Hydrodynamics and Mass Transfer in Bubble Columns

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Hydrodynamics and Mass Transfer in Bubble Columns
by
Onkar N. Manjrekar

A dissertation presented to the
Graduate School of Arts & Sciences
of Washington University in
partial fulfillment of the
requirements for the degree
of Doctor of Philosophy

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Nomenclature

\( a \) Specific interfacial area, \( \text{cm}^2/\text{cm}^3 \)
\( c \) Constant in the holdup radial profile correlation, dimensionless
\( C \) Concentration
\( C_g \) Concentration of a species in the gas phase
\( C_l \) Concentration of a species in the liquid phase
\( C_{l,0^*} \) Dissolved oxygen concentration in liquid saturated by air
\( C_{l,l^*} \) Dissolved oxygen concentration in liquid saturated by oxygen-enriched air
\( d_t \) Column diameter
\( d_b \) Bubble diameter
\( d_p \) Particle diameter
\( D \) Dispersion coefficient
\( D_{AB} \) Gas diffusivity
\( H \) Henry’s constant
\( H_0 \) Static height of the bed
\( H_l \) Dynamic height of the bed
\( k_l \) Liquid side mass transfer coefficient
\( k_{la} \) Liquid side volumetric mass transfer coefficient
\( k_{lad} \) Liquid side volumetric mass transfer coefficient based on dispersion volume
\( k_{lal} \) Liquid side volumetric mass transfer coefficient based on liquid phase volume
\( K_{\text{sensor}} \) Sensor constant of the probe
\( n \) Steepness factor of the radial profiles, dimensionless
\( N \) The total number of gas liquid interfaces passing by the probe during the measurement time
\( P \) Pressure
\( P_e \) Peclet number
\( R \) Radius of the column
\( r \) Distance from the center of the column
\( t \) Time
\( u_g \) Superficial gas velocity
\( u_l \) Superficial liquid velocity
\( V \) Volume
\( v \) Magnitude of bubble velocity cm/sec
\( T_i \) The time interval that Tip \( i \) spend in the bubble (s)
\( \Delta t_i \) Time interval between bubble hitting central tip \( T_0 \) and hitting tip \( T_i \) (s)
\( \Delta t \) Measurement time (s)
\( x_i, y_i, z_i \) The co-ordinates of the tip 1, 2 and 3
Subscripts

avg Average
exp Experimental
g Gas phase
i Counter
l Liquid
0 Central tip
1 Tip one
2 Tip two
3 Tip three

Greek symbols

$\varepsilon_g$ Gas phase holdup
$\zeta$ Dimensionless radius
$\beta$ The angle between the normal of the bubble’s symmetry plane to the probes’ axial direction
$\gamma$ The angle between the projection of the normal vector on the xy plane to the axis x
$\theta$ The angle of the bubbles velocity vector to the probe’s axial direction
$\phi$ The angle between the bubble velocity vector and the normal vector of the symmetry plane of the bubble
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Dedicated to
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ABSTRACT OF THE DISSERTATION

Hydrodynamics and Mass Transfer in Bubble Columns

by

Onkar N Manjrekar

Doctor of Philosophy in Energy, Environmental and Chemical Engineering

Washington University in St. Louis, 2016

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Bubble columns and slurry bubble columns are multiphase reactors used for a wide range of applications in the biochemical, chemical, petrochemical, and metallurgical industries. In spite of their widespread usage, the scale-up of bubble columns remains an ongoing challenge. Various scale-up approaches, based on concepts ranging from ideal mixing to complex 3-D multiphase CFD models, have been used for assessing the effect of column size and gas and liquid flow rates on column hydrodynamics and reactor performance. Among these approaches, phenomenological models based on either single-class or multi-class bubbles that were validated on cold flow systems have been successful in predicting the residence time distributions of gas and liquid in pilot-scale bubble columns (Chen et al., 2004) (Gupta, 2002). However, such models are not entirely predictive, since they are validated using columns having the same size as hot operating units. To provide better predictive capability, we need prior knowledge of local hold-up, transport coefficients, and bubble dynamics. This dissertation provides an improved understanding of the key design parameters (gas hold-up, volumetric mass transfer coefficients, gas-liquid interfacial area, and their spatial distribution) for predictive scale-up of bubble columns.
In this work, a 4-point optical probe is used to estimate local gas hold-up and bubble dynamics (specific interfacial area, frequency, bubble velocity, and bubble chord-lengths) and their radial profiles in a cold-flow slurry bubble column and a bubble column photo-bioreactor. Along with local bubble dynamics, the effect of superficial gas velocity on volumetric mass transport coefficients in several sizes of bubble columns, with and without internals, and in slurry bubble columns and photo-bioreactors are studied.

Key findings:

- In the bubbly flow regime, bubble dynamics in photo-bioreactors with suspended algae were dominated by the physicochemical properties of the liquid, as distinguished from the churn-turbulent flow regime in the slurry bubble columns, where bubble dynamics were mainly affected by turbulent intensities.

- In the bubbly-flow regime, volumetric mass transfer coefficients increased with an increase in superficial gas velocity. However, in the churn-turbulent flow regime, they approached a constant value with an increase in the superficial gas velocity.

- A new methodology was proposed to identify the flow regime from optical probe signals based on the support vector machine algorithm, which can uniquely classify flow regimes for various systems on a single flow regime map.

- A new model for the liquid phase mixing, that with a proper choice of the mass transfer coefficients enables a good match of the predicted and measured tracer response is described. This model provides a better prediction of volumetric mass transfer coefficients than the currently used well mixed model for the liquid phase (CSTR).
The dissertation improves the fundamental understanding of the connection between bubble dynamics and mass transfer. Using the 4-point optical probe as a tool, it demonstrates a connection between bubble dynamics and volumetric mass transfer coefficients. Present work addresses the need of industries to have a method that can be used as an online process control tool to identify flow regime, this method has been tested at cold flow conditions and needs to be implemented at hot flow conditions. The parameters (radial distributions of gas hold-up, bubble velocities, and volumetric mass transfer coefficient) that are evaluated in the present work can be used to validate phenomenological models and CFD results at cold flow conditions, which can later be combined with process chemistry to accomplish scale-up (Chen et al., 2004).

The open literature on multiphase reactors is mainly limited to cold flow condition, and techniques such as the optical probe need to be extended to hot flow conditions. The optical probe described here can withstand high temperature and pressure, but for hot flow conditions it requires a better binding agent to hold the probe tips together, one that will not dissolve in industrial solvents.
Chapter 1
Introduction

1.1 Motivation

Bubble columns (BC) are cylindrical vessels containing liquid through which gas is bubbled. The liquid can be either in batch mode or continuous flow. When solids (typically catalyst particles) are present in the liquid phase, the column is called a slurry bubble column (SBC). Bubble columns have the distinct advantages of good heat and mass transfer coefficients, ease of construction, no moving parts, and a low pressure drop (Kantarci et al., 2005; Wang et al., 2007a). Due to these advantages, they are used for wide range of practical process applications, such as Fischer-Tropsch (FT) synthesis, liquid phase methanol synthesis, biochemical processing, photo-bioreaction, wet-air oxidation, hydrogenation, oxidation, and effluent treatment (Azzopardi et al., 2011; Deckwar, 1992; Krishna and Sie, 2000; Nigam and Schumpe, 1996; Wang et al., 2007a). Bubble columns have an advantage over other reactor types in processing exothermic reactions and slow reactions in which the liquid phase mass transfer is limiting (Levenspiel, 1999).

Nevertheless, scaling up a BC/SBC is difficult, due to the complex gas-liquid hydrodynamic interaction (Dudukovic, 2010; Shaikh and Al-Dahhan, 2013b). Over the past 50 years, bubble columns have been studied by several researchers to develop successful scale-up methodologies. However, successful scale-up of bubble columns is still an ongoing challenge (Dudukovic, 2002; Dudukovic, 2009; Dudukovic and Mills, 2014). A robust approach for scale-up of bubble columns requires a multiscale approach connecting local gas-liquid hydrodynamics to observed macroscale phenomena (Dudukovic, 2010) (see Figure 1-1).
The phenomenological models developed at the Washington University Chemical Reaction Engineering Laboratory (CREL) were successful in predicting gas and liquid phase mixing in pilot scale bubble columns (Chen, 2004; Degaleesan, 1997; Gupta et al., 2001a). These phenomenological models are based on a single liquid recirculation cell superimposed on axial and radial eddy diffusivities that exist in bubble columns as a consequence of the non-uniform gas holdups observed in these reactors (Devanathan et al., 1990; Kumar et al., 1997). In phenomenological models based on single and multi-class bubbles, the liquid stream was compartmentalized into liquid moving upward from the center of the column and liquid moving downward near the walls (Gupta et al., 2001a). It was assumed that the liquid streams moving upward and downward exchange material (see Figure 1-2). To interpret gas mixing, the gas velocity profile was derived under the assumption that some of the gas was drawn downwards by the liquid at near wall regions. Details of these models were provided by Degaleesan (1997) for liquid phase mixing and Gupta et al. (2001a) for gas phase mixing.
The phenomenological models based on single and multi-class bubbles account for accumulation, dispersion, convection, and exchange between upward and downward flowing gas and liquid, the reaction (if any), and the mass transfer of the species. The gas/liquid velocity profiles were obtained by using a 1-D recirculation model with appropriate closures (Gupta et al., 2001a; Hamed, 2012a).

To predict reactor performance using phenomenological models based on single and multi-class bubbles, we need to know several parameters, such as the gas holdup (overall and spatially distributed), eddy diffusivities, mass transfer confident, exchange coefficients, and the average gas/liquid velocity profile. Obtaining these parameters under process conditions is challenging, and has not been completely addressed due the difficulty of measurement and quantification of multiphase flows under process conditions. Degaleesan (1997), Gupta et al. (2001b), and Chen et al. (2006) used CARPT-CT at CREL to obtain these parameters. They used an air-water system and column with the same diameterr as the pilot-scale column to validate the phenomenological model at cold flow conditions. The cold flow model successfully predicted the residence time...
distributions of gas and liquid in hot flow in pilot-scale bubble columns used for DME, methanol, and FT synthesis (Chen et al., 2006). Without any fitting parameters, the validated model was able to predict tracer responses in both gas and liquid phase. To extend the usefulness of these models to columns of other diameters operating under different conditions, we need to know the model parameters used for validation of the model at various process conditions.

Along with the phenomenological models, Chen has elegantly demonstrated how a multi-scale approach can be used to predict the performance of a pilot scale reactor (Chen et al., 2004, 2005). In a complete 3D Euler-Euler model, he implemented a population balance approach in which the bubble population balance equation was solved along with the flow field. In this model, the bubble breakup rates, which were estimated from models that considered the breakup of a single bubble in mildly shearing or elongation flow fields, had to be enhanced 10-fold to match experimental results. This need for adjustment demonstrates that even after taking into account a detailed mechanistic model, the overall model still needed the support of experimental data to be useful for design purposes.

To summarize, both phenomenological models and detailed CFD models require validation with experimental data before they can be used to predict reactor performance. One of the objectives of the present work is to extend our experimental knowledge of these parameters for validation.

1.2 Objectives

The major thrust of this work is to advance the understanding of the connection between bubble dynamics and volumetric mass transfer coefficients, and to provide data at cold flow process conditions that can be used to validate CFD models and phenomenological models for predicting
scale-up. In addition, this work also aims to develop a process for identifying the flow regime in bubble columns that can be used as an online process control tool.

The four objectives of the dissertation are

- Investigate and quantify radial gas holdup profiles and bubble dynamics in slurry bubble columns in the deep churn turbulent flow regime, and relate these changes in bubble dynamics with superficial gas velocity to variations in the volumetric mass transfer coefficient.
- Investigate and quantify bubble dynamics and radial gas holdup profiles in a photobioreactor, and understand the impact of cell culture density on these parameters. Relate the observed changes in volumetric mass transfer coefficients to the changes in bubble dynamics with superficial gas velocity.
- Estimate volumetric mass transfer coefficients in bubble columns of various sizes with and without internals, and study the performance of existing correlations to predict gas holdup and volumetric mass transfer coefficients.
- Develop methods to detect the operating flow regime in a bubble column reactor which can be used as an online process control tool.

1.3 Thesis structure

This thesis consists of the following chapters:

- Chapter – 1: Motivation and objectives of the present work.
- Chapter – 2: Overview of measurement techniques used in this thesis.
• Chapter – 3: Overview of existing methods for classifying flow regimes in bubble columns, and a proposed new method for identifying flow regimes in bubble column reactors.

• Chapter – 4: Application of the 4-point optical probe to slurry bubble columns.

• Chapter – 5: Effect of scale on volumetric mass transfer coefficients in a bubble column with internals. Comparison of the experimentally evaluated gas holdup and volumetric mass transfer coefficients with existing correlations.

• Chapter – 6: Application of the 4-point optical probe to photo-bioreactors, and a new model to evaluate the volumetric mass transfer coefficient in the bubbly flow regime.

• Chapter – 7: Conclusions and recommendations for future work.
Chapter 2
Measurement Techniques

Quantification of flow fields in a multiphase reactor is a challenging task requiring advanced measurement techniques. The available techniques summarized by Mudde (2010) and Mueller (2010), can be broadly classified as invasive techniques, such as local measurement probes, and non-invasive techniques, such as CARPT-CT, γ-ray tomography. The present chapter briefly describes techniques used to quantify bubble dynamics (fiber optical probes) and the volumetric mass transfer coefficient (dissolved oxygen measurement probe).

2.1 Optical probe technique

Optical glass fiber probes are tiny instruments that detect whether gas or liquid is present at a particular point in a multiphase system. One end of the glass fiber is illuminated, and the other end is submerged in the multiphase flow. Depending on the ratio of the refraction indexes of the glass and the surrounding liquid or gas, light is refracted into the multiphase or reflected back into the fiber. The tip of the fiber is around 50-100 µm in diameter, or even less. This small dimension allows interpretation of the signals as if they were coming from a point. The probe offers fast response in combination with a very high signal-to-noise ratio. A typical signature of the passage of a bubble is shown in Figure 2-1. Various studies have been published since the first application of the optical probe by Frijlink (1987) (Groen, 2004; Harteveld, 2005; Mueller, 2010; Wu, 2007; Xue, 2004). Single point or multiple point optical probes were initially used to estimate gas holdup and bubble velocities in bubbly flow, where the gas flow is mainly unidirectional. However, the early algorithms did not allow the application of the probe in systems where bubbles attack the probe at angles. Xue (2004) developed an algorithm that uses a co-ordinate transformation to take
into account bubbles attacking the probe at an angle, so optical probes can measure bubble velocities in churn turbulent flows where flow is not unidirectional. The new algorithm also determines the gas-liquid interfacial area, along with the gas holdup, bubble velocity, and bubble chord lengths. Xue (2004) and Mueller (2010) verified these optical probe measurements via other established techniques, such as $\gamma$-ray tomography, and photographic measurements.

![Optical probe signal](image)

**Figure 2-1** Optical probe signal

In the present work, we have used a 4-point optical probe to study bubble dynamics, gas holdup, bubble velocity, bubble chord length, bubble frequency, and the gas-liquid interfacial area. The following sections discuss algorithms for obtaining these parameters from optical probe signals.

### 2.1.1 Signal processing

A schematic of a 4-point optical probe is shown in Figure 2-2. Three of the four tips of the probe have equal lengths and form an equilateral triangle. The fourth tip is positioned at the inertial center of this triangle, and it is approximately 1 cm longer than the rest of the tips. Figure 2-3 shows a typical response of the 4-point optical probe, where the lower voltage indicates that the probe tip is in contact with liquid and the higher voltage signal indicates that the probe tip is in the gas phase.
(a bubble). It is evident from the signal that the response time of the probe tip is on the order of milliseconds, and essentially a binary signal exists for each tip. Before signal processing, it essential to check that the signal is binary, i.e., it should contain only two voltage values, one representing the gas phase and the other representing the liquid phase. The presence of other voltage values in the signal indicates that the probe is not completely de-wetted when bubbles enclose the tip or that bubbles are not pierced along their axis. All the optical probe signals obtained in this work were binary, as shown in Figure 2-4.

![Figure 2-2 Schematic diagram of a 4-point optical probe (Xue 2008)](image)
Once it is confirmed that the signal does not contain other voltages than those indicating the gas and liquid phases, the time series are transferred to the binary mode via appropriate threshold \((th)\). The threshold can discard the irregular responses caused by a bubble that slips away from the probe instead of being pierced through. These irregular peaks are difficult to define, and may cause errors in measurements. With an appropriate threshold, the responses of the probe are transferred to a binary series, in which the value 1 represents that the probe’s tip is in the bubble, and the value 0 represents that the tip is in the liquid phase.
Once the signals are converted, they can be used to quantify bubble dynamics. Using this binary time series data, we have estimated local gas holdup, bubble frequency, bubble velocity, and the gas-liquid interfacial area, as discussed below.

2.1.2 Gas hold-up

The ergodic hypothesis is invoked for local gas holdup estimation (Lee and Dudukovic, 2014b). According to this hypothesis, when the total measurement time is sufficiently long to provide a good statistical representation of the sampling space, then the ensemble average is equivalent to the time average. Hence, the local gas holdup can be estimated as

\[ \varepsilon_g = \frac{\text{Time spent by the probe's central tip in bubbles}}{\text{Total measurement time}} = \frac{\sum T_0}{\Delta T} = \frac{\sum_{j=1}^{N} n_j(t_j)}{N} \]  

To prove consistency, the gas holdup measured by each probe was calculated and a statistical t-test was performed to compare the gas holdup obtained by each probe. At a significance level of \( \alpha = 0.05 \), the gas holdups measured by each individual tip were equal.

2.1.3 Bubble frequency

Bubble frequency is measured as the number of signal jumps from the liquid phase to the gas phase per unit time in the optical signal, which indicates the frequency of arrival of gas-liquid interphases.
2.1.4 Bubble velocity

Figure 2-3 shows a schematic of an optical probe response when a bubble hits the four-point optical probe. Assuming the bubble shape is ellipsoidal, and considering the surface curvature of the bubble, the time interval between the time when the bubble hits the central tip (Tip0) and the rest of the tips (Tip1, 2 and 3) is given by equations 2.3 a-c.

\[
\Delta t_1 = \frac{T_1 - T_0}{2} = \frac{t_1 \cos \phi}{v} = \frac{x_1 \cdot \sin \beta \cos \gamma + y_1 \cdot \sin \beta \sin \gamma + z_1 \cdot \cos \beta}{v \cdot \cos \phi} \quad [2.3a]
\]

\[
\Delta t_2 = \frac{T_2 - T_0}{2} = \frac{t_2 \cos \phi}{v} = \frac{x_2 \cdot \sin \beta \cos \gamma + y_2 \cdot \sin \beta \sin \gamma + z_2 \cdot \cos \beta}{v \cdot \cos \phi} \quad [2.3b]
\]

\[
\Delta t_3 = \frac{T_3 - T_0}{2} = \frac{t_3 \cos \phi}{v} = \frac{x_3 \cdot \sin \beta \cos \gamma + y_3 \cdot \sin \beta \sin \gamma + z_3 \cdot \cos \beta}{v \cdot \cos \phi} \quad [2.3c]
\]

where

\(x_i, y_i, z_i\) (i=1,2,3) are the coordinates of tip 1, 2, 3 of the probe obtained photographically, and \(T_i\) (i=0,1,2,3) the time tip i spent in the bubble (gas phase) upon entering it.
Figure 2-5 demonstrates how each angle is defined and measured. The three equations are solved numerically for the value of $\beta$, $\gamma$ and $\cos \phi$, instead of $v$ and $\phi$ separately. Since values of the bubble velocity cannot be individually determined, the error in estimation of bubble velocity depends on the value of $\cos \phi$. It has been found that angle $\phi$ has the upper limit of 22° (Kataoka et al., 1986). This limit implies that the maximum error in the calculation of bubble velocity is less than 13.4%. Bubble velocity estimated using this algorithm at various flow conditions has been verified by non-invasive measurements, such as photographic techniques (Xue, 2004) (Mueller, 2010).

2.1.5 Gas-liquid interfacial area

The gas-liquid interfacial area is estimated using the method developed by Kataoka et al. (1986) and Xue (2004), as described by equation 2.4:

$$\alpha = \frac{1}{\Delta T} \cdot \sum_{N} \frac{1}{v \cdot \cos \phi} \approx \frac{1}{\Delta T} \cdot \frac{N}{N_{\text{measured}}} \cdot \sum_{N_{\text{measured}}} \frac{1}{v \cdot \cos \phi}.$$  \hspace{1cm} [2.4]

$$N = N_{\text{measured}} + N_{\text{mixed}}$$

The bubbles that do not hit all four tips of the probe are considered as having the mean value of $v \cos \phi$. This formula is valid both for bubbly flow and for churn-turbulent flow. The gas-liquid interfacial area measured using this algorithm has been verified with non-invasive measurement techniques, such as photographic techniques (Xue, 2004).

A detailed explanation of algorithms for processing 4-point optical probe data can be obtained from Xue (2004) and Mueller (2010).
2.1.6 Bubble time

Bubble time is a new parameter obtained from the optical probe signal that was not previously used by Xue (2004) and Mueller (2010). Bubble time is defined as the time spent by the probe tip in an individual bubble. It is the time between the jump in the signal when the tip enters the gas phase and the drop in the signal when the bubble leaves the tip of the optical probe and the tip is rewetted. (see Figure 2-6).

The shape of the optical probe signal depends on the physical properties of the medium that govern wetting and de-wetting of the optical probe tip, as well as on the distance from the center of the bubble to the point where it is pierced. Harteveld (2005) explains how the shape of the signal depends on the distance from the center of the bubble to where it is pierced (see Figure 2-7).

Note that the optical probe signal is significantly distorted only when the piercing position x/R > 0.88, i.e., near the edge of the bubble where complete de-wetting is not obtained. For these positions, a bell-shaped response is observed. These bell-shaped responses due to imperfect
piercing of the optical probe are disregarded in calculating bubble time by selecting an appropriate
treshold, as shown in equation [2.1], and bubble time is calculated only for bubbles that do not
produce bell shaped responses. As shown in the Figure 2-6, a threshold of 80% was used for bubble
time measurement.

![Image](image.png)

Figure 2-7 Signal shape as a function of piercing position (Harteveld, 2005)

### 2.2 Volumetric mass transfer coefficient measurement

In this work, a dynamic gas disengagement technique was used to measure volumetric mass
transfer coefficients (Chang et al., 1989; Chisti, 1989; Nigam and Schumpe, 1996). While
maintaining the main air flow, a small oxygen flow was added to achieve a switch between air and
oxygen-enriched air. This switch resulted in a small increase in the partial pressure of oxygen in
the gas phase and caused a new equilibrium concentration in the liquid phase. The time rate of
change of the oxygen concentration in the liquid phase was measured using a fast response
dissolved oxygen measurement probe (typical response time of 0.45 sec⁻¹), and it was related to the volumetric mass transfer coefficient. To relate the rate of increase in dissolved oxygen to the volumetric mass transfer coefficient, a mixing model for the liquid phase in the reactor was required, as shown in Figure 2-8.

![Figure 2-8 Evaluation of the mass transfer coefficient](image)

The two common models in the literature for prediction of volumetric mass transfer coefficients are a well mixed liquid phase (CSTR) model and an axial dispersion model (ADM) (Deckwer et al., 1983; Hamed, 2012a; Han, 2007; Vandu et al., 2004b; Vandu and Krishna, 2004).

### 2.2.1 Well mixed liquid phase (CSTR) model

This model assumes the liquid phase to be completely backmixed. The concentration of tracer oxygen in the gas phase is assumed to be constant, because it is slightly soluble in water. Hence, only one equation is needed for the liquid phase:

\[
\frac{dC_L(t)}{dt} = k_L a \left[ C_{L,L}^* - C_L(t) \right] 
\]  

(2.5)

where, the \( C_L \) is dissolved concentration oxygen in the liquid phase.
2.2.2 Axial dispersion model (ADM)

This model assumes an axial gradient of concentration in the gas phase and liquid phase. For volumetric mass transfer coefficient measurement, the 1-D ADM equations are the following:

\[
\frac{\partial C_L(t)}{\partial t} = D_L \frac{\partial^2 C_L}{\partial Z^2} + \frac{k_i a}{\varepsilon_L} [H C_g(t) - C_L(t)], \quad \text{(2.6)}
\]

\[
\frac{\partial C_g(t)}{\partial t} = D_g \frac{\partial^2 C_g}{\partial Z^2} - \frac{u_g}{\varepsilon_g} \frac{\partial C_g}{\partial Z} - \frac{k_i a}{\varepsilon_g} [H C_g(t) - C_L(t)]. \quad \text{(2.7)}
\]

To apply this model, we must know the axial dispersion coefficients (\(D_g\) and \(D_L\)), and these are obtained from correlations (Deckwer et al., 1983). Most studies using ADM use a mass balance equation for the liquid phase (equation 2.6) (Deckwer et al., 1983; Han, 2007), and the concentration in the gas phase is assumed to be constant. In equation 2.6, it is assumed that the liquid phase is in batch mode, hence, there is no liquid velocity term.

As shown in previous work at the CREL (Degaleesan, 1997), no universal correlation exists for prediction of dispersion coefficients, and hence we prefer to use the CSTR model, which requires no parameters.

2.2.3 Procedure to obtain volumetric mass transfer coefficient

To measure the dissolved oxygen concentration [DO], an optical probe developed by Neo-Fox Ocean Optics, Florida, USA, was used. The probe setup consists of an optical probe [model T1000], an optical fiber light source, spectrometer, a USB A/D converter, a PC, and software.

Due to the sensor delay, the measured DO response \(C_{\text{sensor}}(t)\) does not exactly represent the actual DO concentration, \(C(t)\), and needs to be deconvoluted (Han, 2007; Vandu et al., 2004b). As illustrated in Figure 2.9, the sensor response constant, \(K_{\text{sensor}}\), was estimated by a two-point
calibration process using a liquid (A), stripped of oxygen by a nitrogen flow, and another liquid (B), saturated with the oxygen in the air flow. By quickly switching the probe from liquid (A) to liquid (B), a step change in the DO concentration was created, which yielded a response, $C_{\text{sensor}}(t)$, at the probe signal. As shown in Equation 2.8, the measured response followed the actual DO concentration with a certain delay determined by the probe constant ($K_{\text{sensor}}$):

$$\frac{dC_{\text{sensor}}(t)}{dt} = K_{\text{sensor}}[C_l(t) - C_{\text{sensor}}(t)]$$  \hspace{1cm} (2.8)

Here, $C_{\text{sensor}} = 0$ at $t=0$, and $C_l = C_{l,0}^*$ at $t>0$, where $C_{l,0}^*$ is the DO concentration saturated by the oxygen in the air.

By fitting Equation 2.9 to the measured calibration curves, the value of $K_{\text{sensor}}$ was found to be 0.43 s$^{-1}$. This sensor constant is three- to four-fold larger than a typical $k_{\text{ia}}$ value observed for the air-water system, indicating that the time scale of the probe delay is small enough for $k_{\text{ia}}$ measurements (Nigam and Schumpe, 1996). Using Equation 2.9, the probe responses obtained in experiments were deconvoluted to obtain the actual DO concentration profiles by equation 2.10:
\[ C(t) = C_{sensor}(t) + \frac{1}{K_{sensor}} \frac{dC_{sensor}(t)}{dt}. \]  \hspace{1cm} (2.10)

The deconvoluted \( C(t) \) responses were used for to fit the model. The well mixed [CSTR] model described earlier was used to evaluate the volumetric mass transfer coefficient of the liquid phase (Han, 2007).

2.3 Summary

The chapter describes methods that are used to quantify bubble dynamics and volumetric mass transfer coefficients in rest of the thesis. In chapter 3, the optical probe is applied to classify flow regimes. In chapter 4 and chapter 6, the 4-point optical probe technique is used to study bubble dynamics in a slurry bubble column and a bubble column photo-bioreactor. In chapter 5, the dynamic gas disengagement technique is used to quantify the volumetric mass transfer coefficients in a bubble column with internals, and in chapter 6 it is applied to a photo-bioreactor.
Chapter 3
Flow Regime Identification

3.1 Introduction

Bubble columns (BCs) and slurry bubble columns (SBCs) are important multiphase reactors used for contacting gas and liquid phases. Due to their excellent heat and mass transfer characteristics, they are a popular choice for exothermic reactions and reactions where the liquid side mass transfer coefficient is limiting. Common applications of BCs/SBCs include hydrogenation, oxidation, chlorination, biochemical reactions, gas to liquid conversion by the Fisher-Tropsch (FT) – synthesis, and methanol synthesis (Deckwar, 1992; Kantarci et al., 2005; Wang et al., 2007a). The success of these processes depends on maintaining favorable operating conditions: For bioreactors, it is essential to maintain a low shear environment by operating at low superficial gas velocities, whereas for FT synthesis and methanol synthesis it is essential to maintain high throughput and efficient heat and mass transfer by operating at high superficial gas velocities. On a broader level, two different hydrodynamic flow regimes exist at low and high superficial gas velocities.

![Observed flow regimes in the Bubble column](image)

Figure 3-1 Observed flow regimes in the Bubble column
For a gas-liquid system at atmospheric pressure, the bubbly flow regime is observed at low superficial gas velocity when a sparger with narrow openings is used (Ong, 2003). This flow regime is characterized by narrow bubble size distribution, limited or no bubble-bubble interaction, close to uniform radial gas holdup profile in the column, and low liquid phase turbulence (Mudde, 2005). The churn-turbulent flow regime, observed at higher gas superficial velocities, is characterized by broad bubble size distribution, significant bubble-bubble interactions (break-up and coalescence), a parabolic gas-hold up profile in the column, and high liquid phase turbulence (Mudde, 2005). Operating flow regimes in a bubble column depend on the superficial gas velocity, sparger configuration, properties of the liquid phase, density of the gas phase, the operating pressure, and the column dimensions (Azzopardi et al., 2011).

In between the bubbly flow and churn turbulent flow regimes, the transition flow regime is can be observed. This flow regime is not as well defined as the bubbly and churn turbulent flow regimes (Groen, 2004). When it does exist, it is observed in a narrow velocity window between the bubbly flow regime and churn turbulent flow regime. The various flow regimes in bubble columns are shown in Figure 3-1.

Prediction of flow regimes is challenging because reliable theories for their ‘a prori’ prediction are lacking. Measurements to quantify flow regimes are difficult for industrial vessels since they are opaque, and only limited tools are available to quantify even gas holdup at these conditions. Adding to this difficulty, the transition point from bubbly to churn turbulent flow regime changes with operating pressure, and the presence of additional components in the liquid phase (i.e., organic solvents, surfactants, etc.) (Groen, 2004; Joshi, 1998).
The ideal method for determination of flow regime should

- Predict the operating flow regime (bubbly / transition / churn)
- Indicate when the flow regime transition takes place
- Be easy to implement for various industrially important systems.

A summary of methods to determine the flow regime was provided by Shaikh and Al-Dahhan (2007). These methods depend on observing the evolution of a system parameter over a range of superficial gas velocities. Such parameters include the gas holdup $\varepsilon_g$, swarm rise velocity $u_g/\varepsilon_g$, the standard deviation of pressure fluctuation signals, and the Kolmogorov entropy. Along with these methods, advanced signal analysis methods, such as chaos analysis and fractal analysis of pressure fluctuation, are used for determination of the flow regime (Fraguio et al., 2009; Gourich et al., 2006; Joshi et al., 1998; Letzel et al., 1997; Ruzicka et al., 2001; Shaikh and Al-Dahhan, 2013a; Zahradník et al., 1995; Zahradník et al., 1997). However, to predict the flow regime using these methods, experiments need to be performed to generate flow regime maps at each operating condition, similar to the flow regime maps shown in Figure 3-3. In industrial processes, performing extensive experiments is not always feasible. Flow regimes can also be predicted based on linear stability analysis (Bhole and Joshi, 2005; Joshi et al., 2001; Monahan and Fox, 2007a, b; Ruzicka, 2013). Most of the linear stability analysis methods make use of the two-fluid model for flow simulation, and thus use closure forms for interfacial drag. Extensive study of different systems is needed to examine the sensitivity of the results to the closures. Thus, the existing methods for flow regime determination have the following advantages and disadvantages,
Advantages:

- They can identify flow regime transitions.
- Some of them are easy to implement for transparent systems.

However, the main disadvantages are:

- Experiments need to be performed to generate flow maps to predict the flow regime, and the process has to be repeated with changes in the liquid phase or sparger configuration.
- Most of the methods cannot be used as online process control tools.

The current study attempts to develop a method that can be used as a process control tool to predict the operating flow regime without the need for extensive experimentation or changing the operating conditions.

### 3.2 Methodology

To develop a method to identify the flow regime in a BC, we can take advantage of the fact that both bubble size distribution and liquid phase turbulence in the reactor change between the bubbly flow regime and the churn turbulent flow regime. In the bubbly flow regime, bubble size distribution is narrow, individual bubbles are present, the liquid phase turbulence in the column is low, and fewer and very small bubbles are entrained in the wake of larger bubbles (Groen, 2004; Xue, 2004). However, in the churn turbulent flow regime, the bubble size distribution is wide, larger bubbles are present due to very frequent coalescence and break-up, and the liquid phase turbulence in the column is high, with a large number of small bubbles entrained in the wake of the larger bubbles (Wu, 2007; Xue, 2004). These hydrodynamic changes in the behavior of the gas-liquid system can be captured by local measurement techniques, such as optical probes (Groen
et al., 1995; Groen et al., 1996; Harteveld, 2005; Mudde et al., 2009). In the past these probes have been used at the CREL to detect local gas holdup, bubble velocity distribution, bubble chord length distribution, and interfacial area density (Lee and Dudukovic, 2015; Manjrekar and Dudukovic, 2015; Mueller, 2010; Xue, 2004). In this study, we show that the flow regime in BCs can be identified from optical probe signals. Groen (2004) and Lee and Dudukovic (2014b) have demonstrated how the autocorrelation of optical probe signals can be used to study the flow field in mechanically agitated stirred tanks and bubble columns. The present study focuses on the application of time series analysis of optical probe signals to predict flow regimes.

3.3 Methods

3.3.1 Experimental Setup

Two bubble columns were used, one 10 cm in diameter and the other 20.32 cm in diameter. Tap water was the liquid phase, and air was the gas phase. Each column was operated in batch mode for the liquid phase. Along with water, we also studied the effect of the addition of 5% v/v organic solvents, such as isopropyl alcohol and acetonitrile which are commonly used industrial solvents and known to alter bubble dynamics. All the experiments were performed at superficial gas velocities ranging from 1 cm/s to 45 cm/s. A perforated plate distributor of 1.09% open area, with 3 mm diameter holes distributed in a square pitch, was used.

The overall gas holdup was measured by visual measurements. It was defined as

$$\varepsilon_s = \frac{H - H_0}{H}$$
A single point optical probe was used to study hydrodynamic characteristics of the system. Details of this technique are outlined in Xue (2004) and Mueller (2010). The probe was positioned at the center of the column, facing the direction of the gas flow, as shown in Figure [3.2].

![Probe facing downwards](image)

**Figure 3-2** Position of the single point optical probe

### 3.3.2 Data processing

Autocorrelation of a function provides information about how much the function correlates with itself at various time lags. The autocorrelation function is defined by equation (2.1). The normalized autocorrelation function $R_{xx}(m)$ as shown in equation 3.2 was used for data analysis.

\[
r_{xx}(m) = \sum_{n=0}^{N-m-1} x(n)x(n+m) \tag{3.1}
\]

\[
R_{xx}(m) = \frac{r_{xx}(m)}{r_{xx}(0)} \tag{3.2}
\]
3.4 Results and discussion

The gas holdup profile evolved over a range of superficial gas velocities, as shown in Figure 3-3. This evolution was used to identify the flow regime at various superficial gas velocities, using an established method. At each superficial gas velocity, a single point optical probe positioned at the center of the column was used to obtain the time series data. Figure 3-3 shows that the transition velocities are not the same for each condition. The addition of 5% v/v of isopropanol increased the transition velocity, as shown in Figure 3-3 (B), and the width of the transition regime was shorter when 5% v/v of acetonitrile was added. Also, for a 20.32 cm diameter column, there was no inflection point in the gas holdup vs. superficial gas velocity (Figure 3-3 (D)), making quantification of the flow regime difficult. In this case, the flow regime was identified by visual observation of the flow.

Figure 3-3 Gas hold up profiles A) Air-water system Dc = 10 cm B) Air-water + 5% v/v IPA, Dc = 10 C) Air-water + 5% v/v Acetonitrile, Dc = 10 D) Air-water system Dc = 10 cm
The optical probe signals obtained in the bubbly and churn turbulent flow regimes are shown in Figure 3.4. Autocorrelation of these signals is plotted in Figure 3-5. For bubbly flow, Figure 3-5 shows no correlation with itself except at a zero time lag, and it quickly drops to zero at other time lags. The arrival of the bubble at a measuring point is a stochastic process, and hence, there is no correlation between signals at different time lags. These observations can be explained by the turbulence in the bubble column in the bubbly and churn turbulent flow regimes. In the bubbly flow regime, very few smaller bubbles are entrained in the wake of larger bubbles. In contrast, in the churn turbulent flow regime, small bubbles are frequently entrapped in the wake of larger bubbles. This difference gives rise to narrowly spaced signals, since the bubbles in the wake will follow the larger bubbles, causing the weak autocorrelation observed in the churn-turbulent flow regime, as shown in Figure 3-5 at superficial gas velocities of 12 cm/s and 15 cm/s.

![Figure 3-4 Optical probe Signal A) Bubbly Flow B) Churn-turbulent system](image)

The behavior of the autocorrelation function observed in Figure 3-5 was identical for the 10 cm diameter air-water system as well as the 20.32 cm diameter column, and for systems with 5% v/v acetonitrile and isopropanol. The optical probe signal was further processed based on the method of Groen (2004), in which the mean value of the signal ($\alpha$) is subtracted from the signal to redefine the boundaries of the signal from $-\alpha$ to 1 - $\alpha$. Once this transformation is performed, at short time scale autocorrelation appears as shown in Figure 3-6.
Figure 3-5 Autocorrelation function of optical probe signals

Figure 3-6 Autocorrelation function for processed signal
In bubble columns, generally the bubble is followed by liquid (water). At time scales just above the typical single bubble passing time scale, autocorrelation is observed. Due to the stochastic nature of the arrival of the bubble at the fiber tip, autocorrelations quickly approach zero at time scales beyond single bubble passing time scales. As the superficial gas velocity is increased, the level of turbulence in the liquid phase increases, and bubbles start getting entrained in the wake of other bubbles. As a result, the time scale at which the autocorrelation is observed extends beyond the scale of a single bubble (see Figure 3-6, for a gas velocity of 12 cm/s). The observed autocorrelation of a bubble passing time signal can be seen as a contribution of two factors, the triangular shape at low values of time shifts, and, if present, a tail determined by bubble swarm, governed by a larger time scale of turbulence (Groen, 2004). This swarm-related autocorrelation function can be modeled as a decaying exponential, as shown in equation 2.3.

\[ X(\tau) = R(\tau) = a e^{-\frac{\tau}{\tau_0}} \]  

(2.3)

The parameter \( \tau_0 \) is related to the integral time scale of the turbulence (Groen, 2004). The parameter \( \tau_0 \) is also related to the flow regime, and its value increases with an increase in turbulence of the system. Hence, we expect an increase in the parameter \( \tau_0 \) as we increase with the superficial gas velocity. This analysis gives us one parameter that can be tracked to quantify the flow regime.

Bubble size and shape are dominant parameters that govern the hydrodynamics of the bubble column. At low superficial gas velocity and low turbulence, spherical bubbles are observed in the bubble column, travelling vertically in a straight path (Joshi, 1998; Mudde, 2005). At these conditions, due to smaller bubble-bubble interaction, the bubble size is small throughout the residence time of bubbles in the reactor. As the superficial gas velocity is increased, turbulence is introduced in the system, and the number of bubbles in the system increases, resulting in increased
bubble-bubble interaction. The increase in the bubble number density favors bubble coalescence, forming larger bubbles. The larger bubbles have higher velocities and increase the turbulence in the system. Also, it is important to note that as the bubble size increases, the bubble shapes are no longer spherical: They change from ellipsoidal to wobbling to spherical cap shape (Clift et al., 1978). Due to the shape change and larger bubble size, the component of the lift force towards the center of the column acting on these bubble increases, causing them to move toward the center of the column (Mudde, 2005). These bubbles no longer travel in a straight path, rather, their motion is zig-zag and spiral. Because large bubbles prefer to travel through the center of the column, a parabolic gas hold up profile develops, which triggers the large scale liquid circulation observed in these systems in the churn turbulent flow regime (Degaleesan, 1997; Devanathan et al., 1990). This development tells us how changes in bubble size cause a transition from the bubbly to the churn turbulent flow regime. A narrow bubble size distribution likely results in bubbly flow, and a broad bubble size distribution likely results in turbulent flow. However, tracking bubble size distribution in industrial equipment to quantify the flow regime is difficult. Using an optical probe technique, it possible to quantify the amount of time a bubble spends at an optical probe tip. In the bubbly flow regime, due to the narrow size distribution, the variance of the time bubbles spend at the tip (earlier defined as bubble time) will be smaller than in the churn turbulent flow regime.

Based on this hypothesis, the variance of time spent by a bubble at the tip is another parameter that can be used to track flow regime. To compare this parameter within various gas-liquid systems, it is rendered dimensionless by using $t_{\text{mean}}$, which is the mean time the probe tip spends in a bubble (see equation 2.4).
\[ \sigma^2 = \text{Variance of time bubble spends in an optical probe} \]
\[ t_{\text{mean}} = \text{mean time bubble spends in an optical probe} \]
\[ \bar{\sigma}^2 = \text{dimensionless variance} = \frac{\sigma^2}{t_{\text{mean}}^2} \quad (2.4) \]

The two parameters derived from the signal, the time scale \( t_0 \) and the dimensionless variance, were calculated for the various experimental studies described here, including an air-water system, an air-water + 0.5 % IPA/acetonitrile system, and an air-water system in a large column with a diameter of 20.32 cm. Along with these studies, to show the generality of the approach, these parameters were also calculated for a pilot scale bubble column (45 cm column diameter), a slurry bubble column, and a photo-bioreactor. The time scale and the dimensionless variance are plotted against each other in Figure 3-7. It can be seen that the points for the different flow regime lie in a cluster. Machine learning techniques, such as a support vector machine, can identify the flow regime. It is remarkable that the points for very diverse experimental conditions lie in the cluster for a common flow regime.

![Figure 3-7 Representation of flow regime clusters](image-url)
The separation between clusters in Figure 3-7 for the bubbly flow regime and transition flow regime is small, due to a lack of the description of the latter flow regime. Also, obtaining data points belonging to the transition flow regime is difficult, because it is not always clearly observable.

Support vector machines (SVM) are supervised learning models with associated learning algorithms that analyze data used for classification and regression analysis. Given a set of training examples, each marked as belonging to one of two categories, an SVM training algorithm builds a model that assigns new examples into one category or the other. SVM is a proven way to classify binary classes. As there are three different flow regimes; one vs. many approach for classification was used. Accordingly, a binary classifier using SVM to identify the flow regime to which a new test point belongs was developed. A linear classifier kernel outlines the boundaries of each regime. An SVM algorithm developed by MATLAB® was used for classification. The procedure to identify the flow regime is outlined in Figure 3-8.

![Figure 3-8 SVM classification process](image)

To develop a SVM algorithm total of 70 data points from various systems mentioned above were used. The developed classifier was tested using a separate set of data points. Figure 3-9 (a) shows
a linear classification boundary between bubbly flow regime and the non-bubbly flow regime. Figure 3-9 (b) shows the performance of the binary classifier to classify test data points in bubbly or not bubbly flow regime (transition or turbulent flow regime). The data points circled in green are correctly classified data points, and the data points circled in red are incorrectly classified data points. Out of 10 test data points, 9 are correctly classified. All five data points belonging to bubbly flow regime are correctly classified. However, one data point that does not belong to bubbly flow regime was misclassified. This demonstrates the applicability of SVM model to discriminate between bubbly and non-bubbly flow regimes with 90% accuracy in present study. After classification between bubbly and non-bubbly flow regime is completed and if the point belongs to non-bubbly flow regime further classification is needed to identify if it belongs to churn-turbulent or transition flow regime. Figure 3-10 shows the SVM classifier for transition flow regime vs. churn-turbulent flow regime. It can be seen that in this case all 7 test points are correctly identified. This demonstrates our general approach to classifying flow regime in a bubble column.

Figure 3-9 SVM classification of flow regime A) Classification boundary for bubbly Vs. non-bubbly flow, B) Classification of test data points for bubbly Vs. non-bubbly flow
3.5 Concluding remarks

In this work we have demonstrated how Support Vector Machine (SVM) classifier can be used for identification of flow regime in bubble column reactor. The developed method was successful in classifying flow regime for various systems (such as air-water system with different column diameters, air-water system with additional components such as 5% IPA or acetonitrile, photobioreactor with algae and pilot scale bubble column with internals). Traditional methods that depend on a flow regime map for regime classification were not able to uniquely classify the flow regime for all the above systems.

The database for development of the SVM model can be broadened in future for more reliable flow regime prediction. In the present work Matlab, was used to develop the SVM classifier. Other popular packages like WEKA can also be used to develop the SVM classifier, the advantage of using WEKA is that it can perform inbuilt multi-level classification, i.e., classifying between
bubbly, transition and churn turbulent flow regime at the same time. The disadvantage of this package is the difficulty in obtaining visual representation of classified points.

The approach developed in this work provides a classification method that can predict flow regime without changing operating conditions. The method is easy to implement, and the parameters required to identify flow regime can be calculated within seconds from the optical probe signal. Hence, the method can be further developed as online process control tool to detect flow regimes at industrial conditions.
Chapter 4 Bubble Dynamics in a Slurry Bubble Column

4.1 Introduction

Slurry bubble column (SBC) are frequently used in industry for gas-liquid-solid contacting (Deckwar, 1992; Dudukovic et al., 1999; Wang et al., 2007b). In spite of their numerous industrial applications, limited data is available in the open literature on their local bubble dynamics and gas holdup. Vandu et al. (2004b), and Behkish et al. (2002) reported that the overall gas holdup was reduced by 15 to 20% and the liquid side volumetric mass transfer coefficients were lower by 5 to 10% in the presence of solids. Using the dynamic gas disengagement technique, Li and Prakash (2000) observed a decrease in overall gas holdup and an increase in bubble rise velocity in a system with solids. However, Lee et al. (1999) have shown that the dynamic gas disengagement technique is not suitable for identifying holdup profiles and bubble size distributions in bubble columns operating in the churn turbulent regime. Video imaging techniques are not useful in a systems such as a SBC (where micro-size catalysts are used as solid) because these are opaque. In these systems, micro-probe techniques, such as a 4-point optical probe, can be used. Wu et al. (2008) have applied this technique to evaluate local parameters in the presence of alumina-based F-T catalytic solids. In work on SBC, Hooshyar et al. (2010a) found that in the presence of solids, the transition velocity from bubbly flow to churn turbulent flow is decreased. It was also observed that the presence of solids broadens the bubble velocity distribution, but it has a lesser effect on the mean bubble chord length. In a study of a single rising bubble it was observed that the bubble velocity increased in presence of micron sized solid particles; however, as the particle size becomes comparable with the bubble size, particles collided with the bubbles and reduced their velocity (Hooshyar et al., 2013b). Previous studies on local bubble dynamics in SBCs largely dealt with the bubbly flow...
regime (Hooshyar et al., 2010b; Hooshyar et al., 2013b) and did not fully cover the high superficial gas velocity range, which is of industrial interest. Hence, the effect of solids on the key design parameters, such as distribution of gas hold up and bubble velocities, is not well understood at high superficial gas velocities.

In earlier studies on bubble columns, it was observed that in churn turbulent flow regime the liquid exhibits a single recirculation cell in most of the column (from 1.5 to 2 diameters above the distributor to less than 1 diameter below the top free surface) (Degaleesan, 1997; Devanathan et al., 1990). This liquid circulation is promoted by non-uniformities in the radial gas distribution in the bubble column at these operating condition. The gas hold up distribution is parabolic, and it becomes steeper with an increase in superficial gas velocity causing stronger recirculation in the column. This liquid circulation carries back smaller gas bubbles with itself and is responsible for increasing the back mixing of gas and liquid phase. Hence, stronger liquid circulation causes higher degree of back mixing in both liquid and gas phase. In order to successfully scale up bubble column and avoid oversizing the reactor, it is essential to quantify back mixing of each phase.

It was observed that presence of solids reduces gas holdup in all the regions of the column except at the walls of the column (Hooshyar et al., 2010a; Wu, 2007). This indicates weaker liquid recirculation and reduced backmixing exists in presence of slurry compared to air water system. Knowledge of radial gas holdup profile in presence of slurry would provide parameters to phenomenological models to predict reduction in circulation at these systems and improved reliability of scale up of the reactor.
This chapter focuses on partly filling this knowledge gap by addressing the following objectives:

- Quantify the radial variation in gas holdup in a system with solids and compare with a system without solids.
- Study the radial variation in the gas-liquid interfacial area, which can be used to estimate mass transfer coefficients.
- Determine the effect of solids on bubble velocity.

### 4.2 Experimental set-up

Experiments were carried out in an 8 inch [20.32 cm] diameter transparent plexiglass column. Water was used as the liquid phase and air as the gas phase for all the experiments. The height of liquid dispersion was kept constant at 145 cm above the sparger level with an aspect ratio of 7.1. The column was operated in batch mode for the liquid (slurry) phase, and experiments were performed in the churn turbulent regime at gas superficial velocities ranging from 10 cm/sec to 45 cm/sec. Aluminum oxide particles with an average diameter 60 µm ($6 \times 10^{-5}$ m) average diameter and density 3650 kg/m$^3$ or glass spheres in the 0.3 mm ($3 \times 10^{-4}$ m) to 0.35 mm ($3.5 \times 10^{-4}$ m) size range and density 2500 kg/m$^3$ were used separately to study the effect of solids.

The 4-point optical probe was used to determine the radial distributions of the gas holdup, bubble velocity and bubble frequency. The probe was positioned at four dimensionless radial locations ($r/R = 0, 0.3, 0.6$ and $0.9$) along a straight line, with zero representing the center of the column and 0.9 representing a position at 9/10 of the inner radius from the center, which is close to the wall of the column. Figure 4-1 [A] shows the positioning of the probe inside the bubble column. As seen in this figure, two probe orientations were selected, one with the probe tips facing downward to capture bubbles moving upward, and another with the probe tips facing upward to capture bubbles
moving downward. The location of the probe to measure bubble velocities in upward and downward direction is not identical since two probes are 5 centimeters apart in axial distance from each other. However, both probe locations are within the well-developed flow region of the column, since they are more than two column diameters above the sparger zone. In the fully developed flow region, as shown by numerous studies in our laboratory (Degaleesan, 1997; Ong, 2003; Xue, 2004) a small change in the axial position of the probe compared to total medium height does not affect the liquid velocity measurements or local holdup (Xue et al., 2008a). Moreover, the radial distribution of these quantities are independent of the axial position of the measurement and planeand azimuthal angle of the radius along which the probes are located in well developed section of the column (Degaleesan, 1997; Ong, 2003; Xue, 2004).

Figure 4-1 Optical probe position. [A] Probe facing downward to measure velocity of bubbles flowing upward [B] Probe facing upward to measure velocity of bubbles flowing in downward
4.3 Results and Discussion

The observed effect of solids on local gas holdup profile in this work is shown in Figure 4-2. We note that local gas holdup was reduced everywhere in the presence of solids. This reduction in gas holdup was found to be the greatest at the center of the column, and no significant reduction in gas holdup was observed near the wall. Similar gas holdup profiles were observed by others (Degaleesan et al., 2001; Gupta et al., 2001b; Hamed, 2012a; Li and Prakash, 2000; Xue et al., 2008a, b; Youssef et al., 2013). The reduction in gas holdup is the result of the increased bubble velocities observed in the presence of fine solids. Figure 4-3 shows the effect of solids addition on the overall bubble velocity distribution in the column. Bubble velocities were measured at 4 radial positions \((r/R = 0.0, 0.3, 0.6, 0.9)\), collective data of all the positions is used to obtain the distributions shown in figure 4.3, later we will analyze data in central and near wall region. It is clear that bubbles have higher velocities in the slurry bubble column (SBC) system than in the bubble column (BC). The positive values of velocity represent bubbles travelling upward and negative values of velocity represents bubbles travelling downward. The bubble velocity distribution is broader in SBC compared to air water system.

In Figure 4-4 we compare the cumulative distribution of bubble velocities traveling upward in the center region and near wall region for both gas–liquid (BC) and gas-liquid solid (SBC) systems. Velocities obtained at radial positions at \(r = 0\) and 0.3 are considered as the central region, and at radial positions of \(r = 0.6\) and 0.9 are considered as near wall region. As shown in Table 4-1, the mean velocity of bubbles in the central region is higher than the mean velocity of bubbles in the wall region. The percentage change in bubble velocity due to the addition of solids is higher in the wall region.
In both regions, the bubble velocity in the presence of solids is larger. The average velocities of bubbles traveling in the upward and the downward directions are presented in Figure 4-5 [only the magnitude of bubble velocity is plotted]. At a given superficial gas velocity, the average velocity of bubbles travelling upward decreases from the center of the column to the near-wall region [Figure 4-5 [A]]. The opposite trend is observed for bubbles travelling downward, as their velocity is the highest at the wall of the column and lowest in the central region.

![Figure 4-2 Effect of solids on radial gas hold-up profile](image)

Figure 4-3 Axial bubble velocity distribution. [A] Bubble velocity distribution at 40 cm/sec in SBC, [B] Bubble velocity distribution at 40 cm/sec in air-water system, [C] Bubble velocity distribution at 20 cm/sec in SBC, [D] Bubble velocity distribution at 20 cm/sec in air-water system
Figure 4-4 Cumulative axial bubble velocity distribution comparison. [A] Superficial gas velocity 20 cm/sec, wall region [B] Superficial gas velocity 20 cm/sec, center region, [C] Superficial gas velocity 40 cm/sec, wall region, [D] Superficial gas velocity 40 cm/sec, center region

Figure 4-5 Average axial bubble velocities. [A] Bubbles travelling upward, [B] Bubbles travelling downward
### Table 4-1 Axial Bubble velocities in the central and wall regions of a bubble column at different superficial gas velocities

<table>
<thead>
<tr>
<th>Superficial gas velocity</th>
<th>Region</th>
<th>Air-Water (cm/sec)</th>
<th>SBCR (cm/sec)</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 cm/sec</td>
<td>Central</td>
<td>81.26</td>
<td>128.75</td>
<td>58.45</td>
</tr>
<tr>
<td></td>
<td>Wall</td>
<td>66.96</td>
<td>112.51</td>
<td>68.02</td>
</tr>
<tr>
<td>40 cm/sec</td>
<td>Central</td>
<td>95.92</td>
<td>125.63</td>
<td>30.97</td>
</tr>
<tr>
<td></td>
<td>Wall</td>
<td>79.38</td>
<td>114.62</td>
<td>44.40</td>
</tr>
</tbody>
</table>

The radial gas hold-up profile can be represented using a power law function suggested by Kumar et al. (1997) which fits the experimental data:

\[
\varepsilon_g(\xi) = \varepsilon_g \left( \frac{m + 2}{m + 2 - 2c} \right) (1 - c\xi^m) \]  \[1.\]

In equation[1], \(\xi = r/R\) is the non-dimensional radius, and parameters m and c are evaluated using experimental data. Values for these parameters are reported in Table 4-2.
Figure 4-6 Bubble frequency comparison [A] Frequency of bubbles travelling in upward direction [B] Frequency of bubbles travelling in downward direction.

Figure 4-7 Mean bubble chord length

Table 4-2 Gas Hold-up profile

<table>
<thead>
<tr>
<th>Superficial gas velocity</th>
<th>Average gas hold-up</th>
<th>m</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 cm/sec 10% slurry</td>
<td>27.55</td>
<td>2.79</td>
<td>0.92</td>
</tr>
<tr>
<td>20 cm/sec 10% slurry</td>
<td>15.9</td>
<td>1.62</td>
<td>0.72</td>
</tr>
<tr>
<td>40 cm/sec no solids</td>
<td>32.03</td>
<td>2.35</td>
<td>0.9</td>
</tr>
<tr>
<td>20 cm/sec no solids</td>
<td>21.6</td>
<td>1.85</td>
<td>0.72</td>
</tr>
</tbody>
</table>
In gas liquid flows, such as bubble columns, at a given superficial gas velocity, bubbles have a certain amount of kinetic energy to transmit via gas-liquid interactive forces to the liquid causing liquid flow and circulation. The bigger the holdup difference between the center of the column and the wall region the stronger the liquid circulation. Larger bubbles formed due to coalescence experience negative lift force which directs these larger bubbles to the center of the column, these larger bubbles travel higher velocity. This results in density difference between core of the column and walls and causes the large scale liquid circulation to set in. While moving upward, bubbles transfer momentum to liquid phase and carries upward along with it. However, in near-wall region smaller bubble are carried downward by down flow of liquid.

The average bubble velocity in the presence of solids is about 40-60 % higher than for the air-water system. This increase could be partly due to an increase in apparent viscosity of the liquid due to the addition of solids, as a higher liquid viscosity promotes bubble coalescence. Figure 4-6 shows that the bubble frequency in the presence of solids is lower, which could be the result of coalescence. Radial variation of the mean bubble chord length is shown in Figure 4-7; due to the overlapping error bars we can only conclude that in SBC and BC bubble chord length is unchanged. Small increase in bubble chord length distribution in 2-D SBCRs were previously reported by Hooshyar et al. (2010a), however they did not observe clear increase in bubble chord length. Hence, reduction in the bubble frequency is the only indicator of bubble coalescence in SBC which could be responsible for increased bubble velocity. Based on findings of this study and previous studies, it can be concluded that an increase in the bubble velocity is due to effect of increased liquid phase density by addition of solids which would increase the buoyancy force on the bubble. Along with bubble coalescence increased density of the liquid phase, changes in the liquid circulation pattern due to changes in radial gas holdup profiles can also be responsible for
the increase in bubble velocity in SBC (Hooshyar et al., 2010a). However, it not clear how the changes in radial gas holdups increase bubble velocity, and detailed study of liquid circulation velocities and dynamic vertical structures in slurry systems need to be done before making any conclusive claims. Addition of solids along with increasing density also increases viscosity if the liquid, as shown by Hooshyar et al. (2013a) the increase in effective viscosity by addition solids reduces bubble velocity at high solid loading and has minimal effect at low solids loading (below 10%).

4.4 Experiments with glass spheres

In the presence of aluminum oxide particles of average diameter 60 µm, the assumption of a pseudo homogenous phase was made for the slurry phase. We also performed experiments with glass spheres, with diameters ranging between 0.3 mm ($3 \times 10^{-4}$ m) to 0.35 mm ($3.5 \times 10^{-4}$ m) size range and density 2500 kg/m$^3$. In this case, the size range of the glass spheres was comparable with bubble diameter. The experiments were performed at superficial gas velocity 10 cm/sec. At these conditions, glass spheres would collide with bubbles and reduce their kinetic energy, resulting in reduction of bubble velocity (Hooshyar et al., 2013b). Figure 4-8 shows that the average velocity of bubbles [upward direction] in the presence of glass spheres is indeed lower than in either the air water system or the slurry system with aluminum oxide catalytic particles. The radial gas holdup profiles are compared in Figure 4-9, no appreciable change in gas holdup was observed in the three cases.
In the churn turbulent flow regime, gas holdup decreases in the presence of micron size aluminum oxide catalyst particles. The increase in bubble velocity in the slurry system (due to bubble coalescence and changes in radial gas hold up distribution) is responsible for the reduction in gas holdup. Micron size catalyst particles, which have a small Stokes’ number (follow the liquid flow;
however, when the size of particles is increased to 0.3 mm [glass spheres] the bubble velocity decreases, due to collision of bubbles with larger particles. In a single bubble experiment, larger particles were found to reduce bubble velocity (Hooshyar et al., 2013b). The same effect is expected in the SBC, but the systematic study of the effect of larger particles on the radial distribution of bubble velocity, gas holdup and interfacial area in the churn turbulent flow regime remains to be conducted.

Further research on quantification of liquid velocity profile in SBC at high superficial gas velocity with techniques like CARPT is necessary to understand how addition of solids alters liquid velocity profile inside SBC. This will give us insight into mechanism increase bubble velocities in SBC.

The parameters [gas holdup profile, bubble velocity, and volumetric mass transfer coefficient] evaluated in the present work can be used for validation of CFD results, which can later be combined with process chemistry to accomplish scale-up (Chen et al., 2004). The parameters can also be used for development of phenomenological models to explain lab scale as well as pilot scale observations on large columns. Such application has been demonstrated at the Alternative Fuels Development Unit [AFDU], La Porte, TX for dimethyl ether, methanol, and FT synthesis (Gupta et al., 2001a; Gupta et al., 2001b).
Chapter 5
Mass Transfer Coefficient Measurement in Bubble Column

5.1 Introduction

Gas-liquid multiphase reactions are widely used in the chemical industry. A typical gas-liquid reaction is shown below.

\[ A_{(g \rightarrow l)} + bB_{(l)} \xrightarrow{k} R \text{ (s or g or l)} \quad (5.1) \]

In the reaction, reactant A, which is in the gaseous state, dissolves in the liquid phase where it reacts with reactant B to give product R (Levenspiel, 1999). Hence for reactor design, knowledge of the rate of transfer of reactant A in the liquid phase is necessary. In fast reactions, the transfer of reactant from the gas phase to liquid phase becomes a limiting step: for example, in the reactive absorption of carbon dioxide in amine solution, the rate absorption of carbon dioxide into the liquid phase is the rate-limiting step (Astarita, 1967). In the case of bioreactors, knowledge of volumetric mass transfer coefficients is essential to maintain a steady flux of nutrients (oxygen for an aerobic system, carbon dioxide for photobioreactors, hydrogen and carbon monoxide for an anaerobic system) in the liquid phase to avoid starving cells. F-T synthesis and methanol synthesis are two large-scale catalytic processes used for the production of methanol and liquid fuels using synthesis gas. In these processes, the reactants are in the gas phase, and the products are in the liquid phase at reaction conditions. For the reaction to progress, the reactants must transfer from the gas phase to the liquid phase to reach reactive sites on the catalyst. Accordingly, knowledge of the volumetric mass transfer is very critical for reactor design for FT-synthesis and methanol synthesis (Dry, 2002).
Fischer-Tropsch (FT) synthesis is practiced in large scale for production of liquid fuels. This key reaction has gained importance due to its ability to convert synthesis gas, derived from natural gas or biomass sources, to liquid transportation fuels (see Figure 5-1). This reaction is highly exothermic: About 170 kJ of heat is released in the conversion of one mole of carbon monoxide (Krishna and Sie, 2000). The primary motivation for temperature control is the increased selectivity to the undesired byproduct CH₄ at a higher temperature, and the need to avoid a higher temperature that speeds catalyst disintegration by carbon deposition (Dry, 1996). To effectively remove the heat generated during the reaction, vertical heat exchanging internals are installed in the reactor. Previous work revealed that the presence of internals affects both gas and liquid velocity profiles as well as bubble dynamics (Hamed, 2012a; Youssef, 2010b). The effect of the internals on the liquid circulation velocity has been studied by Larachi et al. (2006) using CFD simulations. Youssef (2010a) pointed out that the dense internals structure causes an enhancement in liquid phase mixing. Hamed (2012b) found that radial, as well as axial diffusivity, decreases in the presence of vertical internals. These changes are expected to affect the volumetric mass transfer coefficient (k_La). It is important to understand the influence of these parameters on the mass transfer coefficient. Some of the existing correlations for volumetric mass transfer coefficient are shown in Table 5-1 In the recent literature on prediction of the volumetric mass transfer coefficient, advanced machine learning techniques, such as artificial neural networks, support vector regression, and hybrid genetic algorithms are employed (Gandhi et al., 2009; Gupta et al., 2009; Han, 2007). Along with the machine learning approaches, semi-empirical models based on Higbie’s penetration theory are also used to predict volumetric mass transfer coefficients for air-water systems and systems with organic solvents (Nedeltchev et al., 2007, 2010).
Despite this development of new models, a popular correlation for prediction of volumetric mass transfer coefficients remains the one proposed by Shah et al. (1982), (Martín et al., 2009). The correlation is given in equation 5.1.

\[ k_i a_p = k U_G^\beta \]  

(5.1)

Here, \( k \) and \( \beta \) are adjustable parameters depending on the gas-liquid system and geometry. For an air-water bubble column, the value of \( k \) was found to be 0.007, and the value of \( \beta \) was 0.76. It was proposed that the value of \( \beta \) ranges from 0.7 to 1.1 depending on the system turbulence.
Table 5-1 Correlations for volumetric mass transfer coefficients

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{k_{L}a_{D}d_{L}^{2}}{D_{L}} = 0.6 \left( \frac{\mu_{L}}{\rho_{L}D_{L}} \right)^{0.5} \left( \frac{gd_{L}^{2} \rho_{L}}{\sigma_{L}} \right)^{0.62} \left( \frac{gd_{L}^{3} \rho_{L}^{2}}{\mu_{L}^{2}} \right)^{0.31} \varepsilon_{G}^{1.1} )</td>
<td>(Akita and Yoshida, 1973)</td>
</tr>
<tr>
<td>( \frac{k_{L}a_{D}d_{L}^{2}}{D_{L}} = 0.09 \left( \frac{\mu_{L}}{\rho_{L}D_{L}} \right)^{0.5} \left( \frac{gd_{L}^{2} \rho_{L}}{\sigma_{L}} \right)^{0.75} \left( \frac{gd_{L}^{3} \rho_{L}^{2}}{\mu_{L}^{2}} \right)^{0.39} \left( \frac{U_{G}^{2}}{gd_{t}} \right) \left( 1 + \chi \left( \frac{U_{B}^{2}}{d_{B}} \right) \right)^{-0.45} )</td>
<td>(Nakanoh and Yoshida, 1980)</td>
</tr>
<tr>
<td>( k_{L}a_{L} = 0.32U_{G}^{0.7} )</td>
<td></td>
</tr>
<tr>
<td>( \frac{k_{L}a_{L}d_{L}^{2}}{D_{L}} = 0.021 \left( \frac{\mu_{L}}{\rho_{L}D_{L}} \right)^{0.5} \left( \frac{gd_{L}^{2} \rho_{L}}{\sigma_{L}} \right)^{0.21} \left( \frac{gd_{L}^{3} \rho_{L}^{2}}{\mu_{L}^{2}} \right)^{0.6} \left( \frac{U_{G}^{2}}{\sqrt{gd_{t}}} \right) )</td>
<td>(Heijnen and Van't Riet, 1984)</td>
</tr>
<tr>
<td>( \frac{k_{L}a_{L}d_{L}^{2}}{D_{L}} = 0.555 \left( \frac{Kd_{L}^{1-n}}{\rho_{L}D_{L}U_{G}^{1-n}} \right)^{0.5} \left( \frac{gd_{L}^{2} \rho_{L}}{\sigma_{L}} \right)^{3/5} \left( \frac{U_{G}^{2}}{gd_{t}} \right) \left( \frac{d_{G}^{n}U_{G}^{2-n}}{K/\rho_{L}} \right) \left( n + 2 \right) \left( 2n - 3 \right) \left( \frac{20(1 + n)^{2}}{\varepsilon_{G}^{0.5}} \right) )</td>
<td>(Deckwer and Schumpe, 1985)</td>
</tr>
<tr>
<td>( k_{L}a_{L} = \frac{14.9gf}{U_{G}} \left( \frac{U_{G}^{0.467U_{G}^{0.82}}}{\rho_{L}} \right) \left( \frac{\mu_{L}^{1.76}}{\rho_{L}^{1.76}} \right) \left( \frac{\mu_{G}}{\mu_{L}} \right) \left( \frac{\mu_{G}}{\mu_{L}} \right) \left( \frac{\mu_{L}}{\rho_{L}D_{L}} \right) \left( \mu_{L}^{0.243} \right) \left( \mu_{L}^{0.243} \right) )</td>
<td>(Kawase et al., 1987)</td>
</tr>
<tr>
<td>( f=1 ) for non-electrolyte; ( f=10^{0.0681I} ) for electrolytes ( I=) ionic strength</td>
<td></td>
</tr>
<tr>
<td>( k_{L}a_{D} = 0.467U_{G}^{0.82} )</td>
<td></td>
</tr>
<tr>
<td>( \frac{k_{L}a_{D}d_{L}^{2}}{D_{L}} = 0.452 \left( \frac{v}{D_{L}} \right)^{0.5} \left( \frac{DU_{G}^{1/3}}{v} \right)^{3/4} \left( \frac{gd_{L}^{2} \rho_{L}}{\sigma_{L}} \right)^{3/5} \left( \frac{U_{G}^{2}}{D_{G}^{1/3}} \right)^{7/60} )</td>
<td>(Kang et al., 1999)</td>
</tr>
<tr>
<td>( k_{L}a_{D} = K \times 10^{-3.08} \left( \frac{DU_{G}^{1/3} \rho_{G}^{1/3}}{\mu_{L}} \right)^{0.254} )</td>
<td>(Schumpe and Grund, 1986)</td>
</tr>
<tr>
<td>( k_{L}a_{D} = KU_{G}^{0.82} \mu_{eff}^{-0.39} )</td>
<td></td>
</tr>
<tr>
<td>( K=0.063 ) for water salt solution, ( K=0.042 ) (0.8 M Na₂SO₄)</td>
<td></td>
</tr>
<tr>
<td>( k_{L}a_{L} = 2.39 \times 10^{-4} \left( \frac{P_{G}}{V_{L}} \right)^{0.86} )</td>
<td>(Chisti, 1989)</td>
</tr>
</tbody>
</table>
Since these correlations are established on laboratory scales, and the parameters $k$ and $\beta$ would change from system to system, there is need for experimental studies to evaluate these parameters for variety of systems. Studies have been performed from laboratory scale to pilot scales to test these correlations, and provide better understanding of the systems (Behkish et al., 2002; Deckwer et al., 1983; Godbole et al., 1984; Han and Al-Dahhan, 2007; Jordan and Schumpe, 2001; Lau et al., 2004; Nedeltchev et al., 2010; Vandu et al., 2004b; Vandu and Krishna, 2004). Even though numerous studies have been performed, the effect of vertical cooling has not been taken into account, except far a few studies (Hamed, 2012a; Youssef, 2010b). The prediction of volumetric mass transfer coefficients for systems with vertical cooling internals using correlations still need to be tested. Hamed (2012a) studied studied variation in volumetric mass transfer coefficients with superficial gas velocity in the presence of internals using the ADM for liquid phase mixing. However, effect of scale on prediction of volumetric mass transfer coefficient and performance of existing correlations to predict the volumetric mass transfer coefficients is not tested.

The research objectives for this work are:

- Evaluate mass transfer coefficients at different radial and axial positions.
- Investigate the effect of superficial gas velocity and vertical heat exchanging internals on volumetric mass transfer coefficient.
- Study the effect of scale on mass transfer coefficient in the presence of vertical heat exchanging internals, and compare it with existing correlations.
5.2 Experimental Setup

Experiments were carried out in a transparent plexiglass column with and without vertical heat-exchanging internals. Column diameters of 20.32 cm (8’’) and 45 cm (18’’) are used. Compressed filtered air entered the column through a perforated plate distributor of 1.09% open area with 241 holes of 3 mm diameter distributed in a square pitch for the 18-inch diameter reactor and 1.09% open area with 225 holes of 3 mm diameter arranged in a triangular pitch for the 8-inch diameter reactor. The liquid phase (water) was kept in a batch mode while air was blown continuously. The dynamic height of the gas – liquid mixture (bed) was kept constant at 2.54 m (100-inch) for the 45 cm (18-inch) diameter column, and 1.12 m (44-inch) for the 20.32 cm (8-inch) diameter column for all the experiments. Figure 5-2 shows experimental set-up for dissolved oxygen measurement. The experiments were performed with 22% cross-sectional area occluded by internals and in the absence of internals. The internals solid PVC rods used for the 45 cm (18’’) diameter column had 1’’ outer diameter. For the 20.32 cm (8-inch) diameter column plexiglass rods of 0.5-inch outer diameter were used. The configuration of internals is as shown in Figure 5-3, 75 internals rods were arranged in equilateral triangular pitch to cover about 22% of the total column’s cross-sectional area. In order to ensure the stability of the structure, three spacers were used in addition to the top plate. The bundle of rods was hung 13 cm (5-inch) above the sparger and height could be modified by lifting the top plate.

The experimental conditions for oxygen mass transfer experiments were designed to cover range of superficial gas velocities in the churn turbulent regime. Experiments were performed at different axial and radial positions. Table 5-2 lists the different axial and radial positions at which experiments were performed.
Figure 5-2 Experimental setup

Table 5-2 Experimental conditions and positions of the probe

<table>
<thead>
<tr>
<th>$D_c$ (cm)</th>
<th>Internals (%CSA)</th>
<th>$U_g$ cm/s</th>
<th>Axial Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>0%</td>
<td>20,25,30,35,40,45</td>
<td>$x/L = 0.3,0.5,0.65$</td>
</tr>
<tr>
<td>45</td>
<td>22%</td>
<td>20,25,30,35,40,45</td>
<td>$x/L = 0.3,0.65$</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>20,25,30,35,40,45</td>
<td>$x/L = 0.6$</td>
</tr>
<tr>
<td>20</td>
<td>22%</td>
<td>20,25,30,35,40,45</td>
<td>$x/L = 0.6$</td>
</tr>
</tbody>
</table>

Figure 5-3 Design of Internal bundle 25% coverage (Dimensions in inches)
5.3 Results and Discussions

Dissolved oxygen (DO) concentration profile measured at three axial positions in a 45 cm column without internals are as shown in Figure 5-4. The concentration evolution profiles in time at different locations in the reactor are identical, and there is no change in dissolved oxygen concentration profiles in time along the axial direction. This supports the assumption of complete mixing of the liquid phase.

![Figure 5-4 Dissolved oxygen concentration profile at different axial positions in 45 cm diameter column without internals](image)

Dissolved oxygen (DO) concentration profiles at two axial positions in the presence of vertical cooling internals are shown in Figure 5-5, no change in DO concentration profiles with change in axial position was observed. The observed complete backmixing of the liquid phase in a column with and without internals is the result of intense large scale liquid circulation that exists in large column diameter with large aspect ratio as a result of non-uniform gas hold up (Degaleesan, 1997; Devanathan et al., 1990).
5.3.1 Gas Hold-up

Figure 5-6 compares the overall gas holdup with and without internals for 18-inch diameter column. It can be seen that the presence of internals significantly increases the overall gas holdup at higher superficial gas velocities. Youssef (2010a) observed a similar increase in a gas holdup in the presence of internals; local gas holdup profiles studied by him follow a similar trend.

In the 8-inch bubble a column larger increase in gas holdup was observed in the presence of internals. As shown in Figure 5-7, we can see that at a superficial gas velocity of 20 cm/sec in the
presence of internals, gas holdup is increase by 30%, compared to 5% increase in 18-inch diameter column.

The gas hold-up in bubble column reactors in the absence of experimental data are predicted using correlations. Out of various correlations available, performance of three widely used correlations in the literature for calculating gas hold up in bubble columns with air-water systems was tested. They are popular due to their simple form, equation 5.2, 5.3 and 5.4 states these correlations.

\[
\varepsilon_g = 0.672 \left( \frac{V_g \mu_L}{\sigma_L} \right)^{0.578} \left( \frac{\mu_L G}{\rho_L \sigma_L^3} \right)^{-0.131} \left( \frac{\rho_G}{\rho_L} \right)^{0.062} \left( \frac{\mu_G}{\mu_L} \right)^{0.107} 
\]  

(Hikita et al., 1980)  

\[
\varepsilon_g = 0.62 V_g^{0.56} \left( \frac{\sigma_w}{\sigma_L} \right)^{0.15} \left( \frac{\mu_w}{\mu_L} \right)^{0.15} \left( \frac{\rho_G}{\rho_{\text{air}}} \right)^{0.15} \left( \frac{\rho_W}{\rho_L} \right)^{0.15} 
\]  

(Joshi, 1998)  

\[
\varepsilon_s = \frac{V_g}{0.3 + 2V_g} 
\]  

(Joshi and Sharma, 1979)

Figure 5-8 compares the performance of these correlations against experimental data in the present study. Points in red color correspond to 8 in column diameter and points with blue color correspond to 18-inch column diameter. The gas holdup for an air-water system without internals in both the
columns are predicted well with all three correlations. However, in the presence of internals the gas holdup for 8-inch column is under-predicted by all the three correlations, but for the 18-inch diameter column gas holdup is predicted reasonably well by the correlations. The gas holdup is affected more by the presence of internal in the smaller column than in the larger 18-inch column.

![Graph showing predicted vs. experimental gas holdup](image)

Figure 5-8 Predicted vs. Experimental gas holdup comparison, red color represents 8-inch column diameter, blue color represents 18-inch column diameter

The changes in gas holdup are directly responsible for changes in the gas-liquid interfacial area. Hence, we can expect higher gas-liquid interfacial area in the presence vertical internals. The increase in interfacial area could result of increase bubble break up in the presence of vertical cooling internals.

5.3.2 Volumetric mass transfer coefficient

The overall volumetric mass transfer coefficients without internals are shown in Figure 5-9 (Different axial positions). The overall volumetric mass transfer coefficients are independent of axial position as the concentration profiles were similar at all axial positions. This justifies the selection of CSTR model to evaluate mass transfer coefficient. It can be seen that the value of volumetric mass transfer coefficient does not differ significantly from each other at different
superficial gas velocities, which is unlike the trend in a bubbly regime where the value of mass transfer coefficient increases with an increase in superficial gas velocity. The change in interfacial area is mainly responsible for changes in $k_{L,a}$ (Vandu et al., 2004b). The interfacial area is related to gas holdup and bubble size. However, in the churn turbulent flow regime, the increase in the gas-liquid interfacial area with an increase in superficial gas velocity is relatively low (Xue, 2004). Moreover, in the churn turbulent regime the mean bubble size remains constant due to rapid bubble breakup and coalescence, as demonstrated by De Swart et al. (1996) using video imaging experiments in a two-dimensional column. Thus, it can be concluded that due to no significant change in mean bubble size the gas-liquid interfacial area remains nearly unchanged, and no significant change in the volumetric mass transfer coefficient was observed.

Volumetric mass transfer coefficients in the presence of internals are slightly less in the without internals, but the values are not statistically different as indicated by error bars in Figure 5-10. Similar results were obtained in 8-inch bubble column reactor as shown in Figure 5-11. We expected internals to affect overall volumetric mass transfer mass transfer coefficient. The volumetric mass transfer coefficient $k_{L,a}$ is a combination of mass transfer coefficient ‘$k_L$’ and interfacial area ‘a’. Higbie’s theory for mass transfer is well accepted to calculate mass transfer coefficient in bubble column (Kawase et al., 1987; Nedeltchev et al., 2010), according to this theory, mass transfer coefficient is given by equation 5.5, ‘$t_c$’ is the contact time of liquid surrounding the bubble which is defined as time taken by bubble to travel its own length (Nedeltchev et al., 2007), it is inversely proportional to bubble rise velocity.

$$k_L = 2 \sqrt{\frac{D_{AB}}{\pi t_c}} \quad (5.5)$$
It is well known that larger bubbles have higher rise velocity than smaller bubbles. Hence larger bubbles are expected to have a higher value of \( k_L \). The work of Youssef (2010a) showed that the average chord length is reduced in the presence of internals decrease in the average bubble velocity, implying that the mass transfer coefficient \( k_L \) should also decrease. Volumetric mass transfer coefficient \( k_L \) is also a function of turbulent intensity, which suggests that the presence of internals should decrease \( k_L \) due to a decrease in turbulent intensity. Hamed (2012b) also showed that the presence of internals, radial as well as axial turbulent diffusivity is decreased, which are responsible for the low value of mass transfer coefficient. On another hand, interfacial area, which is directly proportional to gas hold up, it has increased in the presence of internals due to increase in gas hold up as shown in Figure 5-6 and 5-7. Youssef (2010a) has also found an increase in gas-liquid interfacial area in the presence of internals. Therefore, it can be concluded that the decrease in \( k_L \) is balanced by an increase in interfacial area, and the volumetric mass transfer coefficients are unchanged in the presence of internals at the experimental condition for the study.

Figure 5-9 Mass transfer coefficients at different axial positions, radial position \( r/R=0.38 \) in 18-inch BCR
Figure 5-10 Mass transfer coefficients with and without internals at superficial gas velocity $x/L=0.5$ and $r/R=0.38$

Figure 5-11 Volumetric Mass transfer coefficients with and without internals superficial gas velocity in 8 inch Bubble column reactor

A comparison of correlation to predict volumetric mass transfer in churn turbulent flow regime is tested; Figure 5-12 shows the comparison. Points in red correspond to 20.32 cm (8 inch) column diameter and points in blue correspond to 45 cm (18-inch) column diameter. The correlations used for testing are modified form of correlation proposed by Shah et al. (1982) and correlation proposed by Letzel et al. (1999). The correlations are shown in equation 5.6 and 5.7.

$$k_L a = 0.007 V_g^{0.76} \quad [5.6]$$

(Martín et al., 2009)

62
\[
\frac{k_l a}{\varepsilon_g} = 0.5 \quad [5.7] \quad \text{(Letzel et al., 1999)}
\]

From Figure 5-12, it can be seen that mass transfer coefficients are not predicted well. Both of the correlation have more than 30% error, and the correlation proposed by Letzel et al. (1999) over predicts them. Inability of correlation to predict the volumetric mass transfer coefficient is due to leveling of volumetric mass transfer coefficients with superficial gas velocity as seen in Figure 5.10 and 5.11 in churn turbulent flow regime is not taken into account in the correlations. The general form of correlation by Shah et al. (1982) is represented in equation 5.15,

\[
k_l a = k U_G^\beta \quad [5.15]
\]

The k and \( \beta \) are adjustable parameters depending on the gas – liquid system and geometry. We have collected the data on volumetric mass transfer coefficients evaluated in churn turbulent flow regime in present chapter and in the literature (Hamed, 2012a; Han, 2007; Letzel et al., 1999; Vandu et al., 2004a, b; Vandu and Krishna, 2004) to come up with value of k and \( \beta \) which are applicable for churn turbulent flow regime.

Figure 5-12 Predicted vs. Experimental volumetric mass transfer coefficient comparison, red color represents 8-inch column diameter, blue color represents 18-inch column diameter
The value of k and β were found by least square method using about 50 data points in churn turbulent flow regime from the studies mentioned above. The expression obtained is represented by equation 5.16, the value of parameter k was found to be 0.0973, and the value of parameter β was found to be 0.0862.

\[ k_L a = 0.0973 \times U_G^{0.0862} \]  \hspace{1cm} (5.16)

The expression shows a weaker dependence of volumetric mass transfer coefficient than the original equation proposed by Shah et al. (1982) and modified form of the equation proposed by Martín et al. (2009). The weaker dependence of volumetric coefficient on superficial gas velocity is necessary due to leveling effect of volumetric mass transfer coefficients with superficial gas velocity in churn turbulent flow regime. It should be noted that the above correlation is valid only in churn turbulent flow regime, the data used for the preparation of the correlation ranges from a superficial gas velocity 10 cm/sec to 45 cm/sec and column diameter 0.1 m to 0.45 m. The correlation is formed for air-water system. The performance of the equation to predict volumetric mass transfer in churn turbulent flow regime is shown in Figure 5-13.

Figure 5-13 Predicted vs. Experimental volumetric mass transfer coefficient comparison
The performance of the correlation in present flow regime is no different than original correlation proposed by Shah et al. (1982) and modified form of the equation proposed by Martín et al. (2009). Hence, improved form of correlations to predict volumetric mass transfer coefficients is required in churn turbulent flow regime. Advanced correlation can be obtained using machine learning. However these correlation do not give closed from equation.

5.4 Conclusion

Based on the current study we have illustrated that for column with higher aspect ratios the concentration profile of dissolved oxygen in the liquid phase are identical at different axial locations in the column. This is a result of intense liquid recirculation observed in a column with a large aspect ratio (Chen et al., 2006; Degaleesan and Dudukovic, 1998; Degaleesan et al., 1996). As a result, no variation in volumetric mass transfer coefficients was observed at different radial and axial positions, justifying the use of CSTR model.

It was observed that the existing correlations were able to predict gas hold-ups with reasonable accuracy without internals. In the presence of internals, the correlations well-predicted gas hold up for 18-inch diameter column. However they under predicted for 20.32 cm (8-inch) column. The prediction for volumetric mass transfer coefficients by the existing correlation was more inconsistent than the gas hold-ups. This was mainly due to leveling effect of volumetric mass transfer coefficients in churn turbulent flow regime, which the correlations fail to capture. Modified correlation of the form proposed by Shah et al. (1982) was unable to represent the experimental data. A general correlation to prepresent volumetric mass transfer coefficients in churn turbulent flow regime is required.
The value of volumetric mass transfer did not change significantly due to the presence of internals in the churn turbulent flow regime. Hence, a well-defined correlations for air-water system in churn turbulent flow regime can be used to predict them.
Chapter 6
Bubble Dynamics and Mass Transfer Coefficients in a Photo-bioreactor

6.1 Introduction

Microalgae are rich in lipid content which makes them a potential valuable source of biofuels (Chisti, 2007; Georgianna and Mayfield, 2012). However, there are significant technological and commercial challenges to overcome in scaling up to commercial production both of the systems that envision the use of open ponds, and enclosed equipment (Mayfield and Wong, 2011). Microalgae are also potential sources of high-value products such as carotenes, omega-3 fatty acids, and pharmaceuticals (Markou and Nerantzis, 2013; Skjånes et al., 2012) (see Figure 6-1).

In order to commercially produce high-value chemicals from microalgae, it is necessary to cultivate them in a sterilized and well-controlled environment, such as a photo-bioreactors. Preferred configurations for these reactors are bubble columns that enable recycle either with internal draft tubes, or by coupling of an external up-leg and down-leg. These reactors contain no moving parts in them, and hence microalgae are exposed to a mild shear stress environment. The successful design and scale-up of these photo-bioreactors is a key in the production of high-value compounds using microalgae (Luo, 2005). For successful design and scale-up of a reactor, it is necessary to develop at least a phenomenological model that captures the interactions of key parameters (Dudukovic, 2009, 2010; Dudukovic et al., 1999; Dudukovic and Mills, 2014). For bubble columns, this has been illustrated by Degaleesan (1997), Gupta et al. (2001b), and Chen et al. (2006).
Figure 6-1 Applications of algae for production of high-value products

The past success of the phenomenological models for prediction of bubble columns performance was due to the fact that the systems of interest (e.g., liquid phase methanol synthesis, dimethyl ether synthesis and Fischer Tropsch synthesis) all operated deep in churn turbulent flow regime where turbulent mixing is dominant which enabled the key features of the system, such as radial bubble size and velocity distribution possible to be validated with air water system (Chen et al., 1998; Chen et al., 2005; Degaleesan et al., 1996; Gupta et al., 2001a). In contrast, in scale up of bioreactors and photo-bioreactors, bubbly flow regime is of interest in which the effect of physicochemical properties of the liquid (slurry), should be much more pronounced on the measured quantities that describe bubble dynamics (Clift et al., 1978). The presence of microorganisms in these systems modifies the properties of the liquid phase further by excreting metabolites as they grow. Along with the metabolites, the pH of the liquid phase also changes during their growth, e.g. during growth of cyanobacterial algae the pH of the medium increases from 7.5 to about 9.5. To maintain optimum pH, buffer solutions are added in the preparation of microalgae cultures. The electrolyte and hydroxyl compounds in the buffer solution are expected to alter bubble coalescence rates, which would modify bubble dynamics (Joshi et al., 1998; Kantarci et al., 2005; Mudde, 2005; Mudde et al., 2009). Hence, results from air-water system may not be directly extrapolated to scale-up these systems. To develop a scientific basis for
scale-up of these reactors, it is of interest to determine how bubble dynamics in such systems differs of those detected in air-water under similar hydrodynamic conditions, and whether it changes with the cell culture density. Moreover, one needs to assess whether the transport coefficients in such systems follow the previously established trends. Knowledge of transport coefficients is essential as the oxygen produced in the photosynthesis must be efficiently removed from the liquid phase. Otherwise, excess dissolved oxygen in the liquid phase can suppress photosynthesis (De Mas et al., 1988; Torzillo et al., 1986). Unfortunately, at present, there are no reliable correlations that can predict a priori the effect of the key variables on bubble dynamics and resulting transport coefficients. Thus, one needs to establish what measurements are needed for improved understanding of the system.

In the past, Miron et al. (2000) have tested the applicability of existing correlations to predict the overall gas hold-up and volumetric mass transfer coefficients for bubble column and air lift photo-bioreactor. It was observed that the overall gas hold up in bubble column photo-bioreactor was accurately predicted using correlations by Chisti (1989), which was developed for bubble columns with non-Newtonian fluids. For predicting gas hold-up in airlift photo-bioreactor as a function of gas velocity, the correlations by Akita et al. (1994) could reasonably describe variations in overall gas hold-up. However, correlations by Kawase et al. (1995) and Miyahara et al. (1986) did not capture the trend well, and the empirical constants in these equation needed redefining to make reasonable predictions. For prediction of volumetric mass transfer coefficients, fitting of empirical parameter in the correlation proposed by Chisti (1989) was required for both bubble column and airlift photo-bioreactor. The inability of correlation to a priori predict design parameters highlights the necessity of experiments to further understand these systems.
In this work, first bubble velocities and gas-hold up were examined in a photo-bioreactor over a range of cell culture densities and compared to an air-water system. The bubble chord-length distributions and the gas-liquid interfacial area in a photo-bioreactor at different cell culture densities are then compared with values in air-water. Finally, the variation in volumetric mass transfer coefficient with cell culture density, and superficial gas velocity in a photo-bioreactor is discussed.

Four point optical probes have become a favored tool for measuring local gas holdup, frequency, chord length distribution and interfacial area distribution in bubble columns and other gas liquid contactors, because they work reliably in opaque systems also (Groen, 2004; Harteveld, 2005; Hooshyar et al., 2010a; Manjrekar and Dudukovic, 2015; Mueller and Dudukovic, 2010; Xue, 2004). At the moment, no theory is available for a priori prediction of the local bubble dynamic quantities measured by the optical probes as a function of liquid properties and for their distribution spatially in the vessel of interest. These probes have been used successfully to study bubble dynamics in air-water systems both with and without vertical cooling internals and suspended solids (Hamed, 2012a; Manjrekar and Dudukovic, 2015; Wu, 2007; Youssef et al., 2013). In this work, we extend their application to photo-bioreactors.

6.2 Experimental Set-up

A bubble column reactor 10 cm in diameter was used. For the air-water system, fresh tap water was the liquid phase and air was the gas phase. The column was operated in a batch mode for the liquid phase. All experiments were performed at low superficial gas velocities (bubbly flow regime) ranging from 1 cm/s to 3 cm/s to maintain a low shear environment. The dynamic height of the system was maintained 115 cm above the sparger (aspect ratio of 11). Experiments were
performed at algae cell densities of 0.1 g/L, 0.17 g/L and 0.2 g/L (dried biomass weight). For the photo-bioreactor system, *Synechocystis* PCC 6803 was the cyanobacterial model strain. Batches were first grown in a BG 11 medium in shake flasks at 30°C and 180 rpm under continuous light illumination until one of the three selected optical densities was reached, and then transferred to the cylindrical PBR. The carbon dioxide enriched air was continuously bubbled into the bioreactor to provide CO₂. The optical density was measured at a wavelength of 730nm as an indicator of cell density. Tris Sucrose EDTA (TSE) free acid buffer solution is present in the solution to maintain pH between 7.5 and 9.5. Actual pH of the solution was found to be 8.2 and remained fairly constant over the cell culture densities used in this study.

The probe was positioned at four dimensionless radial locations \[r/R = 0, 0.5, 0.75 \text{ and } 0.9\] along a straight line, with 0 representing the center of the column and 0.9 representing a position at 9/10 of the inner radius from the center that is close to the wall of the column. Figure 6-2 (a) shows the positioning and orientation of the probe inside the bubble column. The probe was oriented in a downward direction to capture bubbles traveling upward (Lee and Dudukovic, 2015).

To obtain bubble dynamics using the algorithm developed by Xue (2004), the signal from the probe must be binary, i.e., signal should only contain two voltages values, one representing gas phase and other representing the liquid phase. In the present case, the presence of any other voltage value in the signal would indicate that the algae are interacting with optical probe signal, producing a voltage signal that is not representative of either gas or liquid phase. Figure 6-3 is a histogram of the signal over the collection time. It can be seen that the signals from both the air – water system and the photo-bioreactor are binary i.e., it only contains value around 1.8 V (liquid) and 3.6 V (gas) for both air water and photo-bioreactor (Lee and Dudukovic, 2014a). The mass transfer coefficients were measured using the dynamic gas oxygen-enriched-air method.
Figure 6-2 Experimental setups (a) Location and orientation of optical probe (b) Experimental setup for mass transfer coefficient measurement.

Figure 6-3 Binary optical probe signals

6.3 Model for the volumetric mass transfer coefficient

To calculate the volumetric gas-liquid mass transfer coefficient both a well-mixed [CSTR] model and axial dispersion model [ADM] are commonly used for the liquid phase (Akita and Yoshida, 1973; Han, 2007; Harmsen, 2007; Lau et al., 2004; Letzel et al., 1999; Vandu et al., 2005; Vandu et al., 2004a) when high gas velocities result in churn turbulent flow in the bubble column.
However, at low superficial gas velocities (bubbly flow regime), such models are unable to fit the observed concentration profile, as shown in Figure 6-4.

![Figure 6-4 Poor fit of the CSTR model to the measured tracer response](image)

The traditional CSTR model overestimates early responses to step inputs of the tracer oxygen, since it assumes that mass transfer occurs at the same rate throughout the entire vessel immediately upon injection of the tracer at the bottom of the column. However, it takes time for the gaseous tracer to travel from the bottom to the top of the column, during which the part of the liquid phase that is not in contact with the gaseous tracer is not participating in mass transfer. The CSTR model agrees well with data only after the gaseous tracer “front,” the moving cross section that roughly divides the column into two parts, one containing the oxygen and the other devoid of it, reaches the top of the column.

To overcome the above shortcomings, the CSTR-PFR model is introduced in which the liquid phase is still assumed to be well mixed, but the gas phase is in plug flow. In this model, the tracer concentration in the gas phase at time $t$ is assumed uniform below the height $H_{g}(t)$, which is the height of the gaseous tracer “front” as illustrated in Figure 6-5. Above $H_{g}(t)$ where the gaseous tracer has yet to reach, its concentration is zero, as is the rate of mass transfer. Thus, only part of
the liquid phase is subject to mass transfer at a uniform rate. The volume of this liquid region is $A_l H_g(t)$, where $A_l$ is the cross-sectional area of the liquid phase, equal to the total volume of the liquid divided by the dynamic height of the bed, $H$. Therefore, the mass balance equation for the tracer concentration in the liquid phase is formulated as follows:

$$\frac{\partial C}{\partial t} A_l H = k_l a_l (C_{sat} - C) A_l H_g (t)$$

$$H_g (t) = \begin{cases} \frac{u_g t}{u_g}, & 0 \leq t \leq H/u_g \\ H, & t \geq H/u_g \end{cases}$$

where $a_l$ is interfacial area per unit volume of the liquid phase, and $u_g$ is the characteristic velocity of the gaseous tracer "front", which for simplicity is approximated as the superficial gas velocity $U_g$, i.e.,

$$u_g = U_g$$

It is noted that the CSTR-PFR model is reduced exactly to the traditional CSTR model when $t \geq H/U_g$.

For the purpose of non-dimensionalization, let

$$F = \frac{C}{C_{sat}} \text{ and } \theta = \frac{t}{\tau}$$

where

$$\tau = \frac{H}{U_g}$$

Then, the dimensionless mass balance equation is
\[ \frac{\partial F}{\partial \theta} = \begin{cases} k_a \sigma (1 - F) \theta, & 0 \leq \theta \leq 1 \\ k_a (1 - F), & \theta \geq 1 \end{cases} \]

The above ODE is easily solved with the initial condition \( F(0) = 0 \) and the result is

\[
F(\theta) = \begin{cases} 1 - \exp\left( -k_a \sigma \cdot \frac{1}{2} \theta^2 \right), & 0 \leq \theta \leq 1 \\ 1 - \exp\left( -k_a (\theta - \frac{1}{2}) \right), & \theta \geq 1 \end{cases}
\]

Figure 6-5 Schematic of the CSTR-PFR model

To validate the developed CSTR-PFR model, it was first used to fit the data from the tracer experiment operated under a superficial gas velocity of 2 cm/s. The dynamic bed height was measured to be 1.24m. The curve fitting was performed in MATLAB®. The experimental and model-predicted F-curve is shown in Figure 6-6 which illustrates that the CSTR-PFR model provides a good agreement with the experimental data for the entire range of \( \theta \), including small
values. Thus, the CSTR-PFR model developed in this work is adequate for determining mass transfer coefficients using tracer experiments.

![Graph](image)

Figure 6-6 Experimental and model-predicted F-curve. \(U_g=2\ cm/s, H=1.24\ m.\)

### 6.4 Results and Discussion

In this section, the effect of the cell culture density on bubble chord length distribution is described, followed by a discussion of observed changes in bubble chord length on bubble velocity, gas hold-up, bubble frequency, gas-liquid interfacial area and volumetric mass transfer coefficients.

#### 6.4.1 Bubble chord length

When gas is passed through an orifice into a pool of liquid, it breaks into bubbles, the size of which depends upon orifice diameter, gas velocity, fluid properties such as viscosity and surface tension at the interphase (Azzopardi et al., 2011). It is well-known that additional mixture components alter surface tension (Joshi et al., 1998; Kantarci et al., 2005; Mudde, 2005). For example, the average bubble size is reduced when alcohol is added to an air-water system but increased when electrolytes are added. In preparing the microalgal culture for the photobioreactor, Tris Sucrose EDTA (TSE) free acid was used as the buffer solution. The addition of TSE is expected to alter
the bubble chord length distribution. It is evident from Figure 6-7 (A) that in the photobioreactor compared to an air-water system operated at identical superficial gas velocities, the average bubble chord length at the center of the column was reduced by 40-70%, and at the wall of the column by 30-50%. The effect of the increase in the cell culture density is not significant, as no observable change in bubble chord length is found (see Figure 6-7 (B)). Moreover, the bubble chord length distributions in a PBR compared to the air-water system are narrower in both the center and the wall region of the column, as shown in Figure 6-7 (C) and (D), respectively.

In the bubbly flow regime for the air-water system, when the superficial gas velocity is increased, the increase in the rate of bubble coalescence is more significant than the increase in the rate of bubble breakup. Thus Figure 6-7 (a) shows an increase in the mean bubble chord length with an increase in the superficial gas velocity at all radial locations. In contrast, no significant change is observed in bubble chord length with increase in superficial gas velocity in the PBR system.

For the air-water system, the bubble chord lengths are larger at the center of the column, as large bubbles formed by coalescence tend to move toward the center of the column due to the action of lift force (Mudde, 2005). In the photo-bioreactor, the average bubble chord lengths are uniform throughout the cross-section of the column and are smaller than in the air-water system, indicating reduced bubble coalescence. The average chord length of bubbles in PBR is 0.2 cm, which is smaller than the critical size of 0.58 cm beyond which lift force acting on the bubbles towards the center of the column becomes significant (Harteveld, 2005).

It should be noted that in a PBR, even though the average chord lengths are uniform throughout the cross-section their distribution is different in the center of the column and the wall region. The frequency of occurrence of bubbles is also different along the cross section of the column as later shown in Figure 6-9 (B).
6.4.2 Bubble velocity distribution in PBR

As a consequence of change in the bubble chord length distribution, the bubble velocity distribution changes as well. Figure 6-8 compares the average bubble velocities and the distribution of bubble velocities in a PBR at the center of the column and at the wall region. Compared to the air water system, at identical superficial gas velocities, the average bubble velocities at the center of the column were reduced by 30-40%; a similar reduction in the bubble velocity was observed in the wall region as well (see Figure 6-8 (A)). In the air-water system, the average velocity of bubbles is higher at the center of the column, because larger bubbles formed by coalescence tend to move toward the central region of the column. However, in
photobioreactors, the average bubble velocities do not vary with radial position, which is the result of reduced bubble coalescence causing more uniform bubble size. In the photo-bioreactor, there was no observable effect of increasing cell density on bubble velocity in the range we studied (see Figure 6-8 (B)). Figure 6-8 (A) and (B) show changes in average bubble velocities, the changes in bubble velocity distribution at the center of the column, and near wall region are shown in Figure 6-8 (C) and (B) respectively. The bubble velocity distribution is broader for air water systems at both the region, the broader velocity distribution is a result of broader bubble size distribution in air-water system (Figure 6-7 (C), (D)).

**6.4.3 Bubble frequency**

Bubble frequency is determined as the number of signal jumps from the liquid phase to the gas phase per unit time in the optical signal. It is represented as the number of gas-liquid interphases arriving per unit time. In a non-coalescing medium, such as PBR, larger number of smaller bubbles are present i.e., larger number gas liquid interphases. Hence, the bubble frequency was larger at all radial locations in a PBR compared to air water system (see Figure 6-9 (B)). The bubble frequency was higher at the center of the column, than near wall region, indicating even though the bubble size is uniform throughout the column, more bubbles exist at the center of the column. The radial profiles of bubble frequency, gas hold up and interfacial area, and their variation with superficial gas velocity are strongly correlated (Xue, 2004). Hence, we can expect similar profiles for gas hold-up and interfacial area.
6.4.4 Gas hold-up

As shown in the Figure 6-9 (A), radial gas hold up profiles follow trend similar to bubble frequency. The gas hold up at the center of the column was found higher than near wall region. Even though the gas hold up profile is not flat, the difference between the gas hold up at the center of the column and near wall region is much less that what is observed in the churn turbulent flow regime (Kumar et al., 1997). Due to a reduction in the bubble velocity, the residence time of the gas phase in the PBR has increased, resulting in higher gas hold up compared to air-water system.
6.4.5 Gas-liquid interfacial area

Gas-liquid interfacial area has increased in PBR due to reduced bubble size. Figure 6-9 (C) shows the gas-liquid interfacial area was increased by about 50% at the central region, and about 10% in the wall region, for the PBR. The radial variation of the gas-liquid interfacial area follows similar trend to bubble frequency. The gas-liquid interfacial area decreases from the center of the column to the wall region, due to the lower bubble frequency in the wall region. Once again, there was no significant effect of an increase in cell culture density.

Figure 6-9 (A) Variation in radial gas holdup with superficial gas velocity (B) Variation in bubble frequency with cell culture density at Ug = 2 cm/s (C) Variation in interfacial area concentration with cell culture density at Ug = 2 cm/s (D) Variation in volumetric mass transfer coefficient with superficial gas velocity

The observed changes in bubble dynamics and the gas-liquid interfacial area in PBR, compared to the air-water system, are caused by the presence of algae, buffer solution and the difference in
the pH of the liquid phase. As can be seen from earlier results, the increased cell culture density did not have a significant effect on either bubble dynamics or interfacial area concentration. Hence, to quantify the effect of buffer solution and alkaline pH, an experiment was performed where the buffer solution was added to the air-water system and the pH of the solution was maintained close to that in a PBR (pH ≈ 8.2). Figure 6-10 compares the results of the air-water system, PBR and air-water system with buffer solution at similar pH of the PBR. It clear that bubble dynamics of the PBR and air-water with the buffer solution at similar pH are comparable. Table 6-1 compares the averages of bubble velocity and bubble chord lengths at the center of the column for all three systems at superficial gas velocity of 2 cm/s. Based on the means and standard deviations, a t-test was performed. On basis of t-test, the mean bubble velocity and bubble chord length for system with buffer solution and basic pH is different from both air-water system and PBR, at significance level of α = 0.05. The mean of bubble velocity and bubble chord length for system in buffer solutions are closer to PBR system than air water system. Based on these observations, we conclude that addition of buffer solution and alkaline pH significantly alters bubble dynamics of air-water system, and addition of algae further changes bubble dynamics. The additional changes in bubble dynamics would be due to presence of algae and metabolites present in the system.
Table 6-1 Average bubble velocity and Bubble chord length at the center of the column (Ug = 3 cm/sec)

<table>
<thead>
<tr>
<th></th>
<th>AW</th>
<th>PBR</th>
<th>Buffer solution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average</strong></td>
<td>32.6</td>
<td>19.5</td>
<td>21.3</td>
</tr>
<tr>
<td><strong>Standard</strong></td>
<td>0.2</td>
<td>0.03</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>deviation</strong></td>
<td></td>
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</tbody>
</table>

Figure 6-10 (A) Bubble chord length distribution at the center of the column r/R = 0 (Ug = 2 cm/s) (B) Bubble chord length distribution at the wall of the column r/R = 0.9 (Ug = 2 cm/s) (C) Comparison of bubble velocity with air-water system, PBR and Basic solution with TES buffer (Ug = 2 cm/s)
6.4.6 Volumetric mass transfer coefficients

The changes in bubble dynamics and gas-liquid interfacial area are expected to be reflected in the interphase transport coefficients. The volumetric mass transfer coefficient $k_{la}$ is a combination of two parameters, the mass transport coefficient $k_l$ and interfacial area concentration $a$ (interfacial area per unit volume of the gas-liquid mixture, $m^2/m^3$). It is noted that $a$ and $a_l$ (interfacial area per unit volume of liquid) differ by a factor of liquid holdup i.e. $\varepsilon a_l = a$. A reduction in the bubble chord length increases the interfacial area concentration. At the same time, a reduction in the bubble chord length reduces the bubble velocity, which increases the contact time of the bubbles (defined in bubble columns as the ratio of bubble diameter to bubble velocity) with the liquid phase (Nedeltchev et al., 2007, 2010). According to penetration theory and surface renewal theory, contact time is inversely proportional to mass transfer coefficients. Hence a reduction in the bubble velocity will reduce the mass transport coefficient $k_l$. The overall change in the volumetric mass transfer coefficient depends on the relative change in the mass transport coefficient and interfacial area concentration. Whether it will increase or decrease depends on which term dominates.

Volumetric mass transfer coefficients in the air-water system and photo-bioreactor are compared in Figure 6-11 where a significant increase in the coefficient in the photo-bioreactor is observed. The increase in gas-liquid interfacial area concentration is responsible for this increase in the volumetric mass transfer coefficient. The coefficient slightly increases with an increase in the cell culture density, and also increases with an increase in superficial gas velocity due to the increase in gas hold-up and interfacial area concentration with the increase in the superficial gas velocity.
6.5 Concluding remarks

This work illustrates the application of a 4-point optical probe technique to study bubble dynamics in a photo-bioreactor.

- The bubble dynamics in photo-bioreactors (PBR) is different from those in an air-water system, mainly because of the presence of buffer solution in the photo-bioreactor, the difference in the pH of the liquid phase, and the presence of algae.
- An increase in the gas-liquid interfacial area in a PBR increases the volumetric mass transfer coefficients. Hence, one cannot directly use the correlations developed for air-water systems to predict volumetric mass transfer coefficients in a PBR.
- No effect of an increase in the cell culture density of the solution was found over the range investigated (1 g/L to 2 g/L). This finding implies that the properties of the bubble dynamics, including the interfacial area concentration, will not affect transport coefficients much during algae growth, as long as the cell mass concentration is not much more than...
doubled. In this work, we studied changes in bubble dynamics and transport coefficients in a system where bubble coalescence is hindered.

- The present work introduces the CSTR-PFR model to predict volumetric mass transfer coefficients in the bubbly flow regime. The model needs additional testing in reactive systems. The challenge to performing this task is the unavailability of a fast response probe for measurement of the dissolved gas concentration in the liquid phase, with the exception of oxygen. This limitation is currently a bottleneck to extensive testing of the developed model. Improvements in the measurement technique for dissolved gases are needed to obtain a deeper understanding of the volumetric mass transfer coefficients.

- The key bubble column parameters [gas holdup profile, bubble velocity, and volumetric mass transfer coefficient] evaluated here can be used for validation of CFD results, which can later be combined with an algae growth model in a scale-up analysis (Chen et al., 2004).
Chapter 7
Summary of Findings and Recommendations

This work investigated bubble dynamics and volumetric mass transfer coefficients in a slurry bubble column, a bubble column photo-bioreactor, and bubble columns of various sizes with and without internals. Distinctively, this work relates changes in volumetric mass transfer coefficients to observed changes in bubble dynamics. In addition, it introduces a model for tracer responses in the liquid phase bubbly flow regime for better prediction of volumetric mass transfer coefficients, and develops a method to identify flow regimes in bubble columns. The present section summarizes the key findings and makes recommendations for future work to advance bubble column design fundamentals.

7.1 Bubble dynamics

Bubble dynamics for two distinct flow regimes were studied here: deep churn turbulent flow in a slurry bubble column and bubbly flow in a photo-bioreactor. Bubble dynamics in the slurry bubble column were primarily affected by turbulent intensities. Buoyancy forces had a larger impact on bubble velocities, and were affected less by the size of bubbles. In contrast, bubble dynamics in the photo-bioreactor in the bubbly flow regime were primarily affected by the physical properties of the liquid, and bubble dynamics were chiefly determined by the bubble size.

In the future, interactions between bubble velocities and liquid recirculation in the bubble column need to be investigated. Knowledge of this interaction will provide insight into the mechanism that increases bubble velocities in slurry bubble columns.

This work has shown that, in the bubbly flow regime, bubble dynamics quantified from the cold flow model are not able to predict bubble dynamics at hot flow conditions for a bubble column.
photo-bioreactor. Hence, along with studies of the cold flow models, we should expand the optical probe technique to hot flow systems. In this way we can test our ability to predict bubble dynamics at these conditions and better understand the connections between hot flow and cold flow models, enabling predictable scale-up.

To apply optical probes to hot flow models, this technique must be modified. The existing technique functions well at high temperature and high pressures (Xue, 2004). However, when optical probes deployed in harsh industrial solvents, the binding epoxy resin of the probe tip dissolves. We need a better binding agent to withstand these conditions.

### 7.2 Mass transfer coefficients

We need a much better understanding of volumetric mass transfer coefficients to predict mass transfer coefficients using correlations. This work has shown that the present correlations are unable to predict the effect of internals on volumetric mass transfer coefficients and gas holdup. They were also unable to predict increases mass transfer coefficients in photo-bioreactors resulting from changes in bubble dynamics.

The model developed here better predicts tracer response in the bubbly flow regime, enabling estimates of the volumetric mass transfer coefficient. This model has been tested by predicting volumetric mass transfer coefficients for a slightly soluble gas, oxygen. The model needs to be further validated to predict tracer responses for more readily soluble gases, such as carbon dioxide. One major problem here is the unavailability of tools to measure the dissolved concentration of gases other than oxygen. This limitation has restricted research in volumetric mass transfer coefficient prediction, because all the work available in the literature focuses on evaluating the volumetric mass transfer coefficients for oxygen (Behkish et al., 2002; Hamed, 2012a; Han, 2007; Lau et al., 2004; Vandu et al., 2004b). We still need to know the transport coefficients for other
gases, such as hydrogen and carbon monoxide (syngas), to advance the syngas fermentation processes (Acharya et al., 2014; Drzyzga et al., 2015; Liu et al., 2014).

In a recent study, Schuhfried et al. (2016) described an alternate technique for measurement of the mass transfer coefficient for bubble columns. Instead of liquid phase measurements, an inert gas was used to strip the liquid phase containing a volatile compound. The volatile compound concentration coming off the liquid phase was detected in the effluent gas. The volumetric mass transfer coefficient was estimated by measuring the time evolution of the concentration profile of the volatile compound in the gas phase. The method was tested in a laboratory scale bubble column, and needs further testing and development before it can be used to estimate volumetric mass transfer coefficients for industrial-scale reactors.

7.3 Flow regime identification

The support vector machine algorithm method developed in the present work demonstrates an approach to classifying flow regimes for various cold flow systems on a single flow regime map. The approach needs to be evaluated at hot flow conditions in a high-pressure bubble column to confirm its performance. Once proven at hot flow conditions, the approach can be used as an online process control tool to predict the operating flow regime in a bubble column, since the parameters required to detect the operating flow regime can be obtained within seconds from an optical probe signal.

To conclude, after years of research on bubble columns, we still do not have an established procedure to scale them up. Various models, ranging from phenomenological models to detailed CFD models, have been developed to predict the performance of bubble columns (Chen, 2004; Degaleesan, 1997; Fan et al., 1999; Inga and Morsi, 1997; Krishna et al., 2001; Macchi et al., 2001; van Baten et al., 2003; Wilkinson et al., 1992; Youssef, 2010b). However, there is a lack of
experimental data to support these models, even under cold flow conditions is a big concern. The largest column supporting fundamental studies on bubble hydrodynamics and mass transfer coefficients is 0.45 m in diameter (Akita and Yoshida, 1973; Chen et al., 2006; Degaleesan, 1997; Hamed, 2012a; Krishna et al., 2001; Youssef, 2010b). This is rather small compared to industrial needs, where columns of 1 m to 5 m in diameter are used (Espinoza et al., 1999). We need detailed studies on hydrodynamics and mass transfer in hot flow pilot scale bubble columns. Such appropriately scaled studies would allow us to validate the existing models under these conditions, as well as help us to understand the link between hot flow models and cold flow models.
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