid concentration. The number of data (sampling) points, N_p , is about 1000.

Time domain fitting of the model prediction with the average detector response at every level is performed, for each injection, to estimate the model parameter D_L . It is noted here that the tracer injections are point injections, not cross sectional injections, and therefore do not truly satisfy Equation 9 (uniform injection in a cross section), since a finite time is required for the tracer to spread radially.

4.2 Gas Phase Tracer

Since the radioactive argon tracer is soluble in the liquid phase, the one dimensional axial dispersion model with interfacial mass transfer resistance, is considered for modeling the argon tracer distribution in the reactor. The mass balance equations for the tracer in the vapor and liquid phase are as follows :

$$\frac{\partial C_G}{\partial t} = D_G \frac{\partial^2 C_G}{\partial z^2} - \frac{U_G}{\epsilon_G} \frac{\partial C_G}{\partial z} - K_L a \left(\frac{C_G}{H} - C_L \right) \quad (13)$$

$$\frac{\partial C_L}{\partial t} = D_L \frac{\partial^2 C_L}{\partial z^2} + \frac{\epsilon_G}{\epsilon_L} K_L a \left(\frac{C_G}{H} - C_L \right) \quad (14)$$

The initial and boundary conditions are :

$$t = 0, \quad C_L = 0; \quad C_G = 0 \quad (15a)$$

$$z = 0, \quad \frac{\partial C_L}{\partial z} = 0; \quad \frac{U_G}{\epsilon_G} C_G = D_G \frac{\partial C_G}{\partial z} + \frac{U_g}{\epsilon_G} \delta_i(t) \quad (15b)$$

$$z = L, \quad \frac{\partial C_L}{\partial z} = 0; \quad \frac{\partial C_G}{\partial z} = 0 \quad (15c)$$

D_G is the gas phase axial dispersion coefficient, D_L is the liquid axial dispersion coefficient, H is Henry's law constant for the gas tracer, $K_L a$ is the overall volumetric gas-liquid mass transfer coefficient based on the volume of gas in the reactor, U_G is the inlet superficial gas velocity, and ϵ_G and ϵ_L are the gas and liquid (slurry) holdups, respectively. The function $\delta_i(t)$ describes the pulse of tracer injected and has an area under the curve of unity. For a perfect impulse injection $\delta_i(t) = \delta(t)$ where $\delta(t)$ is the Dirac delta function.

It should be noted that Henry's constant in this study is defined as

$$H = \left(\frac{C_G}{C_L} \right)_{eq} \quad (16)$$

and represents the ratio of the argon molar concentration in the gas and liquid phases when the two phases are in equilibrium. Thus H , as defined in this report, is dimensionless. This can be readily related to the more customary expression

$$H' = \left(\frac{p_G}{C_L} \right)_{eq} \quad (17)$$

by using an equation of state to relate the partial pressure of the tracer gas, p_G , to its gas phase concentration C_G . If C_L is measured in (mol/m^3) and p_G in atmospheres, the units for H' are ($\text{atm m}^3/\text{mol}$).

The overall liquid volumetric mass transfer coefficient is defined by

$$\frac{1}{K_L a} = \frac{1}{k_L a} + \frac{1}{H' k_G a} \quad (18)$$

where k_L (m/s) is the liquid side mass transfer coefficient, while k_G ($\text{mol}/\text{m}^2 \text{ s atm}$) is the gas side mass transfer coefficient. For slightly soluble gases the second term in Equation 18 can be ignored, and liquid side resistance is dominant. The interfacial area, a , as used in the present model, is the gas-liquid area per unit volume of the gas.

We have constrained ourselves here to examining the ADM with constant holdup and constant gas superficial velocities as this has been traditionally used for assessment of reactor performance. We wanted to determine whether such a model can provide a consistent set of reactor parameters when fitted to observed tracer responses.

The model was solved numerically using NAG subroutines for solving the system of partial differential equations. Basically, if one assumes that D_L is known from liquid phase experiments, there are five model parameters, D_G , ϵ_G , H , $K_L a$ and U_G . Three additional parameters are available from independent measurements or calculation: ϵ_G is known from DP (and NDG) measurements, and H can be evaluated from thermodynamics. The superficial velocity at the inlet and outlet is known. In this report, six different parameter estimation trials were conducted in order to estimate the parameters of the model. The details and reasons for this will be discussed in the next section.

Impulse response measurements were performed for the Argon-41 tracer injected into the vapor phase. The tracer was injected as a pulse into the inlet gas line upstream of the sparger. A detector was placed approximately 10 cm (which is close) from the injection point, upstream of the reactor, to monitor the nature of the input pulse. Thus, the detected pulse did not necessarily describe the true shape of the input at the inlet of the reactor since it was detected prior to the inlet. However, due to lack of any better information, this was used to simulate the input pulse to the reactor for the purpose of modeling.

The observed input tracer pulse for the model can be represented well by the following Gaussian function, with adjustable variance to match it to the response of

the inlet detector:

$$\delta_i(t) = \frac{N_c}{\sqrt{2\pi D_i t}} \exp\left(-\frac{(l_i - U_G t)^2}{2D_i t}\right) \quad (19)$$

where D_i and l_i are the parameters used to match the simulated pulse with the measured response of the inlet detector, and N_c is the normalization constant. This model provides good fits to the inlet detector response, i.e., the input pulse to the reactor. (see Figure 2 for an example - run 14.7-1. Fits for other process rates are in Appendix VI.) Since the model responses and parameters were found to be sensitive to the input function used, care should be taken when simulating the input pulse for a given experiment.

As in the case of the liquid tracer data, the detector responses and the model predictions were normalized with respect to the maximum height of the response curve before the model response was fitted to data.

Figure 2: Simulation of Input Pulse to the Reactor

5 Parameter Estimation by Fitting the Model to Data

5.1 Liquid Tracer

Four liquid tracer injections were made at two axial levels for each process rate. For an injection at a given level, responses of the detectors closest (two levels on

either side) to the point of injection showed overshoots and lack of symmetry (see Figure 3, where 'CEN' refers to the center injection). Presently, the model is used to fit only the data of the detectors located at the three levels farthest away from the point of injection that do not exhibit overshoots. The results of the fitting (D_L), for all cases, are tabulated in Table 2. Typical fits to the experimental data are shown in Figure 4 for run 14.7 - N2 center injection. The actual starting time for each experiment (injection) was different from (later than) the zero time of measurement for the detector counts. This was reflected in the offset in the time axis of the tracer response curves shown. The actual injection times were known from the response of the detectors at the point of injection. In the model the time is counted from the injection time. All figures, however, show a brief history prior to injection. The graphs for all the remaining experiments are shown in Appendix III.

Figure 3: Impulse Response Measurements for N2 CEN Injection

5.1.1 Discussion

The fits of the model to experimental responses are, in general, good. The following observations can be made, regarding the values of D_L obtained:

- Level of injection - N1 and N2 :

The values of D_L obtained from the top injection, i.e., injection nozzle N1, are different from those obtained by fitting the tracer data from the bottom injection, nozzle N2. This suggests the nonsymmetric axial distribution of the tracer about its point of injection, contrary to the nature of the ADM.

Figure 4: Liquid Impulse Response Measurements for Run 14.7, N2-CEN Injection, Injection Time: 7.8 s

- Point of injection - Wall and Center:

There are differences in D_L obtained for a given process rate, from a wall injection and a center injection response. For example, considering the injection at nozzle N1; N1 - wall yields higher dispersion coefficients than N1 - center. This occurs because the tracer injected at the wall is carried down sooner by the downflowing liquid at the wall, while for the center injection of the tracer, the liquid tracer is transported down predominantly by the turbulent motion, and its arrival by convection is retarded as it first has to reach the top of the reactor. When the tracer arrives earlier, the apparent dispersion coefficient is larger. Similarly for the injection at nozzle N2, which is at the bottom of the reactor, D_L obtained from the center injection response is higher since the tracer is carried up to the detector faster by upward convection of the liquid in the core region of the column.

The effects discussed are most prominent for the lowest superficial gas velocity, i.e., run 14.7, and are found to decrease with increasing gas velocity. This is to be expected as turbulent mixing starts to dominate convective effects at high gas velocity.

In order to quantitatively assess the differences in the various D_L values obtained for a given process rate, a statistical analysis is carried out using the ANalysis Of VAriances (ANOVA). Details of the analysis are presented in Appendix IV. The D_L values from a particular injection response are considered to belong to a group or treatment. The differences in the D_L 's from within the treatment (the values obtained at different detector levels) are considered to arise due to random error within the treatment. For each run there are four such treatments due to the measurements from four injection points (top - center and wall, and bottom - center and wall). The purpose of the analysis is to determine if there are any significant differences in the averages of the different treatments. This is done by comparing the variances in the treatment means with the variance within each treatment. The results of this analysis (Appendix IV, Table A.4.1) suggest that for runs 14.6 and 14.7 the four treatment means (three for run 14.6) are significantly different so that they belong to different classes, whereas for run 14.8 they all belong to the same category. The results from ANOVA thus confirm our earlier assertion that the differences in the D_L obtained from the top and bottom injection and the center and side injections are real. This means that the liquid flow and mixing phenomena cannot be captured adequately by the axial dispersion model (ADM), except perhaps at the highest gas velocity. The results for the mean $\overline{D_L}$ for all treatments in each run are reported in Table 3, along

Table 2: Parameters for Liquid Phase Tracer Experiments

Run No.	U_G cm/s	P MPa	Gas Holdup	Injection	Det. Lev.	D_L cm^2/s
14.6	25.3	5.2	0.39	N1 - CEN	1	2879
					2	2751
					3	2717
				N1 - WAL	1	3563
					2	5433
					3	5776
				N2 - CEN	5	7081
					6	4313
					7	4696
				N2 - WAL	5	not
					6	avai-
					7	lable
14.7	14.3	5.2	0.33	N1 - CEN	1	1828
					2	2045
					3	1962
				N1 - WAL	1	2466
					2	3183
					3	3377
				N2 - CEN	5	4171
					6	2831
					7	3051
				N2 - WAL	5	2911
					6	2465
					7	2270
14.8	36.0	3.6	0.37	N1 - CEN	1	4432
					2	5117
					3	4742
				N1 - WAL	1	4924
					2	5331
					3	5403
				N2 - CEN	5	5501
					6	5163
					7	5925
				N2 - WAL	5	4741
					6	4441
					7	5991

with the standard deviations $\overline{\sigma_L}$ ¹.

In order to study the effect of superficial gas velocity on the dispersion coefficient, and assess whether any statistically significant variation exists, given that the values vary so widely in a given run, a similar analysis (ANOVA) is performed. In this case, the D_L from all injection responses of a given run were considered to belong to a single group or treatment. The results in Table A.4.2 of Appendix IV suggest that the three treatments (runs 14.6, 147 and 14.8) have different means and therefore fall into different categories. The overall mean $\overline{D_L}$ and standard deviations are also reported in Table 3. This demonstrates that there is a distinct increase in the mean liquid dispersion coefficient, D_L , with superficial gas velocity. However, it is clear that the error, or standard deviations, are relatively high, indicating a wide spread in the model parameter D_L . We ascribe this to the inability of the ADM to describe accurately the measured tracer response.

In general, the overall magnitudes of the liquid phase axial dispersion coefficients suggest a reasonable degree of liquid (slurry) mixing in the column under the existing process rates. The characteristic liquid mixing time based on the entire dispersion height L is in the range L^2/D_L : 350 - 650 seconds. The effect of this extent of mixing on reactor performance naturally depends on the characteristic reaction time and level of conversion.

The liquid dispersion coefficients obtained in this study were compared with correlations from the literature (Kato et al., 1972; Baird and Rice, 1975; Deckwer et al., 1974). The correlations are listed in Table 4. These are the few correlations that apply for the column diameters and superficial gas velocities of interest to us. The liquid dispersion coefficients predicted by these correlations are in the range D_L : 1300 (U_G 14 cm/s) to 2000 (U_G 36 cm/s) cm^2/s . All the above correlations were obtained at atmospheric pressure. Therefore a direct comparison cannot be made with the present experimental results, which were performed at elevated pressures. Clearly the correlations based on atmospheric pressure data underpredict the observed liquid axial dispersion coefficients at all gas velocities.

There is evidence that gas holdup in a bubble column increases at higher pressure due to an increase in the number of small bubbles. The increase in gas density with pressure affects bubble formation sizes, and bubble coalescence and breakup rates, all of which lead to smaller bubble sizes (Wilkinson, 1991). This, in effect, delays transition from bubbly flow to churn - turbulent flow (Krishna et al., 1991). At

¹ $\sigma = \sqrt{\sum(y - \bar{y})^2/(n - 1)}$

Table 3: Results of ANOVA - Average D_L and Standard Deviations

Run	Injection	$\overline{D_L}$ cm^2/s	$\overline{\sigma_L^2}$ cm^2/s	$\overline{\overline{D_L}}$ cm^2/s	$\overline{\overline{\sigma_L}}$ cm^2/s
14.6	N1 - CEN	2782	85	4355	1532
	N1 - WAL	4924	1191		
	N2 - CEN	5300	1499		
14.7	N1 - CEN	1945	109	2713	678
	N1 - WAL	3008	479		
	N2 - CEN	3351	718		
	N2 - WAL	2550	328		
14.8	N1 - CEN	4764	343	5143	516
	N1 - WAL	5219	258		
	N2 - CEN	5529	381		
	N2 - WAL	5057	822		

sufficiently high gas velocities, as in the runs studied in this report, a bubble column operating under high pressure (3-5 MPa) is already in the churn turbulent regime, and the presence of a bimodal bubble size distribution with large and small bubbles is usually seen (Krishna, 1994). It has been reported by Krishna et al. (1991) that beyond transition, in the churn turbulent regime, the gas holdup due to small bubbles is independent of gas velocity. It is the holdup of the large bubbles that increases with increase in gas velocity. However, the effect of pressure, and thereby gas density, on the holdup of these large bubbles in the churn turbulent regime is negligible. As a result, at high pressures and high gas velocities, the overall gas holdup is higher than in a reactor operating at atmospheric pressure and the same gas velocity due to the excess of small bubbles in the system caused by delayed transition, while the holdup of large bubbles is comparable to the holdup of large bubbles for similar gas velocities at atmospheric pressure (Krishna et al., 1994). There is, hence, an additional interaction between the gas and liquid at high pressure. The axial dispersion coefficient is due to liquid recirculation and turbulent (radial and axial) mixing. Therefore, the liquid dispersion coefficient is expected to increase with pressure at such high gas velocities.

Table 4: Correlations for Liquid Dispersion Coefficient in Bubble Columns

Investigator	Equation (in SI)	Range of Variables
Kato and Nishiwaki (gas-liquid-solid)	$D_L = \frac{U_G D_c}{\frac{13Fr^{0.5}}{1+8Fr^{0.425}}}$ $Fr = \frac{U_G^2}{g D_c}$	$0.066 \leq D_c \leq 0.214 \text{ m}$ $0.02 \leq U_G \leq 0.3 \text{ m/s}$
Baird and Rice (gas - liquid)	$D_L = 0.35 D_C^{4/3} (g U_G)^{1/3}$	$0.003 \leq U_G \leq 0.45 \text{ m/s}$ $0.082 \leq D_C \leq 1.53 \text{ m}$
Deckwer et al. (gas - liquid)	$D_L = 0.678 D_C^{1.4} U_G^{0.3}$	—

The relatively low increase in D_L from U_G of 25 cm/s (Run 14.6 at 5.3MPa) to U_G of 36 cm/s (Run 14.8 at 3.6 MPa) may be accounted for by the decrease in pressure between the two runs, which to some extent masks the effect of U_G on the D_L obtained by fitting the tracer curve.

5.1.2 Conclusions and Future Work

The ADM, which has presently been fitted only to the tracer data that do not exhibit overshoots, appears to provide satisfactory fits. However, there is a large variation in the axial dispersion coefficient obtained at different detector levels, which is seen in standard deviations reported in Table 3. Our analysis clearly established the asymmetry of the actual response, contrary to the ADM predictions, and the effect of injection point on the calculated liquid axial dispersion coefficient. All this indicates that while ADM may match a particular response well, it does not represent liquid mixing well.

Figure 5: (a) Experimental Detector Responses for Wall Injection at N 1 (Run 14.7)

Figure 5: (b) Model Calculated Responses at Detector Levels (similar to experiment), for Qualitative Comparison with Fig 5(a) (time scale is arbitrary)

To match the data better, a phenomenological model that captures the essence of the fluid dynamic behavior of the system should be used. The Recycle with Cross Flow and Dispersion Model (RCFDM) recently suggested by us (Degaleesan et al., 1996) provides an attractive alternative in the description of liquid mixing. Preliminary analysis indicates that such a model, with a consistent set of parameters, is able to capture qualitatively all the features of the experimentally observed tracer responses at various detector levels. Figure 5 exhibits the actual tracer responses and simulations based on the RCFDM. The similarities between model and experiments are evident, as well as the ability of the RCFDM for predicting a variety of responses at different column locations. Quantitative evaluation of parameters based on the RCFDM is part of the future planned work.

5.2 Gas Tracer

Two experiments were carried out at each process rate, with the gas tracer being injected at the inlet of the reactor. The axial dispersion model is used to fit the data measured at all detector levels. Six types of parameter estimations were conducted with different sets of floating parameters. For all cases, the liquid phase dispersion coefficient was fixed to the value obtained from the liquid tracer experiments. The value of D_L used for each process rate was that obtained for the bottom center injection (N2 - center) with the response measurement made at detector level 7. It was found that moderate changes in D_L do not affect the results of the model fits to data and the model parameters for the gas tracer experiments significantly.

The ADM that describes the spatial and temporal history of an injected soluble tracer is given by Equations 13, 14 and 15. The two coupled partial differential equations have to be solved for the gas concentration, C_G , and liquid concentration, C_L . The temporal history at a given position z , of the combined response presented by Equation 7 has to be matched to the average detector response at the same axial location.

Parameter estimation is again accomplished by minimizing the sum of the square of errors

$$\min_{\underline{P}} \sum_{i=1}^{N_p} \left(\frac{R(t_i, z)}{R_{max}} - \frac{C_t(t_i, z)}{C_{tmax}} \right)^2 \quad (20)$$

where $R(t_i, z)$ is the average detector response at location z at time t_i , R_{max} is the maximum detector response at z . $C_t(t_i, z)$ is the total argon concentration defined by

Equation 7, evaluated at the axial position z and time t_i , and C_{imax} is its maximum value at z . $\underline{P}$ is the vector of parameters that is used to minimize the sum of square errors, and N_p is the number of data (sample) points, which is approximately 1000.

The model contains seven parameters, D_L , D_G , ϵ_G , ϵ_L , H , K_{La} and U_G . Due to our consideration of the slurry as pseudohomogeneous, $\epsilon_L = 1 - \epsilon_G$ so that the number of free parameters is reduced to six. As already mentioned we take the liquid dispersion coefficient to be given by the liquid phase tracer experiments. The five parameters D_G , ϵ_G , H , K_{La} and U_G have to be determined either by fitting the tracer data, or, from independent observations or calculations. Thermodynamics can provide us with an estimate for the Henry's constant, H . Holdup measurements can be used for estimation of the average holdup, ϵ_G . Superficial gas velocity at the entrance and exit is known. With the exception of the gas superficial velocity, which is known to drop by 18% from the inlet value, and the Henry's constant H , which can be calculated reasonably accurately, none of the other parameters can be assessed 'a priori' with certainty. We examined the ability of the model to match the observed tracer responses based on several approaches using a different number of floating parameters as shown in Table 5.

The following is a comparison of the results obtained by each of the approaches represented as Case 1 - Case 6 in Table 5 and provides the rationale for each approach.

5.2.1 Case 1: Model with Three Floating Parameters, D_G , H and K_{La}

In this case, ϵ_G (from DP measurements) is used as input to the model, by considering the axial average holdup up to the measurement level ($\overline{\epsilon_{G,z}} = \int_0^L \epsilon_G dz / L$). This average at each level, z , is found to vary only slightly from the overall average holdup reported in Table 1. Results for the model parameters obtained by fitting the model to the various experimental runs and detector levels are provided in Table 6. Figure 6 shows the results of fitting the model responses to the experimental measurements at all the detector levels for run 14.8-1. As in the case of liquid measurements, the fits of the model to the experimental data are in general very good. The fits for the remaining experiments are shown in Appendix VI. In all the figures, there is an offset in the time axis, which is due to the differences in the zero time of recording the measurement (detectors) and the starting time of the tracer experiment. This is properly accounted for in the model.

Table 5: Different Attempts of Matching Model Predictions and Data at Various Detector Levels

Case No.	Fixed Parameters	Floating Parameters	Interpretation of Detector Response
1	$U_G = U_{G,in}$ $D_L = D_L(\text{liquid})$ $\epsilon_G = \overline{\epsilon_{G,z}}$ (DP)	$D_G, K_L a, H$	Eqn 7
2a	$U_G = U_{G,in}$ $D_L = D_L(\text{liquid})$ $\epsilon_G = \overline{\epsilon_{G,z}}$ (DP) $H = H(\text{thermo})$	$D_G, K_L a$	Eqn 7
2b	$U_G = U_{G,in}$ $D_L = D_L(\text{liquid})$ $\epsilon_G = \overline{\epsilon_{G,z}}$ (NDG) $H = H(\text{thermo})$	$D_G, K_L a$	Eqn 7
3	$U_G = U_{G,in}$ $D_L = D_L(\text{liquid})$ $H = H(\text{thermo})$	$D_G, K_L a, \epsilon_G$	Eqn 7
4	$U_G = U_{G,in}$ $D_L = D_L(\text{liquid})$ $\epsilon_G = \overline{\epsilon_{G,z}}$ (DP)	$D_G, K_L a, \alpha$	$\alpha\epsilon_G C_G + \epsilon_L C_L$
5	$U_G = \overline{U_{G,z}}$ $D_L = D_L(\text{liquid})$ $\epsilon_G = \overline{\epsilon_{G,z}}$ (DP) $H = H(\text{thermo})$	$D_G, K_L a$	Eqn 7
6	$D_L = D_L(\text{liquid})$ $\epsilon_G = \overline{\epsilon_{G,z}}$ (DP) $H = H(\text{thermo})$	$D_G, K_L a, U_G$	Eqn 7

Table 6: Case 1: Parameters for Gas Phase Tracer Experiments

Run No.	U_G cm/s	Gas Holdup	D_L cm^2/s	Det. Lev.	Model Parameters		
					D_G cm^2/s	H	$K_L a$ s^{-1}
14.6-1	25.3	0.39	4696	1	9800	10.0	0.10
		0.39		2	6839	4.41	2.95
		0.38		3	7864	5.82	1.80
		0.37		4	5412	4.47	0.58
		0.38		5	7131	5.33	1.12
		0.39		6	5729	3.87	0.66
		0.40		7	6204	3.32	1.19
14.6-2		0.39		1	9396	10.0	0.10
		0.39		2	4446	4.28	1.16
		0.38		3	6229	5.82	2.50
		0.37		4	3337	3.70	0.56
		0.38		5	5455	4.65	0.79
		0.39		6	4649	3.78	0.49
		0.40		7	4356	3.41	0.65
14.7-3	14.3	0.34	3052	1	6987	10.0	0.10
		0.33		2	4219	4.35	1.69
		0.32		3	4663	5.11	1.58
		0.32		4	3402	4.75	0.43
		0.32		5	2466	3.76	0.56
		0.33		6	1681	3.98	0.56
		0.33		7	1816	3.17	0.63
14.7-4		0.34		1	6274	10.0	0.10
		0.33		2	3048	5.30	0.32
		0.32		3	4313	6.89	3.45
		0.32		4	2379	4.42	0.31
		0.32		5	1903	3.81	0.41
		0.33		6	1861	3.31	0.46
		0.33		7	1865	3.14	0.47
14.8-5	36.0	0.38	5925	1	9800	10.0	0.30
		0.37		2	5229	3.82	2.73
		0.37		3	6567	4.70	1.66
		0.37		4	4253	3.41	0.51
		0.37		5	4771	3.42	0.65
		0.38		6	4059	3.19	0.61
		0.38		7	3546	3.11	0.59
14.8-6		0.38		1	9800	10.0	0.20
		0.37		2	8531	6.80	2.47
		0.37		3	6505	6.85	3.01
		0.37		4	5070	3.61	0.36
		0.37		5	3793	3.41	0.51
		0.38		6	3106	3.21	0.54
		0.38		7	3985	3.00	0.60

Figure 6: Gas Phase Impulse Response for Case 1, Run 14.8-5, Injection Time 24.6s

Figure 6 (contd.): Gas Phase Impulse Response for Case 1, Run 14.8-5, Injection Time 24.6s

Discussion

For pipe flows, the ADM is known to apply when the radial dispersion is significant enough to overcome the effects of convection. This criterion is expressed as $L/D_C \gg 0.08 Pe_r$, where Pe_r is the radial dispersion Peclet number based on the radius of the tube. When applied to gas flow in bubble columns, $Pe_r = U_G R_c / \epsilon_G D_{rr}$, where D_{rr} is the radial turbulent diffusivity for the gas phase. This requires an independent evaluation of D_{rr} . Experimental measurements of D'_{rr} , the radial turbulent eddy diffusivity for the liquid are available using the CARPT (Computer Automated Radioactive Particle Tracking) technique in our laboratory, in smaller size columns (Degaleesan and Duduković, 1995). When extrapolated to larger diameter columns and higher superficial gas velocities (as in the present study), this yields estimated values of D_{rr} ($D_{rr} = D'_{rr}$) in the range 100 - 150 cm^2/s based on the assumption that liquid and gas radial diffusivities are equal. This yields estimates of Pe_r in the range of 10 to 15, and indicates that the above criterion is well established for all higher detector levels. Even for the lowest detector (DET 1 in Figure 1), $L/D_c = 3.3$ is larger than $0.08 Pe_r$, but not sufficiently large to fully justify the use of the ADM.

Using the gas phase axial dispersion coefficients obtained from parameter estimation calculations reported in Table 6, the dispersion Peclet numbers were calculated. For detectors at the farthest level, $Pe \sim 25$, while for the the lowermost detector level, $Pe \sim 1$. Such a range of Peclet numbers suggests that the ADM is more suited at the highest detector levels, where the flow can be considered to have small deviations from plug flow. It is the least suited at the lowermost levels. This may explain why the values of the parameters are quite consistent for the upper three to four levels of detectors, while for the lower levels, although the fits are good, there is a definite variation in parameter values. The parameters at the lowermost level ($L/D = 3.3$) were found to be very different from the other values.

A parametric sensitivity analysis was performed to study the sensitivity of the model to the various floating parameters. This analysis is performed by fixing two parameters at their fitted values and varying the third. The parameters were varied from -30% to +30% of their fitted values. Results for Run 14.8 - 1 at detector level 5 are shown in Figure 7. It is seen that the model is most sensitive to the Henry's constant H when compared with D_G and $K_L a$, and least sensitive to $K_L a$.

Figure 7: Results for Parametric Sensitivity Analysis for Run 14.8 - 5, Level 5

The mass transfer coefficients and Henry's law constants obtained from the above described parameter estimation (Table 6) are almost constant for all gas velocities at all the highest detector levels. Evaluation of the Henry's law constant from thermodynamic calculations yields values of 5.9 at 52 MPa, 250°C (run 14.6 and 14.7) and 8.1 at 36 MPa, 250°C (run 14.8). The details of this calculation are shown in Appendix V. These values are much higher than the model fitted values shown in Table 6. Thus, the results obtained are suspect in spite of the excellent fits to the data. The constant "drift" of H with detector position indicates problems in reconciling the model with the data. Examination of Table 6 at each gas flowrate clearly indicates a trend in H and K_La with detector position. For most of the runs there is also a trend in D_G .

Repeated runs at identical conditions yielded variation in parameters. As with the liquid experiments, the results for all the three parameters are analyzed using ANOVA. It was found that there is good repeatability for K_La and H for all the three runs (Table A.4.3). For D_G the repeatability for Runs 14.7 and 14.8 are good, but Run 14.6 is not satisfactory. The analysis shows that the mean D_G from Runs 14.6-1 and 14.6-2 belongs to two different groups. This can be observed from Table 6, in which the dispersion coefficients for Run 14.6-1 are generally higher than those for 14.6-2. In order to analyze the effect of superficial gas velocity on each of the

parameters, the data from the two runs at each process rate is considered to belong to a group (same as for the liquid runs), and an ANOVA was performed for each parameter. The results in Table A.4.3 indicate that D_G varies with U_G . However, no dependence of $K_L a$ and H on superficial gas velocity is seen.

5.2.2 Case 2: Model with Two Floating Parameters: D_G , $K_L a$

Since the value of the Henry's constant, H , can be reliably obtained from thermodynamics, by fixing ϵ_G (from DP measurements) and H as model inputs, the model was fitted to the experimental data to estimate the remaining two unknown parameters, D_G and $K_L a$. The parameters obtained by the fitting procedure are reported in Table 7.

Figure 8 (Appendix VI contains the figures for all the remaining runs) shows the model fit to the experimental results for Run 14.6-1 at all the detector levels. Clearly the fit of the model to the experimental data is the poorest at the detector level farthest from the point of injection, that is, close to the liquid-free surface, and gradually improves as one approaches the lower levels. Similar trends are seen for the other experimental runs as well. This behavior is counter intuitive, since it is expected that the farther the point of measurement is from the point of injection, the more applicable the axial dispersion model is.

If the gas holdup values for the upper levels are increased as input model parameters, the fits are considerably improved. A possible explanation for this behavior was sought as follows. When ϵ_G is taken to be erroneously low (ϵ'_G) for the case of the dispersion model, this implies that the front moves at a faster velocity (U_G/ϵ'_G) than it should. Using the three-parameter model of Case 1, there is more freedom for the model to predict a response similar to the experimental measurements. As shown earlier, the model is particularly sensitive to H . In Case 1, when the model predicts the pulse moving at a faster value of U_G/ϵ'_G than it should, H is made lower such that more tracer is in the liquid phase, which is in batch mode and has a high degree of mixing. Thus, the model is then capable of matching a broader spread in the tracer distribution with a larger mean residence time, as indicated by the experiment. However, when H is fixed (as is the situation in the present Case 2), the model loses this degree of freedom, and therefore the fits are not good.

Table 7: Case 2a: Parameters with Fixed H for Gas Phase Tracer Experiments

Run No.	U_G cm/s	Gas Holdup	D_L cm^2/s	Det. Lev.	H	Parameters	
						D_G cm^2/s	$K_L a$ s^{-1}
14.6-1	25.3	0.39	4696	1	5.86	9900	0.006
		0.39		2		7641	2.87
		0.38		3		7888	1.88
		0.37		4		7312	2.58
		0.38		5		7720	1.64
		0.39		6		6850	1.23
		0.40		7		5678	0.99
14.6-2		0.39		1	5.86	9006	0.006
		0.39		2		6040	7.32
		0.38		3		6285	2.75
		0.37		4		5750	7.32
		0.38		5		6772	2.28
		0.39		6		6421	1.52
		0.40		7		4868	1.11
14.7-3	14.3	0.34	3052	1	5.86	3345	3.22
		0.33		2		3228	0.70
		0.32		3		5540	0.94
		0.32		4		3114	0.65
		0.32		5		3241	1.17
		0.33		6		2977	1.41
		0.33		7		2987	1.58
14.7-4		0.33		1	5.86	2400	3.52
		0.33		2		2473	3.40
		0.32		3		2419	2.99
		0.32		4		2385	3.45
		0.32		5		2459	1.93
		0.33		6		2552	0.65
		0.33		7		2437	1.11
14.8-5	36.0	0.38	5925	1	8.11	16828	0.032
		0.37		2		11700	8.92
		0.37		3		11848	13.87
		0.37		4		10640	4.29
		0.37		5		10700	2.64
		0.38		6		7889	1.62
		0.38		7		6859	1.95
14.8-6		0.38		1	8.11	19832	0.0032
		0.37		2		10146	0.60
		0.37		3		10373	0.50
		0.37		4		11754	7.78
		0.37		5		9960	3.32
		0.38		6		8522	2.92
		0.38		7		7167	1.70

Figure 8: Gas Phase Impulse Response for Case 2, Run 14.6-1, Injection Time 12.6s

Figure 8 (contd.): Gas Phase Impulse Response for Case 2, Run 14.6-1, Injection Time 12.6s

The increased holdup for which good fits are obtained, even in Case 2, are slightly higher than those reported by DP, but are similar to the NDG measurements. Based on the DP measurements, the gas holdup starts increasing from detector level 4, which is expected to be due to foaming. When the system is foaming, the radial holdup distribution tends to become more uniform, in which case the average holdup obtained from the NDG measurements becomes more reliable. When the following radial gas holdup profile is used (Kumar et al., 1994)

$$\epsilon_G(\xi) = \tilde{\epsilon}_G \frac{m+2}{m} (1 - c\xi^m) \quad (21)$$

with the exponent $m \geq 10$, the average holdup from NDG measurements becomes quite accurate. This is illustrated in Figure A.1.2 in Appendix I, in which a comparison is shown of the NDG-based average and a true cross-sectional average.

In order to accept the NDG measurements as a better indication of the average holdup, one would have to show that the DP measurements are inaccurate in a foaming system with solids (since there is such a large discrepancy between the holdups from the two measurements). We do not have such evidence at present. However, it is clear that better fits can be obtained for the data with fixed H values using the measurements from NDG for the average holdup estimates at the higher detector levels. The parameters estimated under such conditions are provided in Table 8. Figure 9 shows the results for Run 14.6-1 (compare with Figure 8 (e) - (f)). Hence, based on the premise that NDG-based holdup measurements in the foaming region are more accurate than their DP counterpart, reasonable fits are obtained. However, there is no independent experimental verification for the existence of the flat radial holdup profiles in the upper part of the reactor. Therefore, the above approach cannot be completely justified at present.

The above analysis shows that the model is very sensitive to H as well as ϵ_G . It is unable to match the tracer data well when only two unknown parameters are assigned if one or both of the chosen parameters may be in error.

Table 8: Case 2b: Parameters with Fixed H for Gas Phase Tracer Experiments with NDG Measurements for Gas Holdup at Upper Detector Levels

Run No.	U_G cm/s	Gas Holdup	D_L cm ² /s	Det. Lev.	H	Parameters	
						D_G cm ² /s	$K_L a$ s ⁻¹
14.6-1	25.3	0.42	4696	5	5.86	6059	0.35
		0.45		6		5950	0.33
		0.50		7		5504	0.13
14.6-2		0.42		5	5.86	5805	0.71
		0.45		6		5755	0.47
		0.50		7		4825	0.15
14.7-3	14.3	0.37	3052	5	5.86	2416	0.22
		0.39		6		2472	0.21
		0.41		7		1916	0.14
14.7-4		0.37		5	5.86	2403	0.21
		0.39		6		2399	0.17
		0.41		7		2306	0.23
14.8-5	36.0	0.41	5925	5	8.11	9621	2.63
		0.44		6		8325	1.54
		0.46		7		6720	0.832
14.8-6		0.41		5	8.11	9088	3.32
		0.44		6		7710	1.85
		0.46		7		6970	0.84

Figure 9: Gas Phase Impulse Response for Run 14.6-1, Injection Time 12.6s

5.2.3 Case 3: Model with Three Floating Parameters: ϵ_G , D_G and K_La

In order to find out what the model predicts as average gas holdup, the data are fitted with the other choice of three parameters by floating ϵ_G , D_G and K_La , and fixing H at its thermodynamic value. As one would expect the fits are very good. The values for the obtained parameters are shown in Table 9. The estimated values of ϵ_G are higher than those measured by DP. The discrepancy is larger in the upper part of the column than at the lower level, but exists for the lower portions of the column as well. For some cases in runs 14.7 and 14.8, the estimated holdup values are larger than both DP and NDG measured values! Therefore, little can be said about the D_G and K_La values from this case of parameter estimation, unless we can independently confirm a pronounced axial solids concentration profile which would have affected the measured gas holdup profiles.

5.2.4 Case 4: Model with Three Floating Parameters: D_G , K_La and α

In the analysis done so far for the gas phase tracer experiments, the tracer concentration $C_t(t, z)$ was assumed to be given by Equation 7. This relationship holds if one assumes no cross-sectional variation of tracer and gas holdup (as considered by the one-dimensional model). However, in reality there is a radial variation of the gas holdup profile (Hills, 1971; Kumar et al., 1994). This affects the measurement of the total argon tracer concentration because the detector gets its major source of radiation from the tracer close to the wall. If the phase holdups and concentrations C_G and C_L are uniform through out the cross section, then the total concentration of tracer is the average of the gas and liquid phase concentrations, weighted by the respective holdups. If, however, the distribution of phases is not cross-sectionally uniform, but has more liquid at the wall, as is the actual case, then the average should not be weighted by the phase holdups, but must also account for the relatively higher contribution of the liquid, due to higher volume fraction of the liquid at the wall. In other words $C'_t(t, z) = \alpha\epsilon_g C_G + \epsilon_L C_L$ where $\alpha \leq 1.0$.

It is not possible to know what α is without modeling the radiation received by the detector for a given spatial distribution of the phases and tracer concentration. This in itself is a rigorous and time-consuming procedure. For a preliminary assessment of the effect of an uneven cross-sectional distribution, the model fitting is performed using α as the third floating parameter, instead of ϵ_G or H .

Table 9: Case 3: Parameters for Gas Phase Tracer Experiments with Fixed H

Run No.	U_G cm/s	H	D_L cm ² /s	Det. Lev.	Model Parameters		
					D_G cm ² /s	ϵ_G	$K_L a$ s ⁻¹
14.6-1	25.3	5.86	4696	1	20000	0.20	3.158
				2	6790	0.43	2.495
				3	7879	0.39	1.855
				4	5725	0.43	0.36
				5	7473	0.41	1.45
				6	6256	0.45	0.44
				7	6364	0.49	0.67
14.6-2				1	15000	0.24	4.04
				2	5213	0.46	1.32
				3	6361	0.41	2.19
				4	4317	0.48	0.22
				5	5937	0.43	0.77
				6	5574	0.47	0.33
				7	5246	0.49	0.43
14.7-3	14.3	5.86	3052	1	7340	0.34	0.006
				2	4094	0.39	1.39
				3	4533	0.36	1.58
				4	3628	0.38	0.35
				5	2970	0.42	0.32
				6	2462	0.45	0.16
				7	2426	0.45	0.23
14.7-4				1	5929	0.35	0.006
				2	3329	0.38	0.28
				3	4170	0.34	0.42
				4	2954	0.40	0.16
				5	2553	0.42	0.18
				6	3111	0.44	0.13
				7	2606	0.46	0.14
14.8-5	36.0	8.11	5925	1	20000	0.20	1.80
				2	7235	0.46	0.20
				3	7963	0.43	0.29
				4	7425	0.49	0.10
				5	7320	0.49	0.17
				6	7135	0.51	0.10
				7	6689	0.52	0.08
14.8-6				1	20000	0.22	1.58
				2	9442	0.39	0.28
				3	9800	0.38	0.34
				4	8518	0.46	0.09
				5	7027	0.49	0.12
				6	6580	0.51	0.09
				7	7079	0.54	0.15

Table 10: Case 4: Parameters for Gas Phase Tracer Experiments

Run No.	U_G cm/s	Gas Holdup	D_L cm ² /s	Det. Lev.	Model Parameters		
					D_G cm ² /s	$K_L a$ s ⁻¹	α
14.6-1	25.3	0.39	4696	1	9800	0.08	1.0
		0.39		2	7153	2.28	0.198
		0.38		3	7580	2.62	1.00
		0.37		4	5458	0.40	0.22
		0.38		5	7409	0.82	0.17
		0.39		6	6607	0.34	0.07
		0.40		7	6795	0.25	0.00
14.6-2		0.39		1	9800	0.44	1.00
		0.39		2	4854	0.74	0.23
		0.38		3	6428	2.32	0.29
		0.37		4	3763	0.37	0.10
		0.38		5	5863	0.54	0.11
		0.39		6	5729	0.29	0.07
		0.40		7	5544	0.23	0.00
14.7-3	14.3	0.34	3052	1	4949	0.64	1.00
		0.33		2	4678	0.78	0.15
		0.32		3	5026	0.99	0.16
		0.32		4	3697	0.35	0.15
		0.33		5	3216	0.30	0.00
		0.34		6	2467	0.16	0.00
		0.35		7	2274	0.12	0.00
14.7-4		0.34		1	4283	0.51	1.00
		0.33		2	3113	0.29	0.30
		0.32		3	4143	0.40	0.38
		0.32		4	2571	0.26	0.15
		0.33		5	2343	0.29	0.04
		0.34		6	2661	0.16	0.00
		0.35		7	2499	0.12	0.00
14.8-5	36.0	0.38	5925	1	17470	0.14	1.00
		0.37		2	6007	0.43	0.20
		0.37		3	7216	0.44	0.25
		0.37		4	5135	0.28	0.12
		0.37		5	6025	0.30	0.06
		0.38		6	5671	0.24	0.04
		0.38		7	5863	0.22	0.02
14.8-6		0.38		1	18973	0.11	1.0
		0.37		2	8893	0.37	0.38
		0.37		3	9740	0.38	0.42
		0.37		4	5873	0.23	0.17
		0.37		5	4722	0.28	0.08
		0.38		6	4362	0.22	0.05
		0.38		7	7151	0.23	0.05

Again, the fits are good for all conditions. The parameters are reported in Table 10. There is a distinct trend in the values of α , which is zero at the upper detector levels, and increases with a decrease in height. Such low values of α at the higher levels suggest that the detectors at these levels see only the liquid and no gas. These results can have meaning only if this can be verified.

In order to verify the validity of the results in Case 4, the radiation detected by a detector is modeled by accounting for the cross-sectional variation of gas holdup in the column. Details of this calculation are shown in Appendix II. Once an estimate of C_G and C_L is obtained from the model, it is used in the radiation model to calculate the total concentration C_t .

Figure 10 shows the result of fitting the model response to the experimental data for detector level 7 of Run 14.6-1. The fit is similar to the case shown in Figure 8g, for the case of two-parameter fitting, using holdup estimates from DP measurements. This implies that the total tracer concentration C_t resulting from the radiation calculation is approximately the same as defined by Equation 7. The results of Case 4, with $\alpha \sim 0$, are therefore not valid. The reason for this is that the concentration of tracer in the liquid phase is so low that the influence of high liquid holdup at the wall is offset by the low liquid tracer concentration (refer to Figure 11 and Figure A.2.2 in Appendix II). As seen in Figure A.2.2, the contribution of radiation at these low concentrations of liquid tends to become more uniform across the cross-section, and hence, the effect of the assumed radial gas holdup profile on the results is not very significant. This justifies the use of Equation 7 for this specific gas tracer of low solubility.

So far we have considered a combination of D_G , $K_L a$, H , and ϵ_G as the floating parameters of the model. For Cases 1, 3 and 4, where three floating parameters are used, the fits are good, but the values of H , ϵ_G and α for the respective cases do not compare well with corresponding values from independent measurements (or methods of estimation). For Case 2, when NDG-based values for the holdup are used, the fits are reasonably good with two floating parameters - D_G and $K_L a$. As discussed earlier, the poor fits obtained when using ϵ_G from DP measurements are due to the differences in the mean residence times between the experimental data and model predicted results.

Figure 10: Gas Phase Impulse Response for Run 14.6-1 at Detector Level 7, Injection Time 14.6s (Model Uses Simulation of Incident Radiation)

Figure 11: Model Calculated Tracer Concentration in Gas and Liquid Phase (Run 14.6-1 Detector Level 7)

5.2.5 Case 5: Model with Changing Gas Flow Rate and two Floating Parameters, D_G and K_La

Due to reaction in the slurry bubble column reactor, there is a reduction in the gas volumetric flow rate. This affects the superficial gas velocity along the length of the reactor. The conversions for the runs considered in this study result in an average reduction of around - 18% in the gas flow rate. The axial dispersion model in its present form can not account for the axial variation of U_G . However, for the purpose of this analysis, the reduction in gas flow rate is considered by assuming a linear change (decrease) in U_G with axial position along the column, since the inlet and outlet gas flowrate are known from experimental data. This is just an approximation. Once the U_G at the intermediate axial positions corresponding to the detector levels are evaluated, these values, $U_{G,z}$, are used in the model to predict the tracer distribution at different axial positions, and fit the experimental data. The average value of $U_{G,z}$ at a given axial position can be used; however since the axial profile of $U_{G,z}$ is not known, the present variation in $U_{G,z}$ is considered. Thus, instead of using the inlet gas velocity, as done in Case 2, we now employ the gas velocity estimated at the detector level. The resulting parameters are reported in Table 11. Figure 12 shows the fits of the model to experimental data for Run 14.6 - 1. For this case, with only two floating parameters, the fits are much better than for Case 2 (using DP measurements for ϵ_G and inlet U_G), although they are not as perfect as for the three floating parameter cases. However, these fits are acceptable, since only two floating parameters are used.

5.2.6 Case 6: Model with three Floating Parameters, D_G , K_La and U_G

As a final case, regression is performed to fit the experimental data to the model with three floating parameters, a position-dependent superficial gas velocity, $U_{G,z}$, D_G and K_La . This is done in order to estimate the average variation of U_G with axial position z . The resulting fits are as good as the other fits with three floating parameters. The values of the obtained parameters are shown in Table 12. The values of $U_{G,z}$, in general suggest a monotonic decrease of the gas velocity with axial position, especially at the higher detector levels, as expected.

Therefore this set of parameters for D_G , K_La and U_G , along with the independent estimates of ϵ_G and H , form the most reliable set of parameters. Although three floating parameters used, the values of $U_{G,z}$ obtained are reasonable, and fall within the range of experimental values. This case is therefore the one that should be considered for analysis of the model parameters.

Table 11: Case 5: Parameters for Gas Phase Tracer Experiments (Using Variable U_G)

Run No.	U_G cm/s	Gas Holdup	D_L cm^2/s	Det. Lev.	H	Parameters	
						D_G cm^2/s	$K_L a$ s^{-1}
14.6-1	24.82	0.39	4696	1	5.86	9025	0.006
	24.29	0.39		2		5310	0.63
	24.08	0.38		3		5577	0.28
	23.15	0.37		4		4940	0.26
	22.29	0.38		5		5433	0.12
	21.9	0.39		6		4966	0.13
	21.5	0.40		7		4844	0.14
14.6-2	24.82	0.39		1	5.86	7599	0.006
	24.29	0.39		2		4908	1.56
	24.08	0.38		3		4677	0.46
	23.15	0.37		4		3937	0.57
	22.29	0.38		5		4457	0.19
	21.9	0.39		6		4604	0.14
	21.5	0.40		7		4154	0.18
14.7-3	14.0	0.34	3052	1	5.86	5000	3.52
	13.6	0.33		2		3410	0.78
	13.4	0.32		3		2583	0.42
	12.7	0.32		4		3156	0.35
	12.2	0.32		5		3017	0.40
	11.8	0.33		6		2990	0.51
	11.7	0.33		7		2100	0.28
14.7-4	14.0	0.33		1	5.86	5500	3.52
	13.6	0.33		2		3261	0.50
	13.4	0.32		3		2762	0.29
	12.7	0.32		4		2871	0.33
	12.2	0.32		5		2928	0.43
	11.8	0.33		6		2982	0.39
	11.7	0.33		7		2867	0.35
14.8-5	35.3	0.38	5925	1	8.11	13922	0.002
	34.4	0.37		2		8413	1.70
	34.0	0.37		3		7894	0.78
	32.5	0.37		4		6584	0.57
	31.0	0.37		5		6559	0.50
	30.1	0.38		6		5777	0.36
	29.6	0.38		7		5309	0.22
14.8-6	35.3	0.38		1	8.11	16533	0.002
	34.4	0.37		2		8691	0.27
	34.0	0.37		3		9119	0.25
	32.5	0.37		4		7325	0.28
	31.0	0.37		5		5792	0.40
	30.1	0.38		6		5108	0.29
	29.6	0.38		7		5765	0.30

Figure 12: Gas Phase Impulse Response for Run 14.6-1 using Position Dependent Superficial Gas Velocity, Injection Time 12.6s

Figure 12 (contd.): Gas Phase Impulse Response for Run 14.6-1 using Position Dependent Superficial Gas Velocity, Injection Time 12.6s

Table 12: Case 6: Parameters for Gas Phase Tracer Experiments

Run No.	U_G cm/s	Gas Holdup	D_L cm^2/s	Det. Lev.	Model Parameters		
					D_G cm^2/s	$K_L a$ s^{-1}	U_G cm/s
14.6-1	25.3	0.39	4696	1	9800	0.008	25.3
		0.39		2	6907	0.60	24.8
		0.38		3	6970	1.05	25.3
		0.37		4	5282	0.45	23.9
		0.38		5	6974	0.36	24.4
		0.39		6	5817	0.49	23.4
		0.40		7	5885	0.51	22.7
14.6-2		0.39		1	9800	0.001	25.3
		0.39		2	4536	0.99	24.1
		0.38		3	6239	0.63	25.0
		0.37		4	3717	0.44	22.8
		0.38		5	5500	0.23	23.8
		0.39		6	5173	0.42	23.2
		0.40		7	4798	0.53	22.6
14.7-3	14.3	0.34	3052	1	4345	0.23	14.3
		0.33		2	3104	0.36	13.3
		0.32		3	4082	0.44	13.9
		0.32		4	3449	0.43	13.2
		0.33		5	2714	0.47	12.4
		0.34		6	2133	0.33	12.1
		0.35		7	2157	0.43	12.0
14.7-4		0.34		1	3627	0.18	14.3
		0.33		2	3104	0.36	13.3
		0.32		3	4081	0.44	13.9
		0.32		4	2647	0.29	12.8
		0.33		5	2230	0.34	12.4
		0.34		6	2286	0.34	12.1
		0.35		7	2288	0.31	11.9
14.8-5	36.0	0.38	5925	1	16150	0.003	36.0
		0.37		2	6250	0.51	32.7
		0.37		3	7205	0.54	33.3
		0.37		4	6127	0.21	30.9
		0.37		5	6226	0.45	30.6
		0.38		6	5722	0.33	30.0
		0.38		7	5348	0.30	29.9
14.8-6		0.38		1	19247	0.002	36.0
		0.37		2	9044	0.37	34.9
		0.37		3	9660	0.50	35.0
		0.37		4	7281	0.15	31.3
		0.37		5	5636	0.32	30.6
		0.38		6	5092	0.28	30.0
		0.38		7	5868	0.35	29.9

5.2.7 Discussion of Results

The parameters that truly need to be estimated from this model, are the gas phase dispersion coefficient D_G and the gas-liquid mass transfer coefficient K_La . For the sake of analysis of these model parameters, and to study their dependence on superficial gas velocity, the means and standard deviations of D_G and K_La at each process rate are calculated and reported in Tables 13 and 14 for all the cases that have been considered in this study. The averages are calculated for both trials of each run, excluding the parameters obtained by fitting the response of the lowest detector.

Table 13: Average D_G at each Process Rate for the Various Cases Studied

Case No.	Run	D_G cm^2/s	σ_G cm^2/s
1	14.6	5637	1305
	14.7	2801	1010
	14.8	4951	1504
2a	14.6	6601	835
	14.7	2984	873
	14.8	9795	1770
2b	14.6	5650	446
	14.7	2330	204
	14.8	8072	1155
3	14.6	6094	992
	14.7	3236	722
	14.8	7684	1047
4	14.6	6098	1019
	14.7	3223	952
	14.8	6388	1301
5	14.6	4816	473
	14.7	2910	336
	14.8	6861	1392
6	14.6	5649	1022
	14.7	2908	723
	14.8	6621	1437

Except for Case 1, all other cases show an increase in D_G with gas velocity. Case 1 has H as one of the floating parameters. The fitted values of H are considerably lower than their corresponding values from thermodynamics. This may be the reason for this anomaly. In general, there is a very large spread of D_G about the mean value.

Literature correlations for D_G (Mangartz and Pilhofer, 1980; Field and Davidson, 1980; Towell and Ackerman, 1972), reported in Table 15, are valid only for superficial

Table 14: Average K_La at each Process Rate for the Various Cases Studied

Case No.	Run	$\overline{K_La}$ 1/s	σ_k 1/s
1	14.6	1.23	0.81
	14.7	0.91	0.92
	14.8	1.18	0.97
2a	14.6	2.7	2.2
	14.7	1.66	1.00
	14.8	4.19	4.04
2b	14.6	0.358	0.26
	14.7	0.195	0.03
	14.8	1.834	0.99
3	14.6	1.04	0.79
	14.7	0.44	0.50
	14.8	0.161	0.08
4	14.6	0.984	0.99
	14.7	0.349	0.27
	14.8	0.299	0.08
5	14.6	0.413	0.41
	14.7	0.421	0.14
	14.8	0.494	0.41
6	14.6	0.370	0.37
	14.7	0.378	0.06
	14.8	0.359	0.12

gas velocities up to 13 cm/s, which is lower than the range of velocities of interest to us. Therefore a comparison is made only between Run 14.7, which is at the lowest gas velocity, and the correlation predictions from the literature.

The values of D_G predicted by the above correlations are much higher than the mean value of $D_G = 2908 \text{ cm}^2/\text{s}$ at U_G of 14 cm/s obtained in this study. The implications of these results are completely different from those for the liquid phase results, which suggest that an increase in pressure causes an increase in the liquid dispersion coefficients. The correlation equations suggest that an increase in pressure, which increases the holdup, will lower the magnitude of the gas dispersion coefficients. This occurs because the correlations relate the dispersion coefficient to the swarm velocity of the bubbles, which decreases with a decrease in bubble size or an increase in gas holdup. The physical basis for these equations is not completely known. Intuitively it is expected that the presence of an excess of smaller bubbles should only increase the dispersion of the gas as more bubbles follow and recirculate along with the liquid

Table 15: Correlations for Gas Dispersion Coefficient in Bubble Columns

Investigator	Equation (in SI)	Range of Variables	Prediction of D_G at U_G 14 cm/s (cm^2/s)
Towell and Ackerman	$D_G = 19.7 D_C^2 U_G$	$0.00854 \leq U_G \leq 0.13 \text{ m/s}$ $0.0072 \leq U_L \leq 0.0135 \text{ m/s}$ $D_C = 0.406, 1.067 \text{ m}$	5835
Field and Davidson	$D_G = 56.4 D_C^{1.33} (\frac{U_G}{\epsilon_G})^{3.56}$	$0.00854 \leq U_G \leq 0.13 \text{ m/s}$ $0.0 \leq U_L \leq 0.0135 \text{ m/s}$ $0.076 \leq D_c \leq 3.2 \text{ m}$	13435
Mangartz and Pilhofer	$D_G = 50.0 D_C^{1.50} (\frac{U_G}{\epsilon_G})^{3.00}$	$0.015 \leq U_G \leq 0.13 \text{ m/s}$ $0.0072 \leq U_L \leq 0.0135 \text{ m/s}$ $0.092 \leq D_c \leq 1.067 \text{ m}$	11911

phase, while the larger bubbles move up the column. It must be noted that there is also a large variation in the predictions of D_G from correlations. The correlations are shown to have an error of upto 60 %. Therefore, no conclusion regarding D_G can be made based on the comparison with these correlations.

Unlike the consistent trends for the gas phase dispersion coefficients with superficial gas velocity, $K_L a$ values shows no particular pattern (as indicated by the results of ANOVA in Tables A.4.3 and A.4.4 for Cases 1 and 6). In fact the standard deviations indicate the large variation of $K_L a$ from the mean values. This large spread of the data, and the lack of any trend suggests that the model is quite insensitive to $K_L a$. If one looks at the results from Case 5 and Case 6, which are the most reliable cases, it appears that there is no dependence of $K_L a$ on gas velocity. Here again, the spread is significantly large. Unfortunately, there are no existing literature correlations for $K_L a$ under these conditions of pressure and gas velocity, to make any quantitative comparisons.

5.2.8 Conclusions and Future Work

- In general, good fits are obtained with the one-dimensional model using three floating parameters, $(D_G, H \text{ and } K_L a)$, $(D_G, K_L a \text{ and } \epsilon_G)$, $(D_G, K_L a \text{ and } \alpha)$ and $(D_G, K_L a \text{ and } U_G)$. Although the fits are good for these cases, there is a mismatch between the model predicted H , ϵ_G and α from the first three cases (1, 3 and 4) and corresponding independent measurements. Only for Case 6 are the fitted values of U_G reasonable and relate well to independent experimental information.

Since independent estimates of all model parameters except D_G and K_La are available, ideally a two floating parameter model should suffice. When such a two parameter model, with D_G and K_La as floating parameters, is used, reasonable fits are possible only when the variation of superficial gas velocity, due to gas consumption, is accounted for. A linear decrease in U_G over the entire dispersion height is considered for this. This demonstrates the importance of accounting for the varying gas velocity in the column, despite the fact that the observed conversions are quite low. In Equation 13, a decrease in U_G is equivalent to an increase in ϵ_G . This explains the results obtained for Cases 2 and 3. Therefore, by accounting for the change in U_G with axial position in the column, the model is able to provide good fits of data when estimates for ϵ_G from DP measurements are used.

A comparison of the results between Cases 5 and 6 shows that the D_G values are about the same.

- In the process of using the various approaches for fitting the data, it is shown (in Case 4) that the assumptions for estimating the total argon concentration, given by Equation 7, are good approximations for the system under consideration.
- The values of the parameters obtained by model fits of experimental data are more consistent for the top two to three detector levels for all the cases considered. At the lower levels the values of D_G start increasing. Based on the dispersion Peclet number, it is seen that the model is most suitable for interpretation of the measurements at the upper levels, where the deviation from plug flow is the smallest.
- A parametric sensitivity is performed for Case 1, with three floating parameters, D_G , H and K_La , by fixing ϵ_G from DP measurements. It is found that the model is most sensitive to Henry's law constant H , and least sensitive to K_La . Due to this, variations in K_La do not affect the model predictions appreciably. It is noted, however, that K_La values of zero cannot be used as the data then simply cannot be fitted by the model. In addition, based on the results for Case 2 and Case 5, where two floating parameters are used, considerable model sensitivity to gas holdup and superficial gas velocity is evident.
- The average values of D_G indicate that D_G increases with superficial gas velocity. Literature correlations predict gas dispersion coefficients much higher in

magnitude than observed in this study. This is thought to be due to the large error involved in the correlations.

While there is a consistent increase in D_G with gas velocity, the increase between runs 14.6 and 14.8, that is, for velocities 25.3 cm/s and 36 cm/s appears only marginal considering the large difference in gas velocities (when compared to the differences between runs 14.7 and 14.6), as seen in Table 13. Run 14.8 is at a lower pressure (3.6MPa) than the other two runs (5.2MPa). This implies that a reduction in pressure causes a lowering of D_G , which for the case of run 14.8 would be expected to be higher at a pressure of 5MPa. However, there is no sufficient experimental information at present to confirm this hypothesis fully.

- While the gas dispersion coefficient seems to show reasonable trends, the volumetric mass transfer coefficient, K_{La} , shows no pattern. In addition, there are large variations of K_{La} about the mean value.

Overall, the dispersion model is able to match the tracer responses in the column. Judging from all the cases for different floating parameters that are studied, it is clear that an accurate estimate of the average gas holdup and superficial gas velocity is absolutely necessary for good fits of data.

With regard to the two main parameters, a large variation in D_G values is obtained at different axial positions of measurement, which shows an increase of D_G with a decrease in height. The K_{La} values obtained by fitting the data show no consistent patterns and have a very large spread about their means, which basically indicates that the model is insensitive to K_{La} . As a result, the effect of U_G on K_{La} cannot be properly assessed. This is perhaps also due to the lack of a physical basis for using the axial dispersion model for the fluid dynamic situation in the present column.

A model that better captures the nature of flow in bubble columns and distinguishes between the possibly different bubble sizes is required to consistently predict the characteristics of the tracer responses at all levels in the column. For this purpose, we propose to use the phenomenological Two Phase Recycle with Cross-Flow Model (TRCFM), which accounts for the movement of different bubble classes (gas) within the column and their interaction with the liquid phase. The axial variation of superficial gas velocity and gas holdup can be suitably incorporated into such a model.

6 Gas - Liquid Mixing and Scale-Up Issues in Bubble Columns

In bubble columns liquid recirculation is set up in the column in a time-averaged sense (Devanathan et al, 1990; Hills, 1974). The maximum liquid velocity increases with increasing superficial gas velocity, as the gas holdup increases and the radial holdup profile becomes steeper (Kumar et al, 1994). Simultaneously, due to increased turbulence there is an increase in the radial and axial turbulent diffusivities (Devanathan, 1991; Degaleesan et al. 1995). The effective or overall axial liquid dispersion coefficient is a result of convective and turbulent mixing. The overall liquid axial dispersion coefficient can be tentatively approximated by Taylor diffusivity as

$$D_L = \frac{2\bar{U}_{LU}^2 R^{*2}}{D_{rr}} + D_{zz} \quad (22)$$

where $\bar{U}_{LU}$ is the mean upflow liquid velocity calculated as

$$\bar{U}_{LU} = \frac{\int_0^{R^*} u_{Lz}(r) \epsilon_L(r) r dr}{\int_0^{R^*} \epsilon_L(r) r dr} \quad (23)$$

As U_G increases, $\bar{U}_{LU}$, D_{rr} and D_{zz} increase. As long as the increase in $\bar{U}_{LU}^2$ is larger than the increase in D_{rr} , then both terms in Eqn 22 will increase with increasing gas velocity.

We have experimental results for liquid velocities and turbulent diffusivities in smaller diameter columns and lower gas velocities (Degaleesan and Duduković, 1995) velocities. When extrapolated to larger columns, this yields turbulent diffusivities in the range $D_{rr} \sim 100$ to $150 \text{ cm}^2/\text{s}$, and $D_{zz} \sim 1500$ to $2000 \text{ cm}^2/\text{s}$. The mean upflow velocities can be obtained using the one-dimensional model of Kumar et al. (1994) for liquid velocity. This yields $\bar{U}_{LU} \sim 23$ to 35 cm/s . The above values are calculated for the existing conditions from U_G 14 cm/s to 36 cm/s, respectively. When substituted in Eqn 22, this yields values of D_L to be 3300 to $6100 \text{ cm}^2/\text{s}$. It is noted that the expression for Taylor diffusivity is only an approximate one for use in bubble columns. In addition the convective and turbulent parameters are obtained by extrapolation of the existing data for smaller diameter columns. This gives us reasonable results for D_L under the existing operating conditions.

Using the axial dispersion model (ADM) and fitting the model to experimental data, the axial dispersion coefficients for the gas, D_G , and liquid, D_L , have been evaluated from tracer data under methanol synthesis conditions. For the liquid phase,

the relatively larger values of dispersion coefficients obtained, when compared to correlation predictions of liquid dispersion coefficients at atmospheric pressure, are qualitatively justified based on the holdup differences between the two systems. For the gas phase, comparison of the fitted D_G with literature correlations are counter intuitive and opposite to that of the liquid phase experimental results.

It is clear that none of the existing correlations can be used satisfactorily to predict mixing (dispersion coefficients) in the gas or liquid phase under existing conditions. Since the experiments considered here are only for a single column diameter, and since the effect of pressure can not be discerned from these experiments, no correlations can result from the present work. In addition, results of parameter estimation at the various detector levels indicate the effect of L/D ratio on the model parameters, especially at the lower detector levels of the column.

With regard to scale-up to industrial size columns, caution must be exercised in extrapolating the correlations for the dispersion coefficients to large diameter columns.

7 Conclusions

The liquid (slurry) and gas phase tracer data have been interpreted with the one dimensional axial dispersion model (ADM).

For the case of the liquid, the dispersion model is able to give good fits for the detectors that do not exhibit any overshoots. The obtained dispersion coefficients show an increase with gas velocity. However, there is a large scatter in the axial dispersion coefficient obtained at different detector levels, which suggests that the model is inadequate to describe the behavior of the liquid within the entire column with a single dispersion coefficient. For this purpose, we propose to use the Recycle with Cross Flow and Dispersion Model (RCFDM).

For the gas phase tracer analysis, good fits are possible using the ADM at almost all detector levels, but there is a variation in the estimated parameters with detector level. While the gas phase dispersion coefficient shows an increase with gas velocity, no particular dependence is seen with regard to the volumetric mass transfer coefficient. To better represent the flow pattern along with the bubble size distribution and gas - liquid exchange, we propose to use the Two Phase Recycle with Cross Flow model (TRCFM) in the future.

Comparison with literature correlations for the dispersion coefficients shows the lack of any suitable correlations under existing operating conditions. In order to use the correlations for scale-up, additional experiments at different column diameters,

different L/D ratios, and different pressures are necessary. Tracer runs at different gas consumption or gas generation rates are also needed.

8 Nomenclature

c	constant in equation for void fraction profile
C_L	liquid phase concentration, mol/cm^3
C_G	gas phase concentration, mol/cm^3
D_c	column diameter, m
D_L	liquid axial dispersion coefficient, cm^2/s
D_G	gas axial dispersion coefficient, cm^2/s
D_{rr}	radial turbulent diffusivity, cm^2/s
D_{zz}	axial turbulent diffusivity, cm^2/s
g	gravitational constant, cm/s^2
H	Henry's constant
K_{La}	overall liquid side volumetric mass transfer coefficient, cm/s
L	height of liquid dispersion, cm
m	void fraction exponent
U_G	superficial gas velocity, cm/s
$\bar{U}$	liquid circulation velocity, cm/s
z	axial position of detector, cm

Greek

α	fraction of Gas phase tracer detected
ϵ_G	gas holdup
$\tilde{\epsilon}_G$	constant in equation for void fraction profile
ρ	density, gm/cm^3
ψ	non dimensional radial position

Subscripts

G	gas
L	liquid
t	time

U	upflow region
z	axial position

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10 Appendix I: Holdup Measurements

This appendix deals with some of the aspects on holdup measurements, that were discussed in the main report. The differences in gas holdup estimates between the nuclear densitometer and γ ray tomography technique are shown in Figure A.1.1. In nuclear densitometry (left figure), the source emits a narrow beam of γ radiation through the column, with a detector opposite it. This yields a series of chordal measurements. A single line averaged holdup can be obtained across the centerline of the column. In γ ray tomography (CT), a series of scans is obtained at different angular positions to yield a distribution of void fraction across a given cross-section. The average holdups obtained from NDG are thus higher than the true cross-sectional average holdups from CT. More details are presented elsewhere (Kumar et al, 1995).

However, as the void fraction profile becomes more uniform, that is, with larger values for the void fraction exponent m in equation 14, the differences are reduced. This is illustrated in Figure A.1.2.

Figure A.1.3 (a) and (b) shows the axial holdup profiles in the column from DP and NDG measurements at various process rates.

Figure A.1.1: Data Collection for Densitometry and Tomography

Figure A.1.2: Comparison of Assumed Void Fraction Distribution and Centerline Chordal Average

Figure A.1.3 (a) Axial Holdup Profile Measured by DP

Figure A.1.3 (b) Axial Holdup Profile Measured by NDG

11 Appendix II: Simulation of the Radiation Intensity Measured by a Detector

The intensity of eadiation from a point source recorded at a detector is given by the following expression:

$$n_p = AF.BF.\Omega.\eta.S \quad (24)$$

n_p is the count rate (counts/time) at the detector due to a point source. Each factor is defined below.

The attenuation factor AF is defined as

$$AF = \exp[-(\mu_g l_g + \mu_{sl} l_{sl} + \mu_w l_w)] \quad (25)$$

in which μ_g , μ_{sl} and μ_w are the linear attenuation coefficients in the gas, the slurry and the wall of the reactor, and l_g , l_{sl} and l_w are the effective distances or depths of penetration in the respective media. The attenuation coefficient in the gas phase is negligible when compared with the other phases, and so the term for the gas phase is ignored. l_{sl} takes into account the liquid (slurry) holdup. The calculation of l_{sl} depends on the nature of the holdup distribution. This assumes that the slurry is pseudohomogeneous. If that is not the case and if the attenuation coefficients for the solid and liquid are considerably different, then the term $\mu_{sl} l_{sl}$ must be replaced by $\mu_l l_l + \mu_s l_s$, where subscripts s and l refer to solid and liquid, respectively.

The buildup factor BF represents the ratio of the intensity due to all photons to the intensity due to unscattered photons alone. It is defined empirically using the Berger equation (Tsoulfanidis, 1983):

$$BF = 1 + (a_{sl}\mu_{sl}l_{sl} + a_w\mu_w l_w)[\exp(b_{sl}\mu_{sl}l_{sl} + b_w\mu_w l_w)] \quad (26)$$

where a and b are the empirical constants depending on the medium and energy of radiation.

The solid angle Ω is the fraction of photons emitted by the source that is seen by the detector. For a shielded detector, only the front circular surface of the detector is exposed to the γ rays. For such a case, the solid angle is given by:

$$\Omega = \frac{1}{2}(1 - \cos(\tan^{-1}(R_c/d))) \quad (27)$$

where R_c is the radius of the circular face of the detector, and d is the distance between the source and the detector.

η , the efficiency of the detector, is taken to be a constant. S is the source strength. This is proportional to the concentration of tracer at a given location.

The detectors used are 2" x 2" NaI crystals, shielded on their sides. The various material constants at the energy levels of the source used are provided in Table A.2.1 (Tsoulfanidis, 1971).

Our objective is twofold. Initially we estimate the spatial range at a given axial position in the column over which the detector receives its signal. The simulation is done for an assumed uniform distribution of tracer and uniform distribution of phases. Secondly, we proceed to study the effect of the radially non-uniform gas holdup profile on the radiation received at the detector

1. Uniform phase distribution and concentration of tracer in gas and liquid phase

The medium is considered to be homogeneous, with uniform phase and tracer distribution. Therefore the effective distance in the liquid (slurry) medium used in Equation 25 and 26 is given as

$$l_{sl} = l_{sd}(1 - \epsilon_G) \quad (28)$$

where l_{sd} is the distance between the source and center of the detector. The source strength or local activity is the same at all locations, since the concentration of tracer (which is proportional to the local source strength) is uniform. Substituting for all the factors into Equation 24, the count rate recorded at the detector due to the individual uniformly distributed point sources is calculated. The resulting spatial distribution of intensity (counts/time) at a given axial position is shown in Figure A.2.1. The position of the detector relative to the intensity distribution is shown in Figure A.2.2. The perpendicular distance between the face of the detector and the wall of the column is 2.54 cm (1 inch). The shaded region in Figure A.2.2. represents the volume (area) considered for the contribution of the radiation to the overall radiation received at the detector. The total radiation from this shaded region, which forms less than 1 % of the entire reactor volume, is 90 % of the total radiation from the entire domain. Since the detector is shielded on its sides, the contribution of radiation from different axial positions other than the cross-sectional slice (10 cm in thickness) at the axial position of the detector is negligible. Therefore it can be assumed that the radiation

measured at the detector at a given axial position is proportional to the concentration of tracer at that axial location.

2. Uniform tracer concentration and variable gas holdup profile

It is well known that there exists a cross-sectional holdup profile in the column. The effect of this profile, that is, variation in holdup, can be accounted for in the simulation of the radiation measured at the detector. This is done as follows:

- The gas phase model is used to estimate the cross-sectional average gas and liquid tracer concentrations (C_G and C_L) at a given axial location and time.
- A suitable radial holdup profile of the gas $\epsilon_G(r)$ and thereby the liquid $\epsilon_L(r)$ is assumed (Kumar, 1994).
- The attenuation factor (AF) and buildup factor BF are calculated by accounting for the local variation in the phase distribution.

$$AF = \exp(-([\int_{p_0}^{p_d} \mu_{sl}(1 - \epsilon_G(r))dl] + \mu_w l_w)) \quad (29)$$

where p_0 and p_d denote the position of the source and detector. A similar expression is used for the buildup factor, which takes into account the varying phase distribution. Thereby the effects of radial gas holdup profile are properly accounted for in the factors AF and BF . The solid angle and efficiency remain unchanged from the previously discussed values. The source strength at a given point in the cross-sectional plane is calculated as

$$S(r, z, t) = \epsilon_G(r)C_G(t, z) + \epsilon_L(r)C_L(t, z) \quad (30)$$

Substituting for the individual factors into Equation 24 and integrating over the field of view of the detector, the overall count rate is calculated, which gives the total tracer concentration at a given axial location $C_t(t, z)$.

In this simulation, the gas profile given by equation 21 is used with an exponent of $m = 3$. The effect of gas and liquid tracer concentration on the resultant count rate at the detector is shown in Figure A.2.3.(a), (b) and (c). When the gas and liquid tracer concentration are equal, the simulated profile is steep, similar to Figure A.2.1 with a sharp exponential decay. However, as the concentration of liquid tracer is

reduced, the profiles become flatter, and the contribution of the tracer in the shaded region of Figure A.2.2. to the total radiation is reduced (Fig A.2.3.(c)).

Therefore when the concentration of tracer in the liquid phase is low enough, as in the present situation, the (cross-sectional) spatial contribution of radiation from the tracer at a given axial location becomes uniform and the simplified expression for C_t given by Eqn 7 is valid.

Table A.2.1 : Constants for Radiation Simulation

μ_{sl}	0.065 cm^{-1}	μ_w	0.40 cm^{-1}
a_{sl}	1.4	a_w	1.27
b_{sl}	0.027	b_w	0.032

Figure A.2.1: (a) Three-Dimensional view of the (x,y) Spatial Distribution of Intensity in a Cross-Sectional Slice of the Reactor. Each '.' denotes a discrete source point at an (x,y) location. Position of detector is shown in Fig. A.2.2. Contribution of the shaded region in Fig. A.2.2. is 90 %.

cm

Figure A.2.1: (b) Front View (along x-axis) of Fig. A.2.1(a)

Figure A.2.2: Cross sectional view of the column with detector positioned along the 'x' axis. Shaded region represents the region considered for the contribution of radiation to the overall radiation received by detector.

Figure A.2.3: (a) Front View of the (x,y) Spatial Distribution of Radiation with Non-Uniform Gas Holdup, and Equal Gas and Liquid Phase Tracer Concentration. The contribution of the shaded region in Fig. A.2.2. to the total radiation detected is 88 %.

Figure A.2.3: (b) Front View of the (x,y) Spatial Distribution of Radiation with Non-Uniform Gas Holdup, and Ratio of Gas and Liquid Phase Tracer Concentration 1:0.5. The contribution of the shaded region in Fig. A.2.2. to the total radiation detected is 79 %.

Figure A.2.3: (c) Front view of the (x,y) spatial distribution of radiation with non uniform gas holdup, and ratio of gas and liquid phase tracer concentration 1:0.1. The contribution of the shaded region in Fig. A.2.2. to the total radiation detected is 61%.

12 Appendix III: Liquid Tracer Experiments and Model Fits

Figure A.3.1: Liquid Impulse Response Measurements for Run 14.6, N1-CEN, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 7.2s

Figure A.3.2: Liquid Impulse Response Measurements for Run 14.6, N1-WALL, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 30.8s

Figure A.3.3: Liquid Impulse Response Measurements for Run 14.6, N2-CEN, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 16.2s

Figure A.3.4: Liquid Impulse Response Measurements for Run 14.7, N1-CEN, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 26.4s

Figure A.3.5: Liquid Impulse Response Measurements for Run 14.7, N1-WALL, (5.2 MPa, $U_G = 14$ cm/s), Injection Time 25.5s

Figure A.3.6: Liquid Impulse Response Measurements for Run 14.7, N2-WALL, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 9.8s

Figure A.3.7: Liquid Impulse Response Measurements for Run 14.8, N1-CEN, (3.6 MPa, $U_G = 36$ cm/s), Injection Time 22.4s

Figure A.3.8: Liquid Impulse Response Measurements for Run 14.8, N1-WALL, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 39.6s

Figure A.3.8: Liquid Impulse Response Measurements for Run 14.8, N2-CEN, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 20.8s

Figure A.3.10: Liquid Impulse Response Measurements for Run 14.8, N2-WALL, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 39s

13 Appendix IV: Analysis of Variance (ANOVA)

This section discusses the statistical analysis of the model fitted parameters of the liquid and gas phase axial dispersion model using ANOVA (Box et al., 1978). We explain briefly the analysis for the liquid phase dispersion coefficients. The first test considered the data (liquid dispersion coefficients) obtained for a given process rate (run). For each process rate, four different injection points were used. The dispersion coefficients from each injection point were assumed to fall into a separate category or 'treatment'. In each treatment, the dispersion coefficients were obtained for measurements made at three detector levels. The data (dispersion coefficients) from within a treatment are assumed to differ due to random error. The objective is to find out if there are any real differences in the mean values associated with the different treatments. The F statistic, or F ratio, defined as the ratio of the mean square error in the treatments (s_T^2) to the mean square error between treatments (s_R^2), was calculated.

$$F = \frac{s_T^2}{s_R^2}; \quad s^2 = \frac{S}{n} \quad (31)$$

where S is the sum of square errors, and n is the degrees of freedom (size of sample - 1).

The data were tested using the null hypothesis, which states that the treatment means are equal. If the null hypothesis is true, this implies that the F ratio would follow an F distribution, which is defined as a distribution of the ratio of two variances obtained from two groups sampled from a normally distributed population. Each variance depends on the sample size or the degrees of freedom of each group. n_T and n_R are the degrees of freedom of the two groups for this analysis. The null hypothesis is verified by comparing the F ratio with the percentage points from a standard table of the F Distribution (Box et al., 1978) with n_T and n_R degrees of freedom and a certain significance level. In this case the significance level, which indicates the confidence level of the test, is set to be 10%. For 2 and 6 degrees of freedom the value from the F table is 3.46, and for 3 and 8 degrees of freedom, it is 2.92. An F ratio that is lower than the corresponding value from the F Table indicates that the null hypothesis is valid.

Table A.4.1. shows that the null hypothesis is rejected for runs 14.6 and 14.7, that is, the treatment means are different from each other, while for run 14.8, the hypothesis is accepted.

The analysis is then applied to the liquid dispersion data by considering all the data from a given run to belong to a single treatment. The means from the three runs, 14.6, 14.7 and 14.8, are compared as shown in Table A.4.2. Since the F ratio is much larger than the corresponding percentage point from the F Table, i.e., 2.49, the null hypothesis is rejected, which implies that the means of the three runs belong to different categories. Therefore there is a significant difference between the means of a certain process rate, which implies that there is a dependency of D_L on superficial gas velocity.

A similar analysis is performed for the gas phase model-fitted parameters. Two tracer experiments were conducted at each process rate. The parameters obtained from Case 1 were tested for the repeatability of the experiments at each process rate. The resulting F ratios for each of the parameters in Table A.4.3 show that except for D_G from Run 14.6, there is good repeatability of all the parameters at all process rates. As in the case of the liquid dispersion coefficients, an analysis of the effect of superficial gas velocity on the parameters (Table A.4.3 for Case 1 and Table A.4.4 for Case 6) shows that while the gas phase dispersion coefficients are dependent on gas velocity, both H and $K_L a$ show no dependency.

Table A.4.1. ANOVA Table for Comparison of Mean Values within each Run

Run	Source of Variation	Sum of Squares (S)	Degrees of Freedom (n)	Mean Square (s^2)	Ratio s_T^2/s_R^2
14.6	Bet. Treatments (T)	11429238	2	5714619	4.69
	Within Treatments (R)	7358845	6	1226474	
14.7	T	3333876	3	1111291	5.13
	R	1733267	8	216658	
14.8	T	919538	3	306513	1.22
	R	251495	8	251495	

Table A.4.2. ANOVA Table for Comparison of Mean Values between Runs

Source of Variation	Sum of Squares (S)	Degrees of Freedom (n)	Mean Square (s^2)	Ratio s_T^2/s_R^2
Bet. Treatments (T)	36609900	2	18304950	20.5
Within Treatments (R)	26790772	30	89302573	

Table A.4.3. ANOVA Table for Case 1

Parameter	Run	Repeatability of Runs			Effect of of U_G		
		mean	std. dev.	F	mean	std. dev.	F'
D_G cm^2/s	14.6 - 1	6529	920	10.44	5637	1305	14.7
	14.6 - 2	4745	993	0.55	2801	1010	
	14.7 - 3	3041	1251				
	14.7 - 4	2561	974	0.22	4961	1504	
	14.8 - 5	4737	1068				
	14.8 - 6	5165	1032				
K_{La} $1/s$	14.6 - 1	1.38	0.88	0.57	1.23	0.81	0.43
	14.6 - 2	1.03	0.76	0.001	0.907	0.92	
	14.7 - 3	0.91	0.58				
	14.7 - 4	0.90	1.25	1.37	1.18	0.97	
	14.8 - 5	1.125	0.94				
	14.8 - 6	1.25	0.89				
H	14.6 - 1	4.53	0.91	0.257	4.4	0.86	0.34
	14.6 - 2	4.27	0.88	0.20	4.33	1.08	
	14.7 - 3	4.18	0.70				
	14.7 - 4	4.48	1.42	1.23	4.04	1.32	
	14.8 - 5	3.61	0.59				
	14.8 - 6	4.48	1.82				

Table A.4.4. ANOVA Table for Case 6

Run	$D_G, cm^2/s$			$K_La, 1/s$		
	mean	std. dev.	F	mean	std. dev.	F
14.6	5649	1022	23.9	0.37	0.37	0.95
14.7	2908	723		0.38	0.06	
14.8	6621	1437		0.36	0.12	

14 Appendix V: Calculation of Henry's Law Constant

Vapor liquid equilibrium was calculated using suitable equations of state for the liquid and vapor phase, and considering the reactor conditions and composition of the outlet gas stream (more details regarding these calculations and the equations of state used will be provided by B. A. Toseland). The hydrocarbons used in the calculation were an estimate of the composition of the neutral oil phase in the reactor. From the VLE data, Henry's Law constant for the tracer gas, argon, is obtained as :

$$H = \left(\frac{y_A}{x_A} \right) \quad (32)$$

where x_A is the mole fraction of argon in the liquid phase and y_A is the mole fraction of argon in the gas phase at equilibrium conditions.

For Runs 14.6 and 14.7 (press : 52 MPa and temp : 250 ° C), $H = 5.86$, and for Run 14.8 (press : 36 MPa and temp : 250 ° C), $H = 8.11$.

15 Appendix VI: Gas Phase Tracer Experiments and Model Fits

Figure A.6.1 (a): Simulation of Input Pulse to the Reactor, Run 14.6

Figure A.6.1 (b): Simulation of Input Pulse to the Reactor, Run 14.8

Figure A.6.2: Gas Phase Impulse Response for **Case 1**, Run 14.6 - 1, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 12.6s

Figure A.6.2 (contd.): Gas Phase Impulse Response for **Case 1**, Run 14.6 - 1, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 12.6s

Figure A.6.3: Gas Phase Impulse Response for **Case 1**, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.3 (contd.): Gas Phase Impulse Response for **Case 1**, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.4: Gas Phase Impulse Response for **Case 1**, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 45s

Figure A.6.4 (contd.): Gas Phase Impulse Response for Case 1, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 45s

Figure A.6.5: Gas Phase Impulse Response for **Case 1**, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 30.6s

Figure A.6.6 (contd.): Gas Phase Impulse Response for **Case 1**, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 30.6s

Figure A.6.6: Gas Phase Impulse Response for Case 1, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 29.4s

Figure A.6.6 (contd.): Gas Phase Impulse Response for **Case 1**, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 29.4s

Figure A.6.7: Gas Phase Impulse Response for Case 2a, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.7 (contd.): Gas Phase Impulse Response for **Case 2a**, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.8: Gas Phase Impulse Response for **Case 2a**, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 47.4s

Figure A.6.8 (contd.): Gas Phase Impulse Response for **Case 2a**, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 47.4s

Figure A.6.9: Gas Phase Impulse Response for Case 2a, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 33s

Figure A.6.9 (contd.): Gas Phase Impulse Response for Case 2a, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 33s

Figure A.6.10: Gas Phase Impulse Response for **Case 2a**, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24.6s

Figure A.6.10 (contd.): Gas Phase Impulse Response for **Case 2a**, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24.6s

Figure A.6.11: Gas Phase Impulse Response for **Case 2a**, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 29.4s

Figure A.6.11 (contd.): Gas Phase Impulse Response for **Case 2a**, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 29.4s

Figure A.6.12: Gas Phase Impulse Response for **Case 2b**, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.13: Gas Phase Impulse Response for Case 2b, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 47s

Figure A.6.14: Gas Phase Impulse Response for Case 2b, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 33s

Figure A.6.15: Gas Phase Impulse Response for **Case 2b**, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24.6s

Figure A.6.16: Gas Phase Impulse Response for **Case 2b**, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 29.4s

Figure A.6.17: Gas Phase Impulse Response for **Case 3**, Run 14.6 - 1, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 12.6s

Figure A.6.17 (contd.): Gas Phase Impulse Response for **Case 3**, Run 14.6 - 1, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 12.6s

Figure A.6.18: Gas Phase Impulse Response for Case 3, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.18 (contd.): Gas Phase Impulse Response for **Case 3**, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.19: Gas Phase Impulse Response for **Case 3**, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 45s

Figure A.6.19 (contd.): Gas Phase Impulse Response for Case 3, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 45s

Figure A.6.20: Gas Phase Impulse Response for **Case 3**, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 30.6s

Figure A.6.20 (contd.): Gas Phase Impulse Response for **Case 3**, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 30.6s

Figure A.6.21: Gas Phase Impulse Response for Case 3, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24s

Figure A.6.21 (contd.): Gas Phase Impulse Response for **Case 3**, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24s

Figure A.6.22: Gas Phase Impulse Response for **Case 3**, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 28.8s

Figure A.6.22 (contd.): Gas Phase Impulse Response for **Case 3**, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 28.8s

Figure A.6.23: Gas Phase Impulse Response for **Case 4**, Run 14.6 - 1, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 12.6s

Figure A.6.23 (contd.): Gas Phase Impulse Response for Case 4, Run 14.6 - 1, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 12.6s

Figure A.6.24: Gas Phase Impulse Response for Case 4, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.24 (contd.): Gas Phase Impulse Response for **Case 4**, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.25: Gas Phase Impulse Response for Case 4, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 45s

Figure A.6.25 (contd.): Gas Phase Impulse Response for **Case 4**, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 45s

Figure A.6.26: Gas Phase Impulse Response for **Case 4**, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 30.6s

Figure A.6.26 (contd.): Gas Phase Impulse Response for **Case 4**, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 30.6s

Figure A.6.27: Gas Phase Impulse Response for Case 4, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24s

Figure A.6.27 (contd.): Gas Phase Impulse Response for Case 4, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24s

Figure A.6.28: Gas Phase Impulse Response for **Case 4**, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 28.8s

Figure A.6.28 (contd.): Gas Phase Impulse Response for **Case 4**, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 28.8s

Figure A.6.29: Gas Phase Impulse Response for **Case 5**, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24.0s

Figure A.6.29 (contd.): Gas Phase Impulse Response for **Case 5**, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24.0s

Figure A.6.30: Gas Phase Impulse Response for **Case 5**, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 47.4s

Figure A.6.30 (contd.): Gas Phase Impulse Response for **Case 5**, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 47.4s

Figure A.6.31: Gas Phase Impulse Response for **Case 5**, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 33.0s

Figure A.6.31 (contd.): Gas Phase Impulse Response for **Case 5**, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 33.0s

Figure A.6.32: Gas Phase Impulse Response for **Case 5**, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24.6s

Figure A.6.32 (contd.): Gas Phase Impulse Response for Case 5, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24.6s

Figure A.6.33: Gas Phase Impulse Response for **Case 5**, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 29.4s

Figure A.6.33 (contd.): Gas Phase Impulse Response for Case 5, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 29.4s

Figure A.6.34: Gas Phase Impulse Response for Case 6, Run 14.6 - 1, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 12.6s

Figure A.6.34 (contd.): Gas Phase Impulse Response for **Case 6**, Run 14.6 - 1, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 12.6s

Figure A.6.35: Gas Phase Impulse Response for **Case 6**, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.35 (contd.): Gas Phase Impulse Response for **Case 6**, Run 14.6 - 2, (5.2 MPa, $U_G = 25 \text{ cm/s}$), Injection Time 24s

Figure A.6.36: Gas Phase Impulse Response for Case 6, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 45s

Figure A.6.36 (contd.): Gas Phase Impulse Response for **Case 6**, Run 14.7 - 3, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 45s

Figure A.6.37: Gas Phase Impulse Response for **Case 6**, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 30.6s

Figure A.6.37 (contd.): Gas Phase Impulse Response for **Case 6**, Run 14.7 - 4, (5.2 MPa, $U_G = 14 \text{ cm/s}$), Injection Time 30.6s

Figure A.6.38: Gas Phase Impulse Response for Case 6, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24.6s

Figure A.6.38 (contd.): Gas Phase Impulse Response for **Case 6**, Run 14.8 - 5, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 24.6s

Figure A.6.39: Gas Phase Impulse Response for **Case 6**, Run 14.8 - 6, (3.6 MPa, $U_G \approx 36 \text{ cm/s}$), Injection Time 29.4s

Figure A.6.39 (contd.): Gas Phase Impulse Response for **Case 6**, Run 14.8 - 6, (3.6 MPa, $U_G = 36 \text{ cm/s}$), Injection Time 29.4s