ENGINEERING DEVELOPMENT OF
SLURRY BUBBLE COLUMN REACTOR (SBCR) TECHNOLOGY

Thirteenth Quarterly Report
for
April 1 - June 30, 1998

(Budget Year 3: October 1, 1997 – September 30, 1998)

Submitted to
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Contract No.: DE-FC 22 95 PC 95051

Chemical Reaction Engineering Laboratory
Chemical Engineering Department
Washington University
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Budget Year 3 – 13th Quarter
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■ Objectives for the Third Budget Year

The main goal of this subcontract from the Department of Energy via Air Products to the Chemical Reaction Engineering Laboratory (CREL) at Washington University is to study the fluid dynamics of slurry bubble columns and address issues related to scale-up and design. The objectives for the third budget year (October 1, 1997 – September 30, 1998) were set as follows:

• Further development of phenomenological models for liquid and gas flow.

• Testing of the models against available data from La Porte AFDU.

• Evaluating turbulent parameters in 18 inches diameter columns with and without internals using collected CARPT data in these columns.

• Development of relationships between fundamental and simpler practical models for industrial use.

• Further improvement in fundamental computational fluid dynamics models and testing the models against the CARPT/CT data.

• Preliminary assessment of differences in gas-liquid and gas-liquid-solid systems.

• Testing the effect of the gas distributor on flow patterns.

In this report, the research progress and achievements accomplished in the thirteenth quarter (April 1 - June 30, 1998) are discussed.
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OUTLINE OF THE ACCOMPLISHMENTS

• Scale-up Procedure for the Turbulent Eddy Diffusivity

Correlations for the estimation of turbulent eddy diffusivities are developed based on the existing limited database for scale-up and design of bubble columns. The cross-sectional averaged axial and radial turbulent eddy diffusivities obtained by the Computer Automated Radioactive Particle Tracking (CARPT) in air-water in three column sizes (14, 19 and 44 cm diameters) are used to develop these correlations. Because of the limited number of data points available, the developed correlations represent a preliminary attempt to describe the effects of scale and superficial gas velocities on the turbulent diffusivities. The developed scale-up procedure for the gas holdup, liquid recirculating velocity (which are reported in the 12th quarterly report) and eddy diffusivities enables the estimation of these parameters in systems of industrial interest. Accordingly, such procedure allows us to utilize the developed fundamental two-dimensional convection-diffusion model in interpretation of the liquid tracer data obtained in AFDU at La Porte.

• Interpretation of the Liquid Phase Tracer data During Methanol Synthesis at AFDU, La Porte, Using the Fundamental Two-Dimensional Convection-Diffusion Model

The fundamental two-dimensional convection-diffusion model has been developed for interpretation of the liquid phase tracer data taken at AFDU, La Porte, during methanol synthesis. Model parameters were obtained, based on the developed scale-up methodology, from CARPT measurements using as input the estimated radial gas holdup profile at La Porte. The gas holdup profile at La Porte was estimated from the Nuclear Gauge Densitometry and pressure drop measurements. The results show that the model provides a good representation of the internal liquid mixing in bubble columns. The developed scale-up procedure for evaluating the model parameters in the
AFDU slurry bubble column reactor during methanol synthesis, results in fairly good predictions of the characteristic mixing times within the column as measured by the radiation detectors at various axial locations.

- During this quarter, the work has been completed on i) estimation of the liquid phase turbulent mixing length from CARPT and CT measurements for use in simulation with the CFDLIB code and ii) comparison of time averaged liquid/slurry “turbulent” parameters in gas-liquid (G-L) and gas-liquid-solid (G-L-S) slurry bubble columns. However, the findings have been not yet organized in a report format. This will be accomplished during the next quarterly report.
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1. SCALE-UP PROCEDURE FOR THE TURBULENT EDDY DIFFUSIVITY

Studies of the effects of equipment scale and operating conditions on the fluid dynamic parameters by using experimental data obtained by Computer Automated Radioactive Particle Tracking (CARPT) and Computed Tomography (CT) and from the literature will aid in the design and scale-up of bubble column reactors. Our specific focus is on utilizing the available hydrodynamic information to model liquid mixing in bubble columns in the churn-turbulent flow regime. In this regard, the fluid dynamic parameters of interest are the gas holdup and radial holdup profile, the liquid recirculation velocity and liquid turbulence, which can be quantified by the turbulent eddy diffusivities.

Therefore, a scale-up methodology for gas holdup, liquid recirculating velocity and turbulent eddy diffusivity has been developed. The aim is to develop a basis for the approximate characterization of churn-turbulent bubble columns which enables the estimation these fluid dynamic parameters in industrial scale units based on measurements of these parameters in air-water atmospheric systems. This should enable the utilization of the developed two-dimensional convection-diffusion model in interpretation of liquid phase tracer data taken at AFDU, La Porte, during methanol synthesis.

In the last quarterly report (12th quarterly report) the scale-up procedures for the gas holdup and liquid recirculating velocity have been developed and reported. Here, a scale-up procedure for the turbulent eddy diffusivities is outlined.

1.1 Turbulent Eddy Diffusivities

The cross-sectionally averaged axial and radial turbulent eddy diffusivities are defined, respectively, as

\[
\overline{D}_{zz} = 2 \int_0^L D_{zz} \xi \, d\xi, \quad (1.1)
\]

\[
\overline{D}_{rr} = 2 \int_0^L D_{rr} \xi \, d\xi, \quad (1.2)
\]

In this case, the present results from CARPT data in an air-water system and three column sizes, 14 cm, 19 cm, and 44 cm, are considered. The data points shown in Figures 1.1 and 1.2 for \(D_{zz}\) and \(D_{rr}\), respectively are rather limited in their range of superficial gas velocity, \(U_g\). Therefore, this represents only a preliminary attempt at scaling (extrapolating) \(D_{rr}\) and \(D_{zz}\), and needs to be substantiated with further experimental data at higher gas velocities, especially in the largest diameter (44 cm) column.

The following dependencies have been observed for \(\overline{D}_{zz}\) and \(\overline{D}_{rr}\) (based on CARPT data), and apply to large diameter columns (> 10 cm) in the churn-turbulent flow regime (\(U_g > 5\)).
\[
\overline{D}_{zz}(cm^2/s) = -\frac{2325}{D_c^{0.8}} + 106.6D_c^{0.3}U_g^{0.3} \tag{1.3}
\]
\[
\overline{D}_{rr}(cm^2/s) = -\frac{350}{D_c^{0.8}} + 13.0D_c^{0.3}U_g^{0.3} \tag{1.4}
\]

It is emphasized again, that due to the limited number of data points available, these equations represent only a preliminary assessment of the effects of scale and superficial gas velocity on the turbulent diffusivities.

CARPT results for the average radial and axial eddy diffusivities in the churn-turbulent flow regime, indicate that the radial profiles of the turbulent diffusivities can be approximately expressed as follows:

\[
D_{zz}(\xi) = \overline{D}_{zz}P_4
\]
where \(P_4 = -3.4979\xi^4 + 3.2704\xi^3 + 0.4693\xi^2 + 0.00503\xi + 0.5847 \tag{1.5}\)

\[
D_{rr}(\xi) = \overline{D}_{rr}P_2
\]
where \(P_2 = -5.0929\xi^2 + 5.0717\xi + 0.1653 \tag{1.6}\)

\(P_4\) and \(P_2\) are fourth order and second order polynomials which are independent of gas velocity and column diameter. This is illustrated in Figures 1.3 and 1.4, which show the profiles evaluated using Equations 1.5, and 1.6. The reasonably good comparisons suggest that the above equations (1.5 and 1.6) in combination with Equations 1.3 and 1.4 can be used to estimate the profiles for the axial and radial eddy diffusivities as a function of column diameter, \(D_c\), and superficial gas velocity, \(U_g\), in air-water bubble columns operating in the churn-turbulent flow regime.
Figure 1.1: Effect of superficial gas velocity and column diameter on the average axial eddy diffusivity

Figure 1.2: Effect of superficial gas velocity and column diameter on the average radial eddy diffusivity
Figure 1.3: Radial profile ($P_4$) of the axial eddy diffusivity

Figure 1.4: Radial profile ($P_2$) of the radial eddy diffusivity
1.2 Characterization of Churn-Turbulent Bubble Columns

The scale-up equations for gas holdup, and liquid recirculating velocity presented in the 12th quarterly report and the equations for turbulent eddy diffusivities presented above have been developed for air-water atmospheric systems in the churn-turbulent regime. In this regime of flow, the effects of the gas distributor and trace contaminants in water are expected to be small. It is therefore assumed that at sufficiently high gas velocities for air-water systems, the fluid dynamic parameters are predominantly a function of superficial gas velocity and column diameter.

A change in system properties (physical properties of the fluids, presence of solids, etc.) and operating conditions (pressure and temperature) directly affect bubble sizes and their distribution, and thereby the global gas holdup and holdup distribution in the column. This in turn influences the extent of liquid recirculation and turbulence characteristics in the system, which are essentially dictated by the passage and interaction of bubbles. For example, an increase in the system pressure tends to reduce the bubble size, which delays transition to turbulent flow regime and, therefore, results in the increase in gas holdup, compared to values expected at atmospheric conditions. However, when the flow is in the churn-turbulent regime, it is typically characterized by the presence of large and small bubbles, irrespective of system pressure and other such factors (Krishna and Ellenberger 1996; De Swart 1996). Based on interpretation of dynamic gas disengagement (DGD) experiments Krishna et al. (1994) conclude that the characteristics of the large bubbles are unaffected by system properties and pressure. Independent measurements of the local holdup profile in high pressure bubble columns, at high gas velocities (Adkins et al. 1996), indicate that the holdup profile is parabolic (m = 2 in Equation 1.7) in shape, similar to the case for air-water systems at atmospheric pressure.

\[
\varepsilon_g = \tilde{\varepsilon}_g \frac{m+2}{m} (1-c\tilde{\varepsilon}^m) \quad (1.7)
\]

From these observations it is inferred that well into the churn-turbulent flow regime, similar bi-modal bubble size distribution is present in the column, irrespective of system properties (except when viscosity is very high). It is essentially the resulting gas holdup and its radial distribution that dictate liquid recirculation and turbulence. Therefore, the unified characterization of churn-turbulent bubble columns can be employed to approximately evaluate \( \bar{u}_{rec} \), \( \bar{D}_{zz} \) and \( \bar{D}_{rr} \) in industrial systems of interest, based on the knowledge of these parameters in air-water systems, as shown in Figure 1.5. For a given process condition, with prior knowledge of the global gas holdup in the column, an equivalent superficial gas velocity, \( U_{ge} \), that would exist at atmospheric conditions in such a column in an air-water system, can be evaluated using Equation 1.8.

\[
\bar{e}_g = 0.07U_g^{0.474-0.000625D_g} \quad \text{(in cgs units)} \quad (1.8)
\]
The calculated $U_{ge}$ can then be substituted in Equations 1.1 to 1.4, as well as Equation 1.9, to estimate the average turbulent diffusivities and average recirculation rate in the column under the specific conditions of interest.

$$\bar{u}_{rec} (cm/s) = 2.2D_c^{0.4} U_g^{0.4}$$  \hspace{1cm} (1.9)

![Figure 1.5: Method of Characterization of Churn-Turbulent Bubble Columns](image)

The fluid dynamic parameters estimated from the above procedure are used in the phenomenological modeling of liquid mixing in an industrial slurry bubble column reactor namely the AFDU in La Porte, Texas.

1.3 Summary

Using experimental data obtained by CARPT/CT and from the literature, equations have been developed for the prediction of the mean liquid recirculating velocity and average eddy diffusivities in air-water atmospheric systems. Based on the unified characterization of churn-turbulent bubble columns a methodology has been proposed which enables the estimation of the mean liquid recirculating velocity and turbulent eddy diffusivities, in churn-turbulent flow regime, in systems of industrial interest, e.g., high pressure and high temperature, using the data generated in air-water systems. This strategy requires a knowledge of the global holdup and holdup distribution in the system under consideration.
The equations and proposed methodology for scaling up of churn-turbulent bubble columns require substantiation with additional experimental data for the fluid dynamic parameters in large columns, at higher gas velocities and in different systems. Once verified, this will serve as a tool by which data from a limited database can be utilized to model and scale-up bubble columns, under process conditions, in the churn-turbulent flow regime. In this report, an indirect verification of the scale-up strategy is accomplished, by interpreting the experimental liquid tracer data obtained in ADFU at La Porte as discussed in the following section.

1.4 References


2. INTERPRETATION OF THE LIQUID PHASE TRACER DATA DURING METHANOL SYNTHESIS AT AFDU, LA PORTE, USING THE FUNDAMENTAL TWO-DIMENSIONAL CONVECTION-DIFFUSION MODEL

Two-dimensional convection-diffusion model for liquid mixing in bubble columns has been developed for interpretation of the liquid phase tracer data taken at AFDU, La Porte, during methanol synthesis. The model equations were reported in the seventh quarterly report. The model characterizes, in a statistical sense, the large scale flow pattern and mixing in the column, which should prove useful for the design and scale-up of bubble column reactors.

It is noted that, since long time averaging is used to arrive at the model equations, the present model therefore only describes the meso and macro scale mixing in the column. Micromixing phenomena are not captured, but this is not a serious drawback since most of the reactions in bubble columns are slow to moderately fast where the characteristic reaction time is larger than the micromixing time scale.

In this section, the developed two-dimensional convection-diffusion model is used to interpret the liquid phase tracer runs performed during methanol synthesis at AFDU, La Porte. The model parameters were obtained based on the developed scale-up methodology, from Computer Automated Radioactive Particle Tracking (CAPRT) measurements using as input the estimated radial gas holdup profile at La Porte. The gas holdup profile at La Porte was estimated from the Nuclear Gauge Densitometry and pressure drop measurements. The developed scale-up procedure for the gas holdup and liquid recirculating velocity have been reported in the previous quarterly report (12th quarter), while for the turbulent eddy diffusivities are reported in Section 1 of this report.

Although the developed model was described in the seventh quarterly report, we re-state it here for clarity and to make its implementation easy to follow.

2.1 Two Dimensional Convection-Diffusion Model for Liquid Mixing in Bubble Columns

The fundamental two-fluid model mass balance equation for the local, instantaneous tracer species for phase \( k \), is given by the following equation:

\[
\frac{\partial \rho_k C_k}{\partial t} + \nabla \cdot \rho_k C_k \mathbf{u}_k - D_m \nabla^2 C_k = 0
\]  

(2.1)

with an interfacial jump condition for mass transfer across the interface:

\[
\sum_{k=1}^{2} \rho_k C_k \left[ \mathbf{u}_k - \mathbf{u}_{k,i} \right] \cdot \mathbf{n}_k = 0
\]  

(2.2)

In the above equation, the phase density, \( \rho_k \), for incompressible flows such as in bubble columns, can be considered to be constant. \( D_m \) is the molecular diffusivity, which is small and will be neglected hereafter. Phasic or ensemble averaging of the above equation in an axisymmetric system, for an inert, non-volatile tracer, yields:
\[
\frac{\partial}{\partial t} \left( \rho_k \varepsilon_k \langle C_k \rangle^x \right) + \frac{\partial}{\partial z} \rho_k \left( \varepsilon_k \langle u_{\varepsilon, k} \rangle^x \langle C_k \rangle^x + \varepsilon_k \langle u_{\varepsilon, k} C_k \rangle^x \right) + \\
\frac{1}{r} \frac{\partial}{\partial r} \left( r \rho_k \left( \varepsilon_k \langle u_{\varepsilon, k} \rangle^x \langle C_k \rangle^x + \varepsilon_k \langle u_{\varepsilon, k} C_k \rangle^x \right) \right) = \left( \rho_k C_k (\bar{u}_k - \bar{u}_k) \cdot \nabla X_k \right)
\] (2.3)

where \(< >^x\) represents phasic averaging. The right hand side of Equation 2.3 represents the term due to mass transfer across the interface, where \(X_k\) is the phase function and is defined as in Equation 2.4.

\[
X_k(\bar{x}, t) = \begin{cases} 
1 & \text{if } \bar{x} \text{ is in phase } k \text{ at time } t \\
0 & \text{otherwise}
\end{cases}
\] (2.4)

An additional source term to represent reaction, can be added to the right hand side of the equation. For the present situation, considering a non-volatile inert liquid tracer, the right hand side of Equation 2.3 is set to 0. Since the model is primarily concerned with the liquid phase, the subscript \(k = l\), denoting the liquid phase, is dropped. In addition, all symbols denoting averaging are also dropped, in order to simplify notation. All the variables representing the fluid dynamic parameters and the tracer concentration will denote the phase averaged quantities.

The cross-correlation terms between the fluctuating velocity and tracer concentration are closed using a standard gradient diffusion model (Hinze 1975; Tennekes and Lumley 1971; Seinfeld 1986), as

\[
\langle u' C^x \rangle = -D_{zz} \frac{\partial C}{\partial z} - D_{rr} \frac{\partial C}{\partial r}
\] (2.5)

and

\[
\langle u' C^r \rangle = -D_{rr} \frac{\partial C}{\partial r} - D_{zz} \frac{\partial C}{\partial z}
\] (2.6)

but, CARPT experiments show that

\[
D_{zz} = D_{rr} \sim 0
\] (2.7)

Therefore

\[
\langle u' C^x \rangle = -D_{zz} \frac{\partial C}{\partial z}
\] (2.8)

\[
\langle u' C^r \rangle = -D_{rr} \frac{\partial C}{\partial r}
\] (2.9)

where \(D_{zz}\) and \(D_{rr}\) are the CARPT measured axial and radial turbulent eddy diffusivities, respectively. Therefore, the final form of the model equation is:

\[
\frac{\partial (\varepsilon C)}{\partial t} + \frac{\partial}{\partial z} (\varepsilon u' C) + \frac{1}{r} \frac{\partial}{\partial r} (r \varepsilon u' C) = \frac{1}{r} \frac{\partial}{\partial r} [r \varepsilon D_{zz} \frac{\partial C}{\partial r}] + \frac{\partial}{\partial z} [\varepsilon D_{zz} \frac{\partial C}{\partial z}]
\] (2.10)
Standard boundary conditions are used with zero flux at the wall and at the centerline of the column. For the case with continuous flow of liquid through the column, a zero gradient is assumed at the outlet with injection of tracer at the inlet. Equation 2.10 represents the averaged balance equation for the non-volatile liquid species, and is a transient two dimensional convection-diffusion equation. The phasic (or time) averaging refers to any time interval, which may be small or large.

Multiphase flows in bubble columns are highly transient in nature. Hence the length of the time interval considered in the averaging will affect the type of results obtained. Short time averages involve averaging which is done over a small time interval, large enough to smooth the variations across the interface but small enough to capture some of the transient structures in the flow. With this averaging some of the transient structures in the flow can be captured. These transient structures will vary in nature with the time interval of averaging. On the other hand, long time averaging results in a statistically stationary flow field, which is steady in time, in terms of all the fluid dynamic variables.

Two factors are of concern here in deciding the type of averaging to be considered for the above model equation. First, since the flow phenomena in bubble columns is highly turbulent and random in nature, a quantitative comparison of the fluid dynamic parameters, between model predictions and experimental measurements, can only be made with respect to the statistical properties of the flow field. This immediately implies that time or ensemble averaging is required. Second, since the present model is considered in a two-dimensional axisymmetric domain, the type of boundary conditions used (zero gradient at the centerline) will not permit the computation of physically realistic results describing the transient structures. A true transient behavior can only be represented in a fully three dimensional flow model which can capture the inherent vortical and spiraling motion of the flow in bubble columns.

For these reasons, it is proposed to consider long time averaging for the above model equation. The various averaged quantities in the above equation will hence refer to long time averaged quantities and corresponding closure models (Equations 2.8 and 2.9). CARPT data for the long time averaged liquid velocities, \( u_r \) and \( u_z \), and turbulent diffusivities, \( D_{rr} \) and \( D_{zz} \), along with CT data for the time averaged liquid holdup profile, are used as input parameters to the model.

2.2 Numerical Procedure for Solution of Model Equations

A finite volume (also referred to as the control volume) method has been used to solve the convection-diffusion model (Patankar 1983). In this scheme, the calculation domain is divided into a number of non-overlapping control volumes, such that there is a control volume surrounding each grid point. The governing equations are integrated over each volume, with piecewise profiles for the variation of the dependent variables. This results in the discretization equation containing the values of the dependent variables for a group of grid points. The discretization equation obtained as such allows the conservation principle for a given quantity to be expressed for the finite control volume. The most attractive aspect of this method is that the resulting solution guarantees that the integral conservation of a given quantity is exactly satisfied over a single or group of
control volumes, and therefore over the whole domain. Thus, even the coarse-grid solution exhibits exact integral balances.

2.2.1 Discretization considerations

An implicit scheme is used in time, with upwinding for the convection term. Although the upwind scheme is only first order accurate, it has been shown to have advantages in solving nonlinear systems with steep velocity gradients (Patankar 1980) as in the case of bubble column flows. However, if the physical diffusion process is dominant (i.e. if $D_{zz}$ and $D_{rr}$ are very large), upwind differencing loses its advantages and requires finer discretization. A staggered grid configuration is used, by assigning the scalar variables, namely the concentration and holdup to the cell center and the vector velocity variables and diffusivities to the cell faces (Figure 2.1). Advantages of using the staggered grid configuration, for solution of the momentum balance equations, have been discussed elaborately by Verstaag et al. (1995) and Patankar (1983). For solution of the convection-diffusion equation it poses no special advantage.

Figure 2.1: Variable Locations in a Staggered Grid

The above process of discretization results in a set of linear algebraic equations. Since the model equation is a transient convection-diffusion equation, this results in a sparse matrix. Therefore a direct method is used to solve the system of equations, based on LU decomposition. The model is two dimensional, resulting in extremely large number of equations which depend on the size of the domain studied. The SMPAK\textsuperscript{TM} solver, which uses an effective storage scheme to hold large sparse matrices, is used to solve the equations. This significantly reduces the memory and time (five times lower than a standard solver) for computation. The spacing used in the three coordinates, $\Delta t$, $\Delta z$ and $\Delta r$, are the numerical parameters that need to be considered. Although stability is not a concern since an implicit scheme is used, the issue of accuracy should be examined. For this purpose, several trials are made with increasingly fine discretizations, until an accurate solution is obtained.
There is considerable experimental evidence in the literature, including results from CARPT, which show that in columns of high aspect ratios the time averaged flow pattern is axisymmetric with global liquid recirculation in the column. In a time averaged sense, a large scale liquid circulation exists in the form of a recirculation cell, which occupies most of the column, with respect to height, with liquid ascending along the central core region and descending along the annular region between the core and the walls. A single one dimensional velocity profile is always identified in this recirculation cell, which is in the middle part of the column. Axial variations are evident in the distributor and free surface region, where the liquid turns around. In the middle region, there is evidence that all the other fluid dynamic parameters, such as the turbulent eddy diffusivities and the turbulent stresses are also a function of radial position only.

The computation domain is therefore divided axially into three regions: a distributor zone at the bottom, a fully developed region where the radial liquid velocities are negligible and are considered to be zero, and finally the disengagement zone at the top where liquid turns around. The distributor and disengagement zones are assumed to extend over a height equal to one column diameter, based on experimental considerations. However, varying the height from 1 to 2 times the column diameter does not affect the results significantly (Figure 2.6), especially for column aspect ratios greater than 10. In the distributor zone and the disengagement zone, the domain is discretized only in the radial direction, as shown in Figure 2.2. In both these regions where the radial liquid velocities are significant, it is found that the solution of the equations becomes very sensitive to the radial velocities. The velocities assigned to these regions are therefore fitted to a smooth profile in order to satisfy liquid continuity for each control volume or cell, and therefore the entire domain. In the fully developed middle region, the domain is discretized both radially and axially (Figure 2.2), and the radial liquid velocities are set to zero.

Figure 2.2: Schematic of Column Discretization
The other fluid dynamic variables, i.e., the axial liquid velocity, axial and radial turbulent eddy diffusivities are considered to be a function of radial position only and independent of axial location in the middle section of the column. Experimental data from CT for the gas holdup, is first fitted to the power law expression given by Equation 2.11 to obtain the radial liquid holdup profile, which is then used as an input to the one dimensional liquid recirculation model to obtain an axial liquid velocity profile that fits the experimental data from CARPT measurements under the same operating conditions.

\[
\varepsilon_g = \tilde{\varepsilon}_g \frac{m+2}{m} (1 - c \xi^m), \quad \varepsilon_l = 1 - \varepsilon_g \quad (2.11)
\]

These radial profiles for the liquid holdup and velocity are used as input to the model in the middle fully developed section of the column, along with radial profiles for the axial and radial turbulent eddy diffusivities. Using these calculated profiles for the holdup and velocity ensures continuity to be satisfied in the entire domain. The developed model, as represented by equation 2.10, is used to simulate tracer responses for different cases for which experimental data is available.

### 2.3 Case I: Air-Water System

The model is first tested in a column under operating conditions for which experimental data for the fluid dynamic parameters are directly available. The case considered is the tracer data of Myers et al. (1986), whose experiments were conducted in an air-water system in a column of diameter 19 cm, at a superficial gas velocity of 10 cm/s and liquid velocity of 1 cm/s. The mode of operation, in this case, is therefore a cocurrent bubble column with a continuous flow of liquid and gas. The following boundary conditions are used:

\[
r = 0, \text{ and } r = R; \quad \frac{\partial C}{\partial r} = 0 \quad (2.12 \text{ a, b})
\]

\[
z = 0, \ C(r,0,t) = \delta(t); \quad z = L, \ \frac{\partial C}{\partial z} = 0 \quad (2.12 \text{ c, d})
\]

\[
t = 0, \ C(r,z,0) = 0 \quad (2.13)
\]

A time step of 0.5 sec along with a radial grid size of 0.38 cm and an axial grid size of 1 cm were found to be optimum discretizations. In the end zones, the cell heights are assigned to be equal to the column diameter. In order to solve the model for the present case, CARPT and CT experiments were performed under identical conditions to obtain the input hydrodynamic parameters for the system. Results are shown in Figures 2.3, 2.4 and 2.5, for the one dimensional time averaged axial liquid velocity, liquid holdup profile and turbulent eddy diffusivities, respectively.
In Figure 2.3, the solid circles represent the axial liquid velocity axially averaged in the middle section of the column. The curve is the one-dimensional recirculation model prediction, using the input holdup profile from CT measurements (shown in Figure 2.4) along with a mixing length profile obtained from CARPT data. With these profiles for the liquid velocity and holdup, continuity is satisfied within 98%. The experimental data for the turbulent diffusivities, in Figure 2.5, are directly used as input to the model.
Figure 2.5: One Dimensional Turbulent Eddy Diffusivities: Column Diameter 19 cm, \( U_g = 10 \) cm/s

Using the above parameters as input, the model (i.e. equation 2.10) is solved to predict the overall tracer impulse response of the given system, shown in Figure 2.6. Here, \( E(t) \) is evaluated as follows:

i. The model (via equation 2.10) calculates \( C(r, z=L, t) \).

ii. The mixing cup concentration is calculated by equation (2.14 a).

iii. \( E(t) \) is then calculated by equation (2.14 b).

\[
\bar{C}(z=L, t) = \frac{\int_0^R r \varepsilon u_z C(r, z=L, t) \, dr}{\int_0^R r \varepsilon u_z \, dr} \quad (2.14 \text{ a})
\]

\[
E(t) = \frac{\bar{C}(z=L, t)}{\int_0^\infty \bar{C} \, dt} \quad (2.14 \text{ b})
\]

The comparison between the two dimensional model prediction of the normalized exit mixing cup concentration and the experimental tracer response curve from Myers et al. (1986) (Figure 2.6) suggests that the model provides a good representation of the experimental data. Therefore, a fundamentally based model, with experimental data for the fluid dynamic parameters, is able to capture the overall mixing in the system as described by the tracer residence time distribution (RTD).
2.4 Case II: Interpretation of the AFDU Tracer Data

2.4.1 Experimental Details

The radioactive tracer experiments were conducted by Air Products and Chemicals, Inc. in DOE’s Alternate Fuels Development Unit (AFDU), in LaPorte, Texas, which is a slurry bubble column reactor, to study the backmixing characteristics of the gas and liquid phase in this reactor during methanol synthesis. Powdered methanol catalyst (~ 45 wt % loading) suspended in an 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

\[ CO + 2H_2 \rightleftharpoons CH_3OH \]  

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 may be varied by changing the feed ratio, depending upon process requirements. The presence of \( CO_2 \) is usually required, as it serves to initiate the reaction. A side reaction known to occur is the water gas shift reaction:

\[ H_2 + CO_2 \rightleftharpoons H_2O + CO \]
Based on the above reaction stoichiometry (Equations 2.15 and 2.16), there is a reduction in the volume of the gas due to reaction. 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 flow rate are reported in Table 2.1. 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 flow rate is about the same for all the runs, around - 18 %.

Table 2.1: Experimental Conditions (Temp : 250 °C)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>P MPa</th>
<th>Avg. Gas Holdup</th>
<th>Inlet U_g0 cm/s</th>
<th>Feed Compn. mol %</th>
<th>Conv of CO to MeOH</th>
<th>Inlet Vol. Flow Rate SCFH</th>
<th>Change in Flow Rate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.6</td>
<td>5.2</td>
<td>0.39</td>
<td>25</td>
<td>35.4</td>
<td>50.8</td>
<td>12.7</td>
<td>143121</td>
</tr>
<tr>
<td>14.7</td>
<td>5.2</td>
<td>0.33</td>
<td>14</td>
<td>35.0</td>
<td>50.9</td>
<td>12.7</td>
<td>81151</td>
</tr>
<tr>
<td>14.8</td>
<td>3.6</td>
<td>0.38</td>
<td>36</td>
<td>60.2</td>
<td>24.0</td>
<td>10.3</td>
<td>141690</td>
</tr>
</tbody>
</table>

2.4.2 Gas Holdup Measurements

Holdup measurements within the reactor were made using two techniques: 1. Differential Pressure measurements (DP) and 2. Nuclear Density Gauge (NDG) measurements. From the experiments conducted, there is no definite trend for the axial gas holdup at different velocities. In addition, discrepancies exist between the two techniques.

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

$$\rho_g = \frac{\Delta P}{\Delta z}$$  \hspace{1cm} (2.17)

where

$$\rho = \rho_l \epsilon_l + \rho_g \epsilon_g$$  \hspace{1cm} (2.18)

The subscripts ‘l’ and ‘g’ refer to the slurry and gas phase, respectively. Based on experimental evidence 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 1995b). Therefore, from here on the terms 'liquid' and 'slurry' are used interchangeably. The density of the gas phase is very small when compared with that of the slurry, and hence the second term in Equation 2.18 is usually neglected. Equation 2.18 in conjunction with Equation 2.17 can be used to calculate the average holdup between the two measurement sections (Figure 2.7). Assuming that there
is no axial variation of holdup between the measurement sections, the volume average holdup calculated from DP measurements yields a cross-sectional mean holdup, $\bar{\varepsilon}_g$:

$$\bar{\varepsilon}_g = 2 \int_0^1 \varepsilon_g(\xi) \, d\xi$$

(2.19)

Nuclear Densitometry (NDG) is a noninvasive method in which a narrow beam of radiation (γ ray) emitted through the center of the column, with the source on one side (Figure 2.7), is detected using a detector on the opposite side. Such a single chordal measurement obtained across the centerline (i.e. diameter) of the column results in a chordal average, $\hat{\varepsilon}_g$, defined by

$$\hat{\varepsilon}_g = \int_0^1 \varepsilon_g(\xi) \, d\xi$$

(2.20)

which is not necessarily representative of the cross-sectional mean.

Therefore, there is a discrepancy between the average holdups measured by DP and NDG. Using Equation 2.11 for the radial gas holdup profile, the two averages $\bar{\varepsilon}_g$ and $\hat{\varepsilon}_g$ are found to be related by the following expression:

$$\frac{\hat{\varepsilon}_g}{\bar{\varepsilon}_g} = \frac{(m+2)(m+1-c)}{(m+1)(m-2c+2)}$$

(2.21)
Since experimental measurements of \( \varepsilon_g \) and \( \overline{\varepsilon}_g \) are available from NDG and DP, the axial average of these values is used to extract the void fraction exponent \( m \) and \( c \) in Equation 2.11, given above, which then provide the description of the radial void fraction profile existing in the column. Using the average gas holdup, \( \overline{\varepsilon}_g \), in the entire reactor as measured by DP, the resulting void fraction profiles, calculated for all the three process conditions are shown in Figure 2.8.

![Figure 2.8: Radial Gas Holdup Profiles Calculated from Global Gas Holdup Measurements (DP and NDG) in the AFDU During Methanol Synthesis](image)

### 2.4.3 Tracer Experiments

A schematic of the AFDU slurry bubble column reactor is shown in Figure 2.9. 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 \( \mu \)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 2.9. The injections made at 4.5'' (11.4 cm) from the wall are 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 in the time averaged sense.
Radiation measurements from the vapor and liquid tracers were made using thirty 2" by 2" NaI scintillation detectors positioned outside the column, at various axial levels, as shown in Figure 2.9. Sets of four detectors were placed at 90 degree angles at seven axial locations. In addition, detectors were placed at the inlet and outlet of the 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.

![Figure 2.9: Schematic of Reactor for Tracer Experiments](image)

The detectors were shielded on their sides thereby allowing only the front circular surface of the detectors to be exposed to radiation. With this configuration, the spatial range from which a detector received most of its radiation is assessed. Details of these calculations are discussed in the fourth quarterly report for DOE (Degaleesan et al. 1996b). It has been shown that most of the intensity recorded at a detector, shielded on its sides, comes from a slice of volume at the given axial level of the detector. For analyses purposes only the tracer from the cross-section of the reactor at the axial location of the detector is considered here.
2.4.4 Model Parameters

In order to use the present model to predict liquid tracer distribution in the column it is necessary to evaluate the model parameters. Experimental information exists only for the average gas holdup. From the holdup measurements using DP and NDG, there is an axial variation of the gas holdup in the reactor due to reaction. This variation is not very significant as far as the slurry phase mixing is concerned, and as a first approximation, the average gas holdup in the reactor as obtained from DP measurements is considered. The corresponding radial gas holdup profiles calculated using results from DP and NDG are shown in Figure 2.8. Information on the other fluid dynamic variables, namely, the liquid velocity profile and turbulent eddy diffusivities does not exist. Hence, the preliminary scale-up rules and characterization methodology were used to evaluate the mean liquid recirculating velocity and average turbulent eddy diffusivities. Since the present experimental conditions involve high pressure and a slurry system, this significantly alters the overall gas holdup in the reactor (Wilkinson et al. 1992), which for the present case results in gas holdups higher than that at atmospheric conditions for air-water systems. Knowing the average gas holdup in the reactor (Table 2.1) and using Equation 2.22, the equivalent gas velocity, \( U_{ge} \), for the three operating conditions is calculated (shown in Table 2.3).

\[
\varepsilon_g = 0.07 U_g^{0.474 - 0.000626 D_c} \quad \text{(in cgs units)} \quad (2.22)
\]

For Run 14.6, \( U_{ge} = 47 \) cm/s, which is considerably higher than the original inlet gas velocity of 25 cm/s. The estimated \( U_{ge} \) is used in Equations 2.23 to 2.27, to evaluate the mean recirculation velocity and average axial and radial turbulent diffusivities under the existing conditions in the AFDU.

\[
\bar{u}_{rec} \text{ (cm/s)} = 2.2 D_c^{0.4} U_g^{0.4} \quad (2.23)
\]

\[
\overline{D}_{zz} = 2 \int_0^1 D_{zz} (\xi) \xi d\xi \quad (2.24)
\]

\[
\overline{D}_{rr} = 2 \int_0^1 D_{rr} (\xi) \xi d\xi \quad (2.25)
\]

\[
\overline{D}_{zz} \text{ (cm}^2 \text{/s)} = -\frac{2325}{D_c^{0.8}} + 106.6 D_c^{0.3} U_g^{0.3} \quad (2.26)
\]

\[
\overline{D}_{rr} \text{ (cm}^2 \text{/s)} = -\frac{350}{D_c^{0.8}} + 13.0 D_c^{0.3} U_g^{0.3} \quad (2.27)
\]
The liquid recirculating velocity profile, $u_z(r)$, is then calculated by the procedure outlined in Figure 2.10, using as input the holdup profile estimated from DP and NDG measurements (Figure 2.8), and the knowledge of the mean recirculation velocity, $\bar{u}_{\text{rec}}$.

Figure 2.10: Determination of the Liquid Recirculating Velocity Profile, $u_z(r)$, with knowledge of $\varepsilon_z(\xi)$ and $\bar{u}_{\text{rec}}$

The liquid (slurry) recirculation velocity profile, evaluated in this manner is shown in Figure 2.11, for Run 14.6.

Figure 2.11: Calculated Axial Liquid Velocity Profile for Run 14.6, in the AFDU Reactor During Methanol Synthesis
The centerline velocity calculated is of the order of 1 m/s. Due to the large area and higher liquid holdup near the wall, the magnitude of the maximum downward liquid velocity is much lower than the centerline velocity, in order to satisfy mass balance for the liquid (in batch mode). The radial profiles for the axial and radial eddy diffusivity are calculated from Equations 2.28 and 2.29, respectively, along with the estimated average values (Table 2.3).

\[
D_{\infty}(\xi) = D_{ss}P_4
\]

where
\[
P_4 = -3.4979\xi^4 + 3.2704\xi^3 + 0.4693\xi^2 + 0.005035\xi + 0.5847
\]

(2.28)

\[
D_r(\xi) = D_rP_2
\]

where
\[
P_2 = -5.0929\xi^2 + 5.0717\xi + 0.1653
\]

(2.29)

The profiles for the axial and radial eddy diffusivities, calculated in this manner for Run 14.6 are shown in Figures 2.12 and 2.13, respectively.

Heat exchanger tubes are present in the AFDU reactor for cooling the medium. There are 24 one inch (O.D.) tubes, which occupy approximately 7.5% of the cross-sectional area of the reactor, and extend over the entire length of the dispersion. The effect of the heat exchanger tubes are accounted for only with regard to the radial turbulent eddy diffusivity, since the presence of these tubes will physically reduce the radial length scales of turbulence. Liquid recirculation and the axial eddy diffusivity are assumed to be affected to a lesser extent, and for the present calculations these effects are neglected.

Figure 2.12: Calculated Axial Eddy Diffusivity Profile for Run 14.6, in the AFDU Reactor During Methanol Synthesis
A cross-sectional view of the reactor in the presence of these tubes is shown in Figure 2.14. The tubes are present in two annular rings about the center of axis of the reactor, near the region of flow inversion, and will affect the radial turbulent diffusivities in this region by restricting the radial length scale of turbulence in this region. This is accounted for by considering the characteristic spacing between the tubes, which is about 2.25\" (5.7 cm), as an effective diameter and estimating the average radial diffusivity for this diameter (5.7 cm).
Equation 2.27, which was originally developed for large diameter columns (> 10 cm), is modified by retaining the 0.3 power dependence of \( D_{rr} \) on \( D_c \) and \( U_g \) (Equation 2.27) for smaller column diameters. Considering the CARPT data for the 14 cm diameter column as a reference, the following equation for the radial diffusivity for \( D_{ceff} = 5.7 \) cm is used:

\[
D_{rr(Dc=5.7)} = \left( \frac{5.7}{14.0} \right)^{0.3} D_{rr(Dc=14)}
\]

The above equation results in a radial diffusivity of 35 cm\(^2\)/s. The estimated value of the radial diffusivity in the region of the tubes, results in a modified profile for the radial eddy diffusivity, denoted by the dashed line in Figure 2.13. This represents a first approximation in accounting for the effect of heat exchanger tubes in the AFDU reactor. Thereby, all the input fluid dynamic parameters to the model are evaluated.

### 2.4.5 Simulation Results

The initial and boundary conditions are given below. Since the liquid is in batch mode, zero flux conditions are applied at all the boundaries:

\[
\begin{align*}
    r = 0, r = R; \quad & \frac{\partial C}{\partial r} = 0 \quad (2.31) \\
    z = 0, z = L; \quad & \frac{\partial C}{\partial z} = 0 \quad (2.32)
\end{align*}
\]

The initial condition is assigned according to the location of tracer injection during an experiment. In the actual tracer experiment, the injection is made locally at a certain \( (r_i, \theta_i, z_i) \). However, since the model is two dimensional, for modeling purposes the injection is considered to be made in an annular ring \( (r_i, z_i) \). The initial condition is given as:

\[
\begin{align*}
    t = 0; \quad & C(r,z,t) = f_i(t) \quad r = r_i, z = z_i \\
    & = 0 \quad r \neq r_i, z \neq z_i \quad (2.33)
\end{align*}
\]

\( f_i(t) \) describes the pulse of tracer injected (close to an impulse function), and is fitted to the response of the detector close to the location of injection. For a given experimental condition, four tracer experiments were carried out with four different locations of the injection point. These are \( (r_i, z_i) \) are given in cm) given in Table 2.2.

<table>
<thead>
<tr>
<th>Table 2.2: Positions of Tracer Injection in the Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_i ) (cm)</td>
</tr>
<tr>
<td>Wall injection at N1</td>
</tr>
<tr>
<td>Center injection at N1</td>
</tr>
<tr>
<td>Wall injection at N2</td>
</tr>
<tr>
<td>Center injection at N2</td>
</tr>
</tbody>
</table>
In order to compare the experimental results with model predictions, the individual detector responses measured by the four detectors at each axial level are averaged to yield an averaged detector response at each detector level. Averaging is done since the present model is only two dimensional, and cannot distinguish any angular variations in tracer concentration. Responses of the individual detectors at two axial levels indicate that such an (angular) averaging of the four detector responses at a given axial location is a reasonable approximation. The averaged experimental detector responses measured at the seven detector levels, for the wall injection at level N1 in Run 14.6, are shown in Figure 2.15. It is to be noted that the various detector level responses, in Figure 2.15, do not all show equal measurements at large times, which is what is expected if the tracer is eventually uniformly distributed in the reactor. The reason for this is the improper normalization of the detector responses. Specific details and reasons for this are shown elsewhere (Degaleesan, 1997), where suggestions have been made to improve the quality of the tracer data. Due to this, the experimental detector responses cannot be quantitatively compared with the model predictions of the tracer distribution in the column. Only the characteristic mixing times as measured by the times of the peaks of the curves can be compared.

The radiation intensity emitted, per unit volume, by the tracer is directly proportional to the tracer concentration. Since the experiments involve radioactive tracer, the measurements, as detected by the scintillation detectors, represent neither local nor average tracer concentration, but the attenuated cumulative tracer concentration in a given cross-sectional plane.
Figure 2.15: (b) Experimental Detector Responses for Wall Injection at Level N1 for Run 14.6

The detectors are shielded on their sides. Hence, most of the radiation detected, comes from the cross-sectional plane at the axial level of the detector. In order to compare the model predictions with the averaged experimental detector response, the local tracer concentration, in a two dimensional axisymmetric domain, \( C(r,z,t) \), is first integrated along the radial path \( r \) through the column center, using the Beer-Lambert law, to yield a representative radioactive tracer response at a given axial location, \( \bar{C}(z,t) \). Therefore,

\[
\bar{C}(z,t) = \int_{r=0}^{r=R} C(r',z,t) \exp \left( - \int_{r}^{R} \mu_{\text{eff}}(r'') dr'' \right) dr' \tag{2.34}
\]

where

\[
\mu_{\text{eff}}(r) = \mu_g \varepsilon_g(r) + \mu_d \varepsilon_d(r) \tag{2.35}
\]

\( \bar{C}(z,t) \) represents the response measured by the shielded and collimated detectors, which have been used for the present experiments. Since the detectors are collimated, the only significant contribution of the radiation that is measured comes from the tracer along the radial path \( r \) through the column center. Hence, the contribution from the angular and axial direction is neglected in the calculations. The \( Mn^{56} \) particles emit \( \gamma \) radiation at 0.85 MeV. The catalyst loading in the reactor for all the three runs was kept at a constant of 40 % by weight. For a given composition of the catalyst particles resulting in a bulk
density $\rho_s = 2.02 \text{ gm/cm}^3$, and liquid (hydrocarbon oil) density of $\rho_l = 0.667 \text{ gm/cm}^3$, the linear attenuation coefficient of the slurry at 0.85 MeV is $\mu_{sl} = 0.06728 \text{ cm}^{-1}$, and for the gas is $\mu_g = 1.0e^{-5} \text{ cm}^{-1}$.

Figures 2.16 and 2.17 show the comparison of model predictions with the experimental tracer responses for the wall injection at level N1 for Run 14.6. The calculated as well as the measured responses have been normalized with respect to their maximum for the sake of comparison. The results show that the model is able to capture the characteristic overshoots as seen by the detector responses at all the measurement levels. A quantitative comparison of the tracer responses is unfortunately not possible due to the fact that the experimental data do not level off at large times at the same height for all the detectors.

Figures 2.18 and 2.19 show the comparison between model predictions and experimental detector responses for the center injection at level N2, and Figure 2.20 for the center injection at level N1 (Figure 2.9). Experimental data at Levels 5, 6 and 7 for center injection at N1 and all levels for the wall injection at N2, in Run 14.6 were not available for comparison. For all the different locations of injection, since the operating process conditions are the same, the input model parameters are fixed. Therefore, with a consistent set of model parameters the model is able to capture the internal liquid (slurry) and overall mixing in the AFDU reactor, as measured by the detector responses at all the seven locations. Table 2.3 shows the list of the average input parameters calculated for all the three experimental conditions considered. The radial profiles for liquid velocity and turbulent diffusivities are obtained using the developed scale-up procedure.
Figure 2.16: Comparison of Model Prediction with Experimental Detector Responses for Wall Injection at Level N1, Run 14.6
Figure 2.17: Comparison of Model Prediction with Experimental Detector Responses for Wall Injection at Level N1, Run 14.6
Figure 2.18: Comparison of Model Prediction with Experimental Detector Responses for Center Injection at Level N2, Run 14.6
Figure 2.19: Comparison of Model Prediction with Experimental Detector Responses for Center Injection at Level N2, Run 14.6
Figure 2.20: Comparison of Model Prediction with Experimental Detector Responses for Center Injection at Level N1, Run 14.6
Table 2.3: List of Estimated Average Fluid Dynamic Parameters for LaPorte AFDU during Methanol Synthesis

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$U_{g0}$ cm/s</th>
<th>$\bar{g}$</th>
<th>$U_{ge}$ cm/s</th>
<th>$\bar{u}_{rec}$ cm/s</th>
<th>$\bar{D}_{zz}$ cm$^2$/s</th>
<th>$\bar{D}_{rr}$ cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.6</td>
<td>25.0</td>
<td>0.39</td>
<td>47.4</td>
<td>47.6</td>
<td>965.2</td>
<td>114.1</td>
</tr>
<tr>
<td>14.7</td>
<td>14.0</td>
<td>0.33</td>
<td>33.1</td>
<td>41.2</td>
<td>854.0</td>
<td>100.7</td>
</tr>
<tr>
<td>14.8</td>
<td>36.0</td>
<td>0.38</td>
<td>44.7</td>
<td>46.5</td>
<td>946.0</td>
<td>111.3</td>
</tr>
</tbody>
</table>

It is to be noted that while Runs 14.6 and 14.7 are at a higher pressure of 52 atm, Run 14.8, which is carried out at a higher superficial gas velocity of 36 cm/s, is at a lower pressure of 36 atm. The effect of pressure is evident in the gas holdup measurements, which indicate a lower holdup for Run 14.8 in comparison with Run 14.6, although it is operated at a higher superficial gas velocity.

The results of the model predictions for the various injections of Runs 14.7 and 14.8 are shown elsewhere (Degaleesan, 1997). It is clear from these figures that the model is, in general, able to correctly predict the mixing patterns within the reactor shown by the detector responses. By using a single set of input parameters (Table 2.3) for a given experimental condition, the model is able to capture the mixing patterns for the various injection locations, as measured by detectors at all levels. This substantiates using the proposed convective-diffusion model to describe liquid mixing based on liquid recirculation and turbulence, and suggests that the preliminary scale-up rules developed result in a good estimate of the input fluid dynamic model parameters. Such comparisons indirectly justify the proposed methodology of characterization of churn-turbulent bubble columns, by using the gas holdup in the reactor as a means of accounting for the effects of pressure, solids and other system parameters.

The approach used for evaluation of the model parameters stresses the importance of measurement and prediction of the gas holdup and its radial distribution in the column. Several correlations exist in the literature that account for the effects of pressure and liquid properties on overall gas holdup. However, there is no good agreement between the correlations, even at atmospheric pressure. Table 2.4 shows the correlations used to estimate the transition holdup and transition gas velocity based on the bi-modal bubble size distribution in churn-turbulent flow. Measurements of large bubble holdup and rise velocities, using dynamic gas disengagement (DGD) under different process conditions, have resulted in correlations listed in Table 2.5.

A combination of the correlations of Wilkinson et al. (1992) for the transition holdup and velocity (1T. in Table 2.4), along with that of Krishna and Ellenberger (1996) for the dilute phase holdup (2L. in Table 2.5), seems to yield the best estimates for the global gas holdup in comparison to experimental data in the AFDU during methanol synthesis (Table 2.1). The slurry phase properties existing under experimental conditions in the AFDU are considered, instead of the liquid (except for the surface tension, $\sigma$, since no data was available for the slurry), resulting in gas holdups reported in Table 2.6. The...
Table 2.4: Correlations for Estimating the Transition Holdup and Transition Gas Velocity based on the Bi-modal Bubble Size Distribution in Churn-Turbulent Flow (SI units)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reference</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1T.</td>
<td>Wilkinson et al. (1992)</td>
<td>( \varepsilon_{\text{trans}} = 0.5 \exp(-193 \rho_g^{-0.61} \mu_l^{0.5} \sigma^{0.11}) )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \frac{V_{\text{small}} \mu_l}{\sigma} = 2.25 \left( \frac{\mu_l^4 \rho_l}{\rho_g \sigma^3} \right)^{0.273} \left( \frac{\rho_l}{\rho_g} \right)^{0.03} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( U_{\text{trans}} = \varepsilon_{\text{trans}} V_{\text{small}} )</td>
</tr>
<tr>
<td>2T.</td>
<td>Reilly et al. (1994)</td>
<td>( \varepsilon_{\text{trans}} = 4.457 \sqrt{\frac{\rho_g}{\rho_l}} \sigma^{0.12} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \frac{V_{\text{small}}}{1} = \frac{1}{2.84 \rho_g^{0.04}} \sigma^{0.12} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( U_{\text{trans}} = \varepsilon_{\text{trans}} V_{\text{small}} (1 - \varepsilon_{\text{trans}}) )</td>
</tr>
</tbody>
</table>

Table 2.5: Correlations for Estimating the Large Bubble Holdup and Overall Holdup based on the Bi-modal Bubble Size Distribution in Churn-Turbulent Flow (SI units)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reference</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1L.</td>
<td>Wilkinson et al. (1992)</td>
<td>( \frac{V_{\text{lb}} \mu_l}{\sigma} = \frac{V_{\text{small}} \mu_l}{\sigma} + 2.4 \left( \frac{U_g - U_{\text{trans}}}{\mu_l} \right)^{0.757} \left( \frac{\mu_l^4 \rho_l}{\rho_g \sigma^3} \right)^{0.077} \left( \frac{\rho_l}{\rho_g} \right)^{0.077} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \varepsilon_{\text{lb}} = \frac{(U_g - U_{\text{trans}})}{V_{\text{lb}}} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \bar{\varepsilon}<em>g = \varepsilon</em>{\text{trans}} + \varepsilon_{\text{lb}} )</td>
</tr>
<tr>
<td>2L.</td>
<td>Krishna et al. (1996)</td>
<td>( \varepsilon_{\text{lb}} = \frac{0.268}{D_e^{0.18}} (U_g - U_{\text{trans}})^{0.58} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \varepsilon_g = \varepsilon_{\text{lb}} + \varepsilon_{\text{trans}} (1 - \varepsilon_{\text{lb}}) )</td>
</tr>
</tbody>
</table>
estimated values of the overall gas holdup show reasonable agreement with the measured average holdup, especially at the two higher gas velocities. The estimated transition gas velocity from bubbly flow to churn-turbulent flow, however, seems rather low when compared with experimental results for atmospheric air-water systems. This is partly due to the high values of the holdup of the small bubbles. The high holdup of small bubbles (transition holdup), which is the same for Runs 14.6 and 14.7, results in a higher value of the gas holdup for Run 14.7 ($U_g = 14.0$ cm/s), when compared with experimental measurements.

The correlations of Wilkinson et al. (1992) yield much higher values for the large bubble holdup (1L. in Table 2.5). This may be caused by the fact that his correlation does not take into consideration the effect of column diameter on large bubble holdup (which is supposed to decrease with increase in column diameter). Reilly's correlation (2T. in Table 2.4), which resulted in moderate estimates of the transition gas velocity and holdup under atmospheric conditions, greatly overpredicts the transition holdup for the present high pressure data. For example, for Run 14.6, the transition holdup calculated from Reilly's correlation gives $\varepsilon_{trans} = 0.58$, which is much higher than the overall gas holdup measured in the reactor, ~ 0.4. This points to the disparity in the available correlations, which perform well only under a certain range of operating and process conditions.

Table 2.6: Estimation of Global Gas Holdup in the Reactor Using Correlations from the Literature

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$U_{g0}$ cm/s</th>
<th>Press. MPa</th>
<th>Wilkinson (1992)</th>
<th>Krishna et al. 1996</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon_{trans}$</td>
<td>$U_{trans}$ (m/s)</td>
<td>$\varepsilon_L$</td>
<td>$\bar{\varepsilon}_g$</td>
<td>$\bar{\varepsilon}_f$</td>
</tr>
<tr>
<td>14.6</td>
<td>25.0</td>
<td>5.2</td>
<td>0.28</td>
<td>0.056</td>
<td>0.120</td>
</tr>
<tr>
<td>14.7</td>
<td>14.0</td>
<td>5.2</td>
<td>0.28</td>
<td>0.056</td>
<td>0.073</td>
</tr>
<tr>
<td>14.8</td>
<td>36.0</td>
<td>3.6</td>
<td>0.24</td>
<td>0.049</td>
<td>0.160</td>
</tr>
</tbody>
</table>

Correlations such as those presented above are useful in estimating the global gas holdup. There is still no way (empirical or theoretical) of predicting the holdup profiles in the reactor. For such situations, global holdup measurements from DP and NDG prove to be helpful in calculating the gas holdup profile, as discussed earlier.

2.5 Summary

The two dimensional axisymmetric convection-diffusion model provides a good representation of internal liquid mixing in bubble columns. Although the instantaneous flow in bubble columns is highly turbulent and transient in nature, and the time-averaged velocity profile does not exist in the column at any instant in time, by properly accounting for the churn-turbulent flow via the turbulent eddy diffusivities, the model is able to capture, in a statistical sense, the large scale transient flow patterns in the column, thereby yielding the characteristic overshoots seen by the detectors at various axial locations. This represents the meso-scale and macro-scale mixing in the column, which is of importance for modeling bubble column reactors. Results also imply that CARPT measurements for the turbulent eddy diffusivities can provide suitable closure for the
\( \langle u'C \rangle \) terms appearing in the original balance equations. Such model predictions for liquid mixing in bubble columns are the first of their kind, and are truly 'predictions', involving no fitting parameters. The developed model, along with experimental input for the model parameters, therefore allows us to study the influence of fluid dynamics on liquid mixing in bubble columns.

The developed scale-up strategy reported in the 12\textsuperscript{th} and 13\textsuperscript{th} quarterly reports (Degaleesan, 1997) for evaluating the model parameters in the AFDU slurry bubble column reactor during methanol synthesis, results in fairly good predictions of the characteristic mixing times within the column as measured by the radiation detectors at various axial locations. This indirectly substantiates the proposed methodology of using the gas holdup in churn-turbulent flows, at sufficiently high gas velocities, for characterizing the systems of interest.

2.6 References


