Vibrations for improving multiphase contact

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VIBRATIONS FOR IMPROVING MULTIPHASE CONTACT

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
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in

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Department of Chemical Engineering

by
Yogesh G. Waghmare
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Abstract

Present work demonstrates the use of vibrations to enhance performance of two multi-phase contacting systems: a bubble column for gas-liquid contacting (physical absorption) and a Piston Oscillating Monolith Reactor (POMR) for gas-liquid-solid contacting (catalytic reactions).

In a bubble column reactor, enhancements of mass transfer coefficient and gas hold up were experimentally studied for the air-water system. Mass transfer coefficient enhancements up to 500% and gas hold-up improvements up to 200% were achieved under the application of low amplitude (0.5-2.5 mm) vibration at low frequencies (0-25 Hz). A fundamental theory was developed from first principles to explain these enhancements. The theory satisfactorily predicts the mass transfer coefficient and the gas hold-up as a function of operating parameters including the frequency and the amplitude of vibrations, the gas superficial velocity and the viscosity of the system. Effects of vibrations on the bubble size distribution were also investigated and population balance modeling was performed to explain the experimental observations.

Performance of a novel three phase POMR was studied for two reactions: hydrogenation of alpha-methyl styrene to cumene and partial hydrogenation of soybean oil using a monolith catalyst washcoated with Pd/Al₂O₃.

Hydrogenation of alpha-methyl styrene reaction was carried out under external mass transfer controlled conditions in the POMR and also in a stirred tank reactor. Results show activity improvement of up to 84% at 17.5 Hz over no-pulsing conditions. It was shown that the POMR provides for rapid mass transfer rates, superior to traditional reactors, and even superior to a stirred tank when compared on a power-per-volume basis.

Soybean oil was partially hydrogenated in the POMR and also in a stirred tank reactor. The reaction was found to be internal diffusion controlled at these conditions. Activity enhancements up to 112% were achieved at 17.5 Hz over no-pulsing conditions. The
enhancements can be attributed to either the increased intra-pore transport or the improved wetting distribution due to the application of vibrations. Improvement in serial pathway selectivity was observed with increasing frequency but stereo-selectivity remained unaffected by the vibrations.
Chapter 1   Introduction

A large fraction of chemical process operations involve contacting between two or more fluid phases. Systems which consist of two or more fluid phases are known as multiphase systems. Multiphase systems are encountered in non-reactive unit operations such as distillation (gas-liquid), drying (gas-solid), extraction (liquid-liquid) etc. as well as in reactive systems such as catalytic cracking (gas-solid), hydrogenation of vegetable oils (gas-liquid-solid) etc.

For a non-reactive multiphase system, generally the objective is to effectively transfer one of the chemical species from one phase to another. For example in absorption processes, transfer of a species of interest from the gaseous phase to the liquid phase is desired. In the case of multiphase reactive systems, if the intrinsic rate of reaction is much faster than the mass transfer rates, then the observed reaction rate is governed by the rate of mass transfer. Thus mass transfer processes can be of immense importance in multiphase phase systems. The performance of the multiphase contacting equipment is generally evaluated in terms of its mass transfer characteristics.

In general, mass transfer rates can be enhanced by supplying extra energy to the system. This promotes mass transfer by creating higher interfacial area and higher turbulence intensities in the system. The most commonly used mode of energy input is agitation of fluid by stirring, as in a stirred tank reactor. Alternatively vibrational energy or pulsations can be used to enhance mass transfer rates. For example in a bubble column (see Figure 1.1), a typical operation is simple gas injection. Here, mass transfer can be promoted by agitation or oscillation.

Use of oscillations for improving performance of chemical process operations can be dated back to 1938. In 1938 Martinelli and Boelter\(^1\) found that heat transfer due to the natural convection from a tube to water can be increased by up to 400% using vibrations. Since then vibrations have been used in a variety of chemical process operations ranging from mineral
washing to fluidization. In a classic paper, Baird\textsuperscript{2} reviewed various applications of vibrations for the chemical processing industry. Baird summarized the effects of different frequency vibrations and its application to various operations as shown in Figure 1.2.

![Figure 1.1 Various modes of energy input for gas-liquid contacting.](image)

### 1.1 Objective

The objective of this research work is to demonstrate and fundamentally explain observed results when using vibrations as a means of performance enhancement for multiphase systems. Current work is focused on two types of multiphase systems, namely non-reacting gas-liquid systems and reacting gas-liquid-solid systems. A bubble column is chosen as equipment to study effects of vibrations on gas-liquid systems. Effects of vibrations on the bubble column are characterized in terms of mass transfer coefficient, gas hold-up and bubble size distribution. A theory is developed from the first principles to explain the results. A piston oscillating monolith reactor (POMR) is used to study gas-liquid-solid system under the influence of vibrations. Two reactions, namely hydrogenation of alpha-methyl styrene and hydrogenation of soybean oil are tested. Performance of a POMR is measured in terms of both the activity of reaction and the selectivity toward the desired products.
1.2 Thesis Outline

The Thesis outline is presented in Figure 1.3. Discussion is divided into 6 independent chapters. Each chapter focuses on an important aspect of this project. These six chapters are either published in peer reviewed journal or are currently under review. Information regarding the publication of each chapter is listed below:


![Figure 1.2 Scope of application of vibrations for various chemical process operations (source: Baird, 1966^2)](image-url)


Apart from these six chapters, there are two more chapters in the thesis. In Chapter 1 a summary of work accomplished and key results are provided in the thesis outline section. The reader interested in additional details is referred to the appropriate chapter 2-7. Next a literature review of vibrations for the performance enhancements in multiphase systems is presented. The final chapter 8 discusses the overall conclusions from the current work and proposes ideas for the future work.

1.2.1 Mass Transfer Experiments (Detailed in Chapter 2)

Initial work in this project focused on the experimental investigation of effects of vibrations on the bubble column performance. The equipment used for the study is shown schematically in Figure 1.4. Low frequency (0-30 Hz) and low amplitude (0.46-2.46 mm) mechanical vibrations were imparted at the bottom of the column with the help of a piston and motor assembly. Distilled water was used as the liquid phase and air was used as the gas phase. Here the gas flow rate is high such that jetting occurs through the injector nozzle. Bubbles are formed as a result of breakage of this jet.

Mass transfer experiments were performed by measuring the dissolved oxygen concentration as a function of time. The volumetric mass transfer coefficient \( k_{l,a} \) was calculated according to the following expression:

\[
\frac{C(t)}{C^*} = 1 - \exp(-k_{l,a}t)
\]

where, \( C(t) \) is the dissolved oxygen concentration at time \( t \) and \( C^* \) is the saturation concentration of oxygen in pure water.
Figure 1.3 Flowchart illustrating the overview of the current thesis work.

Figure 1.4 Oscillating bubble column reactor.
Mass transfer enhancements as compared to the no vibration case \((k_{La^*/KL_a})\) were calculated. Figure 1.5 shows a plot of enhancements obtained at a gas superficial velocity of 0.5 cm/s. It can be seen that the mass transfer rates can be improved by up to 500% using low frequency and low amplitude mechanical vibrations. It should also be noted that the \(k_{La}\) does not increase monotonically with frequency. Initially \(k_{La}\) increases with increasing frequency, ultimately reaching a plateau at higher frequencies.

![Figure 1.5 Enhancement \((k_{La^*/KL_a})\) as a function of frequency for a solid piston with different cam amplitudes. \(U_{og} = 0.5\) cm/s, Membrane thickness = 3.18 mm.](image)

During the experiments, it was observed that the vibrations at the bottom of the column generated waves at the top free interface between the water and the air. At sufficiently high frequencies, the top surface became unstable. Rigorous sloshing and mixing was observed near the top surface. A first modeling effort was to connect the observed bubble breakage and the enhanced mass transfer inside the column proper with the observed instabilities at the top surface.

A theory developed by Benjamin and Ursell\(^3\) was used to predict the frequencies at which the surface instabilities will occur. Benjamin and Ursell showed, under the assumption of small
vibrational amplitude on an inviscid fluid, the stability of the free surface is given by a series of Mathieu equations, which can sustain unstable behaviors at certain pulsing amplitudes and frequencies:

\[
\frac{d^2 a_m}{dT^2} + (p_m - 2q_m \cos 2T)a_m = 0
\]  

(1.2)

where,

\[
p_m = \left( \frac{4k_m \tanh(k_m h)}{\omega^2} \right) \left( g + \frac{k_m^2 \sigma}{\rho_L} \right)
\]  

(1.3)

\[
q_m = 2k_m A \tanh(k_m h)
\]  

(1.4)

and \(a_m\) is the surface fluid amplitude which is a function of time; \(k_m\) is the characteristic eigenvalue obtained from the derivative of the Bessel function; \(\omega\) is the angular frequency of oscillations; \(A\) is the forcing amplitude; \(h\) is the height of the water, \(\rho_L\) is the water density; \(g\) is the acceleration due to gravity; \(\sigma\) is the water surface tension; \(T\) is the period of oscillation taken as \(\frac{1}{2} \omega t\), where \(t\) is the time. Each frequency produces a constant \(p_m\) value and each fixed amplitude produces a constant \(q_m\) value. From the values of \(p_m\) and \(q_m\), regions of instability and stability of the free surface can be predicted as shown in Figure 1.6.

The predictions from this theory showed a good agreement with experimental free surface instability observations, as shown in Figure 1.6. This theory gives a tool to predict the frequencies and the amplitudes at which the enchantments will be observed but it cannot predict the magnitude of these enhancements or the actual value of the mass transfer coefficient.

There have been efforts in the literature to correlate observed \(k_La\) under vibrations to power input.\(^4,5\) We correlated the mass transfer coefficient to the power input as

\[
k_La \propto P_m^{0.4}
\]  

(1.5)

where power input per unit mass of liquid for an oscillating bubble column can be given as
\[ P_m = \left( g U_{og} + \frac{1}{2} A^2 \omega^3 \right) \]  

(1.6)

where \( U_{og} \) is the superficial gas velocity. The first term on the right hand side of equation 1.6 shows power input due to injected gas. The second term shows the contribution to the power term from the oscillations. Equation 1.5 is in close agreement with Baird\(^4\), where he predicted that \( k_L a \propto P_m^{0.42} \). Although this empirical correlation provides a tool for predicting \( k_L a \), it cannot predict the plateauing behavior observed.

![Mathieu stability chart showing stable and unstable region. Darkened data points represent unstable experimental responses, open points represent stable responses.](image)

1.2.2 Development of Theory for \( k_L a \) (Detailed in Chapter 3)

In order to explain the observed performance enhancements in a bubble column due to vibrations, a first principles theory development was undertaken. The volumetric mass transfer coefficient is a lumped parameter that depends on fundamental hydrodynamic parameters including bubble size and bubble rise velocity. These parameters depend on the operating parameters including the frequency and the amplitude of vibrations and the gas superficial velocity.
There are three major effects associated with the oscillations in a bubble column. The first effect of oscillations is the retardation of bubble rise velocity. Here, the application of vibrations imparts an additional downward force on the gas bubble which causes a reduction in the bubble rise velocity. This force is known as the Bjerknes force or the kinetic buoyancy force. Pulsations impart force on the liquid phase causing pressure oscillations. The volume of bubble changes according to the changing pressure. The oscillating fluid phase also imparts an acceleration, in addition to the acceleration due to gravity. The Bjerknes force arises owing to the interaction between the pulsing bubble volume and the acceleration of the oscillating liquid phase. Equation 1.7 shows the time average Bjerknes force acting on the bubble

\[
< F > = V_0 \rho_L g - \frac{\omega^2 A \Delta V_{\text{max}} \rho_L}{2}
\]  

(1.7)

where \( V_0 \) is the mean bubble volume and \( \Delta V_{\text{max}} \) is the maximum volume change due to the oscillating pressure field. The Bjerknes force not only causes the reduction in the bubble rise velocity but at an appropriate combination of frequency and amplitude, the rise velocity can be forced to zero and hence a bubble can be held stationary in the liquid. This phenomenon is known as the flooding point and this is the physical explanation behind the plateauing behavior of \( k_L a \) observed in the Figure 1.5.

Substituting an expression for \( \Delta V_{\text{max}} \) obtained by using Boyle’s law and an oscillating pressure field, we get

\[
\langle F \rangle = \rho_L V_o g \left( 1 - \frac{1}{2} \frac{(\rho_\ell h) A^2 \omega^4}{g P_o} \right) = \rho_L V_o g (1 - Bj(h))
\]

(1.8)

where \( Bj \) is the dimensionless Bjerknes number defined as:

\[
Bj(h) = \frac{1}{2} \frac{(\rho_\ell h) A^2 \omega^4}{g P_o}
\]

(1.9)
where $P_o$ is atmospheric pressure. Taking a time-averaged force balance around a bubble as $Buoyancy force = Drag force$

$$\rho g V_o g(1 - Bj(h)) = \frac{1}{2} \rho U^2 C_D (\pi R^2)$$

(1.10)

and using the Kunii and Levenspiel\textsuperscript{7} drag law $C_D = 10 / \sqrt{Re}$, the following expression for rise velocity was obtained

$$\frac{U}{d} = \left( \frac{2g}{15\sqrt{\nu}} \right)^{2/3} \left[ 1 - Bj(h) \right]^{2/3}$$

(1.11)

The symbol $U$ is used to denote rise velocity, $d$ denotes mean bubble diameter and $\nu$ is the kinematic viscosity.

The second effect is that the power input from forced oscillations causes enhanced bubble breakage. The formation of smaller bubbles creates higher interfacial areas ($a$), which leads to mass transfer improvements. Figure 1.7 clearly shows improved bubble breakage. This improvement owing to bubble breakage can be attributed to the higher power input arising from the impressed pulsations of liquid.

Figure 1.7 Photograph of bubble column showing improved bubble breakage due to oscillations. Photograph is taken at 350 mm above nozzle. $U_{avg} =$0.6 cm/s: (a) no oscillations; (b) with oscillations, $f = 16$ Hz, $A = 1.36$mm
The effect of vibrations on the mean bubble size was quantified by measuring the Sauter mean bubble diameter at various frequencies and amplitude of vibrations. Figure 1.8 shows a decreasing bubble diameter with increasing power input, where the Sauter mean bubble diameter $d$ is plotted against the power input. In a classic paper, Hinze\textsuperscript{8} proposed a correlation based on the Kolmogorov principle of isotropic turbulence to predict bubble diameter as a function of power per unit mass and the cohesive properties of a fluid including surface tension and density:

$$
d = k \frac{\left( \frac{\sigma}{\rho} \right)^{3/5}}{P_m^{2/5}}
$$

(1.12)

where $P_m$ is the power input per unit mass. The symbol $\sigma$ is the surface tension. The constant of proportionality $k$ was found to be equal to 1.7 after fitting. Figure 1.8 shows good agreement between the experimental data and the predictions from the Hinze formula.

![Figure 1.8 Sauter mean bubble diameter (measured at vertical position, $s = 53.8$ cm) vs power input showing Hinze type of bubble breakage.](image-url)
The individual models for the bubble rise velocity and the mean bubble diameter can now be combined to get an expression for the volumetric mass transfer coefficient. Using penetration theory as a basis, for a spherical bubble one can write

\[ k_L a = \sqrt{\frac{4 \, D}{\pi \, t_c}} \left( \frac{6}{d} \right) \varepsilon \]  

(1.13)

where \( D \) is the molecular diffusivity of oxygen in water and \( t_c \) is the contact time taken as the ratio of the bubble rise velocity to the bubble diameter, \( t_c = d / U \), and \( \varepsilon \) is the gas hold-up given as \( \varepsilon = U_{og} / U \). Using equations 1.11, 1.12 and 1.13 the final expression obtained for the average \( k_L a \) in a bubble column is

\[
\langle k_L a \rangle = 4.58 \frac{U_{og} \sqrt{D} \, P_m^{4/5}}{\left( \frac{\sigma}{\rho_L} \right)^6 \left( \frac{g}{\sqrt{U}} \right)^{1/3}} G(Bj)
\]

(1.14)

where,

\[
G(Bj) = \frac{3}{2} \left[ 1 - \left(1 - Bj \right)^{2/3} \right]
\]

(1.15)

This theory was verified against experimental data. Gas hold-up and mass transfer coefficient measurements were performed for a range of gas superficial velocities, namely, 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 cm/s. Frequency was varied from 0 to 30 Hz. Two amplitudes of 1.66 mm and 2.46 mm were investigated. Figure 1.9 shows that the theoretical predictions for \( k_L a \) are in good agreement with the experiments. It should be noted that the constant of proportionality 4.58 in equation 1.16 is obtained solely from first principles; it is not a fitted parameter. The theory predicts the plateau in \( k_L a \) at higher frequencies when rise velocity \( U \) becomes zero. The theory is strictly applicable to dilute gas systems of low viscosity liquids (such as water).
1.2.3 Effect of Viscosity on $k_La$ (Detailed in Chapter 4)

Previous work on pulsed-flow bubble columns focused on air-water systems. There have been no attempts in the literature to investigate the effects of physical properties of the fluid on the volumetric mass transfer coefficient in bubble column with oscillations. This chapter reports the effects of viscosity on mass transfer coefficient in an oscillating bubble column.

Different concentrations (0-3 wt%) of an aqueous solution of carboxymethylcellulose (CMC) were prepared to obtain different viscosities (1-62 cP). Results of mass transfer experiments are shown in Figure 1.10. Similar to our previous work for air-water systems, the viscous system exhibits an initial increase in mass transfer coefficient as a function of frequency and then leveled to a plateau. This asymptotic behavior can again be attributed to the Bjerknes force acting on a bubble, which slows the bubble rise velocity as frequency is increased. The absolute value of the mass transfer coefficient decreases as a function of increasing viscosity.
The observed decrease in mass transfer coefficient can be attributed to a decrease in diffusivity with increasing viscosity. The Stokes-Einstein equation provides a useful relationship between diffusivity and viscosity, for constant density and constant temperature fluids we have:

$$\frac{D_1}{D_2} = \frac{\nu_2}{\nu_1}$$

Equation 1.16 shows that increasing viscosity leads to a decrease in molecular diffusivity. According to penetration theory\(^9\), the mass transfer coefficient depends on diffusivity as

$$k_L \propto \sqrt{D}$$

Thus, an increase in the viscosity causes a decrease in the diffusivity which results in the decreased mass transfer coefficient.

The theory developed in the previous section was modified to take into account viscosity effects. The diffusivity term \(D\) in equation 1.14 was replaced with \(D_0\nu_0/\nu\) following the Stokes-Einstein equation. Here, \(D_0\) is the diffusivity of oxygen in water at the reference viscosity of \(\nu_0\). With the modified theory, the final expression for volumetric mass transfer coefficient is,
The modified theory predicts that

\[ k_L a \propto \nu^{-1/3} \]  

(1.19)

Figure 1.11 provides a plot of experimental \( k_L a \) data vs viscosity on log-log plot which confirms this dependence.

Figure 1.12 shows all the experimental \( k_L a \) data plotted against the theoretical prediction for the applied amplitude of 1.66 mm. It should be noted that the constant of multiplication, 4.58, is obtained from first principles and not from regression. Considering that no parameter fitting was done and the data was collected for a wide range of operating conditions including various superficial gas velocities and a range of viscosities, it can be concluded that the proposed theory does a good job predicting \( k_L a \) behavior under pulsed-flow conditions. The theory is suitable for design purposes.
Figure 1.12 Comparison between theoretical prediction and experimental data for mass transfer coefficient. The solid line shows the theoretically predicted curve according to equation (1.12); $A = 1.66$ mm.

1.2.4 BSD Experiments and Population Balance Modeling (Detailed in Chapter 5)

In the previous sections as well as in the literature, attempts were made to measure the average bubble size in the oscillating bubble column. In reality, there exists an entire range of bubbles sizes and this is often described statistically as a bubble size distribution (BSD). The objective of the part of the work reported here is to explain the effects of forced vibrations on the bubble size distribution. A high speed digital camera was used to measure BSD at different heights in the column. Effects of operating parameters including frequency (0-20 Hz), amplitude (0.46-2.46 mm) and gas flow rate (0.017-0.17 cm/s) were studied.

Figure 1.13 illustrates the effect of frequency on BSD at a height 53.8 cm above the injector. At low frequencies, the bubble size distribution is broad and the Sauter mean bubble diameter is large. The Sauter mean bubble diameter is the ratio of the third moment to the second moment of the BSD. As the frequency is increased, bubbles undergo breakage which results in a sharper (low variance) bell shaped distribution. With increasing frequency, the peak of the bell curve shifts towards the left indicating smaller mean bubble diameters.
Figure 1.13 Effect of frequency on BSD; $Q_g = 10 \text{ ml/s}, A = 1.66 \text{mm}, H = 53.8\text{cm}$

Figure 1.14 shows evolution of Sauter mean bubble diameter with respect to height at constant gas flow rate and oscillation frequency and amplitude. The mean bubble diameter decreases with increasing height, ultimately reaching an equilibrium size. There are two competing processes which govern bubble size in any dispersed system. Bubbles undergo breakage because of the turbulent or shear forces acting on a bubble. At the same time, bubbles collide with each other and coalesce to form larger bubbles. The bubble size distribution reaches an equilibrium value when the rates of these two processes, breakage and coalescence, become equal.

Population balance modeling (PBM) was used to model the breakage and the coalescence processes. Using PBM, the evolution of BSD with respect to the height and the effect of frequency on the BSD were predicted.

Bubbles can be discretized into number of size classes, each class $i$ representing a bubble volume of $v_i$. The steady state population balance equation for a class $i$ can be expressed as
\[ u_i \frac{d}{dx} n_i = [B_B - D_B + B_C - D_C]_i \]  

Figure 1.14 Effect of height on Sauter mean diameter at high gas flow rate; \( A = 1.66 \text{ mm}, \) \( Q_g = 10 \text{ ml/s}, f = 17.5 \text{ Hz}. \)

Here, \( n_i \) is the number density of class \( i \) defined as the number of bubbles in class size \( i \) per unit volume of dispersion; \( u_i \) is the rise velocity of bubble of diameter \( d_i \) and \( x \) is the distance from injector. Left hand side of the equation is the convective term and right hand side represents the source term which accounts for the change in bubble population due to breakage and coalescence processes. Here, \( B_B \) denotes the birth of a particular size bubble due to bubble breakage, \( D_B \) is the death due to breakage, \( B_C \) is the birth due to coalescence and \( D_C \) is the death due to coalescence.

The coalescence model proposed by Luo\(^{11}\) was used to calculate the \( B_C \) and \( D_C \) terms. For calculating \( B_B \) and \( D_B \), two different breakage models, namely, the Martinez-Bazan (MB) and the Luo-Svendsen (LS) were considered. These two models were chosen because the underlying physical assumptions are significantly different. The LS model favors a single bubble
breaking into a large and a small bubble. The MB model favors a single bubble breaking into two equal size bubbles. As a result they predict completely different shapes for the daughter bubble size distribution.

An illustrative result of PBM simulation is shown in Figure 1.15. We have compared the experimentally observed equilibrium BSD at $H = 67.7$ cm (height above the injector) with the simulation results obtained by solving equation 1.20 for both breakage models. Predictions from the MB model match reasonably well with the experimental results although the MB model shows a slightly broader distribution as compared to the experimental values. The BSD obtained from the LS model is not in agreement with experimental results; the distribution curve is much broader than experimentally observed. We speculate that fluid vibrations enhance the production of nearly equal size bubble breakage, mainly owing to shear effects, and this results in more uniform BSD. Details of this work are reported in chapter 5.

![Bubble diameter, d [cm]]

![Volume fraction/ ∆d [1/m]]

Figure 1.15 Comparison between experimentally observed equilibrium BSD and simulation results for two different breakage models at $H = 67.7$ cm, $f = 20$ Hz.
1.2.5 Alpha-methyl Styrene Hydrogenation in a Piston Oscillating Monolith Reactor (POMR) (Detailed in Chapter 6)

Chapters 6 and 7 report the application of vibrations to improve the performance of gas-liquid-solid reactions. Traditionally these reactions are carried out in stirred tank reactors or packed columns. In a stirred tank reactor fine catalyst particles are suspended in the liquid with the help of stirring. Here, a catalyst separation step is often necessary. In packed columns, the catalyst is coated on the packing and liquid and gas phases are passed through the bed. Packed bed reactors show lower mass transfer rates due to low gas and liquid superficial velocities and they also suffer from phase maldistribution. Monolith reactors overcome the difficulties with stirred tank or packed bed reactor, but uniform distribution of the gas and liquid phases in the monolith can be difficult. In this work vibrations are used to promote gas and liquid distribution in monoliths. Added benefits of vibration include increased mass transfer rates.

Hydrogenation of alpha-methyl styrene (AMS) (Figure 1.16) was studied in piston oscillating monolith reactor (POMR). This is a known kinetically fast, mass transfer controlled reaction. The reaction is very selective with a small amount of side products. The reaction can be operated at relatively mild conditions (~50-100°C and ~0.1-0.68 MPa)

\[
\text{AMS} + \text{H}_2 \xrightarrow{\text{Pd/Al}_2\text{O}_3} \text{Cumene}
\]

*Figure 1.16 Hydrogenation of AMS to cumene*

For this reaction, Pd on alumina catalyst was prepared using an ion exchange technique. The catalyst was washcoated on the walls of monolith creating a very thin layer of catalyst which helps in minimizing internal diffusion resistance. Washcoated monoliths were stacked together
alternating with micro-heat exchangers. Micro-heat exchangers provide high heat transfer area and a good control of temperature in the reactor. Figure 1.17 shows a schematic of the POMR.

![Figure 1.17 Schematic of the Piston Oscillating Monolith Reactor (POMR).](image)

The alpha-methyl styrene reaction was carried out in POMR at three different frequencies (0, 8, 15 Hz) at $T = 46^\circ C$ and $P = 0.44$ MPa. Samples were analyzed using a gas chromatography to obtain product concentration profiles with respect to time. The rate of reaction based on concentration data is shown in Figure 1.18. Results show activity enhancements up to 84% for 17.5 Hz at 2.5 mm amplitude over the no pulsing case. These activity enhancements can be attributed to increased mass transfer rates because of oscillations. The low frequency (~0 Hz) results from the POMR need additional explanation. Hydrogen had to be recycled in the POMR because of the low per pass conversion. The recycle pump imposed a frequency of ~0.5 Hz regardless of the piston oscillations.

For comparison purposes, the reaction was also carried out in a stirred tank reactor at the identical temperature and pressure conditions. The observed reaction rates in the stirred tank
reactor are also shown in Figure 1.18. It can be seen that even without the applications of oscillations, POMR gives more than 200% activity improvement compared to the stirred tank.

![Graph showing comparison between hydrogenation rates in POMR and stirred tank.](image)

**Figure 1.18 Comparison between hydrogenation rates in the POMR and stirred tank.**

The mass transfer coefficient in POMR was calculated based on correlations available in literature. Results of mass transfer coefficient calculations are provided in Table 1.1 where both theoretical mass transfer rates and reaction rates are provided. The mass transfer rates were equated to the rate of reaction to obtain the concentration of the reactants on the catalyst surface ($C_{surf}$) according to,

$$ k_{av}a(C^* - C_{surf}) = \eta r(C_{surf})\rho_c $$

(1.21)

Here, $k_{av}a$ is the overall volumetric mass transfer coefficient, $C^*$ is saturation concentration of hydrogen in reaction mixture, $\eta$ is effectiveness factor, $r(C_{surf})$ is intrinsic reaction rate at catalyst surface concentration and $\rho_c$ is catalyst density. We found that $C_{surf} / C^* < 1$ which suggests that the concentration gradient across the external diffusion film is large and hence the reaction is external mass transfer limited.
The theoretical reaction rates were calculated as $\eta r(C_{\text{surf}})$. This gives the maximum theoretical reaction rate. Minimum reaction rates were also calculated to take into account the fact that the monolith holes are filled with liquid during only half of the oscillation cycle (downstroke). The minimum rate of reaction predicted from these calculations was in agreement with the experimentally observed reaction rates (see Table 1.1).

Table 1.1 Theoretical mass transfer rates and reaction rates.

<table>
<thead>
<tr>
<th>$f$ (Hz)</th>
<th>$k_{\text{m,a}}$ (1/s)</th>
<th>Experimental Rate min (mmol/gPd.s)</th>
<th>Theory Rate min (mmol/gPd.s)</th>
<th>Theory Rate max (mmol/gPd.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.86</td>
<td>16</td>
<td>15</td>
<td>29</td>
</tr>
<tr>
<td>8</td>
<td>1.5</td>
<td>22</td>
<td>25</td>
<td>49</td>
</tr>
<tr>
<td>17.5</td>
<td>2.4</td>
<td>30</td>
<td>40</td>
<td>75</td>
</tr>
</tbody>
</table>

Figure 1.19 Comparison of reactor performance for different types of reactors

The activity of the POMR was compared with the available literature\textsuperscript{13,15-23} which uses other reactor types as shown in Figure 1.9. It was concluded that the POMR provides for rapid mass transfer rates in gas-liquid transport limited reactions, superior to several other reactors of advanced design, and even superior to a stirred tank when compared on a power-per-volume
basis. The POMR comes with the added advantage of a fixed-bed catalyst, in a conventional package – a monolith. It is the type of oscillations (low frequency and amplitude), and how they are generated (by a piston-cam arrangement), that set the POMR apart from previous work in the area of novel gas-liquid contactors.

1.2.6 Partial Hydrogenation of Soybean Oil in Piston Oscillating Monolith Reactor (Detailed in Chapter 7)

The heterogeneous catalyzed hydrogenation of edible oils has long been an important process for the food industry because hydrogenation provides oil with improved resistance to oxidation and better textural properties (e.g. a higher melting point). This reaction is traditionally carried out in a three-phase stirred tank at 0.1-0.7 MPa and 150-200°C using a Ni based catalyst present as a slurry. Ni is used industrially, because it is a low cost catalyst. Pd is more active catalyst, but cost due to catalyst losses from the slurry would be high. Our research allows washcoating of the catalyst on the MR and the use of Pd.

The soybean oil is a mixture of Palmitic acid (C16:0), Stearic acid (C18:0), Oleic acid (C18:1), Linoleic acid (C18:2) and Linolenic acid (C18:3). In the representation CXX:Y, XX indicates the alkyl group chain length and Y represents number of double bonds. A simplified hydrogenation reaction scheme can be presented as

\[
\text{C18:3} \xrightarrow{k_3 \text{H}_2} \text{C18:2} \xrightarrow{k_2 \text{H}_2} \text{C18:1} \xrightarrow{k_1 \text{H}_2} \text{C18:0}
\]  

This reaction is first order in hydrogen concentration and first order in double bond concentration.

In this work, the overall degree of unsaturation was measured in terms of the Iodine value (IV). By measuring the decrease in IV with respect to time, the rate of hydrogen consumption (this is the same as the rate of reaction) was calculated. The soybean oil hydrogenation reaction was carried out in POMR at 110°C and 0.41MPa at three different piston frequencies of 0, 8,
17.5 Hz. Amplitude for 8 and 17.5 Hz was kept constant at 2.5 mm. Results are shown in Figure 1.20. It can be seen that the reaction rate enhancements of 112% can be achieved with 17.5 Hz vibrations as compared to no piston vibration case (real vibration frequency is 0.5 Hz due to recycle pump). For comparison purposes, soy oil hydrogenation was also carried out in a stirred vessel using the same type of monolithic catalyst as in the POMR and under the identical temperature (110°C) and pressure (0.41 MPa) conditions. The reaction rate in the stirred tank is lower than the reaction rate in the POMR for all the frequencies. Operation at 512 rpm in stirred tank represents an equivalent power input per unit volume for POMR operating at 8 Hz. More than 300% enhancement in POMR was achieved as compared to stirred tank on equivalent power per unit volume basis.

![Figure 1.20 Effect of frequency on hydrogenation rate in the POMR. Conditions: T = 110°C, P = 0.4 MPa, A = 2.5 mm.](image)

**Figure 1.20** Effect of frequency on hydrogenation rate in the POMR. Conditions: $T = 110^\circ$C, $P = 0.4$ MPa, $A = 2.5$ mm.
Further experiments were performed with different diameter powdered catalyst ($L = 6-28 \, \mu m$) in the stirred tank at 2000 rpm. Powdered catalyst showed higher activity as compared to the monolith catalyst. In Figure 1.21, a plot of rate against $1/L$ illustrates the effect of diffusion length on reaction rate. It can be seen that the reaction rate is unaffected by the catalyst size for smaller catalyst particles suggesting absence of internal diffusion limitation. Reaction rate decreases rapidly with increasing particle size for large diffusion lengths indicating the presence of internal diffusion limitations. The Weisz-Prater modulus calculated from the observed reaction rates, confirmed that the reaction is internal diffusion limited for large catalyst particles including the monolith catalyst which has a diffusion length scale (100 $\mu m$) larger than the powdered catalyst. Hence, it can be concluded that the oscillations are capable of improving internal diffusion in porous catalyst.

![Graph](image_url)

**Figure 1.21** Dependence of the reaction rate on the diffusion length of catalyst.

In a previous study Chandhok et al.\textsuperscript{24} achieved up to two orders of magnitude enhancement in mass transfer coefficient by pulsating flow through a liquid membrane, at frequencies in the 1 Hz range. Leighton and McCready\textsuperscript{25} explained that the enhancement of diffusive transport in membranes due to oscillating flows can result from enhanced Taylor
dispersion in the pores. They proposed that the mass transfer enhancements are function of Womersley number $\alpha = a(\omega/\nu)^{0.5}$ ($a$ is pore radius) and Schmidt number $Sc = \nu/D$. According to this theory, for a pore radius of 10$\mu$m and assuming that the fluid pulsations only penetrate up to a distance of $1/10^{th}$ of the washcoat thickness, we found that transport enhancements of 93% and 78% can be achieved for 17.5Hz and 8Hz frequency respectively as compared to no piston pulsing. This is in order of magnitude agreement with the experimental data which shows enhancements of 112% and 34% for the 17.5 and 8Hz. The present work suggests that oscillations can induce significant enhancement in pore diffusion/convection in the monolith washcoat.

While a high activity is desired, selectivity is also important for soy oil hydrogenation. Serial pathway selectivity is important because the desired product distribution favors the mono and di- unsaturated fatty acids (partial hydrogenation). Recent health concerns regarding the adverse effects of trans fatty acids (TFA) has spurred further interest into minimizing the formation of TFAs. In this work, both serial pathway selectivity and trans isomer formation were examined. Irrespective of the reactor system used (stirred tank or POMR) the monolith catalyst showed lower serial selectivity and higher TFAs formation as compared to the powdered catalyst. This lower performance can be attributed to intraparticle diffusion limitation with respect to triglycerides. Thus, it was shown that both the activity and the selectivity are governed by intrapartical diffusion limitation for soybean oil hydrogenation reaction.

### 1.3 Literature Survey

This section is divided into three parts. The first part gives an overview of the applications of vibration for a variety of chemical process operations. The present work uses vibrations in two contactors, bubble columns and monolith reactors. Literature is reviewed for these applications in the last two sections.
1.3.1 Applications of Vibrations

1.3.1.1 Solid-Liquid Systems

Vibrations are used in the solid-liquid filtration operation where mechanical vibrations help in the delaying of cake formation at the filtration screen and thus allowing longer uninterrupted operation.\textsuperscript{26} Svarovsky\textsuperscript{27} reported a commercial application of this principle in a pneumatically vibrated tubular pressure filter. The high-frequency, low amplitude vibrations lead to slurry agitation and help dislodge the solids during the backwash process. Sawyer\textsuperscript{28} has patented a similar tubular pressure filter in which a filtration blanket in the form of a membrane is constantly cleaned by sonic waves. Vibrations are generated by a transducer attached to the membrane wall which causes cavitation and continuous cake removal.

There are many well established industrial applications of vibrations in the mineral processing industry. Low frequency fluid pulsations have been used in mineral washing operations to achieve better separation of coal.\textsuperscript{29} It is known that high range ultrasonic frequencies can be used in floatation devices to effectively separate small solid particles from the liquid phase.\textsuperscript{30}

1.3.1.2 Liquid-Liquid Extraction

Fluid pulsation at low frequencies has been found to be very effective in improving the performance of continuous liquid-liquid extraction processes in sieve plate column. Grinbaum\textsuperscript{31} has reviewed the state of the art for design and analysis of pulsed columns for liquid-liquid extraction. There are two possible ways to impart these pulsations. One way is to the vibrate sieve plates in the column and an alternative is to hold the plate stationary and pulse the flow of the continuous phase. Pulsations not only helps in reducing the stage height but it also delays column flooding.\textsuperscript{31} Delayed column flooding allows higher throughput. In liquid-liquid extraction columns, the dispersed phase tends to coalesce near the sieve plates and pulsations
cause it to re-disperse, resulting in the improved column performance. Pulsed liquid-liquid extraction techniques were originally developed in the nuclear industry for refining uranium by solvent extraction. Pulsed sieve plate columns are being replaced with pulsed disc and donut columns.

1.3.1.3 Fluidization

When a bed of solid particles is vertically vibrated it was observed that the bed expands at certain frequencies. It was found that fluidization of a vibrating bed can be achieved at much lower gas superficial velocity as compared to a static bed of solid particles. Very small particles of size smaller than 35 µm (known as Geldart group C particles) are considered not suitable for fluidization because of the strong intraparticle attractive forces. Mechanical vibrations have proved to be useful in fluidizing these cohesive particles. Mechanical vibrations provide extra energy to overcome the intraparticle forces thus avoiding agglomeration and channeling. With the application of vibrations it was found that along with improved fluidization characteristics, the gas-solid contact efficiency and the rates of the heat and mass transfer can be significantly improved.

1.3.1.4 Chemical Reactions

The use of ultrasonic waves (20-100 kHz) to enhance chemical reaction rates has been extensively studied in the literature. Pressure fluctuations in the ultrasonic waves cause bubble formation due to vaporization of the liquid. The bubble subsequently collapses or cavitates, momentarily creating local high temperatures. These momentary high temperatures are responsible for the improved reaction rates. Apart from the cavitation effect, ultrasonic waves are also capable of improving reaction performance by enhancing the mass transfer rates. It has been found that the ultrasound increases the effective diffusivity in the solid-liquid system as the ultrasound reduces the diffusion film thickness.
1.3.1.5 Gas-liquid Contacting

The effect of pulsation on gas-liquid systems has been mainly studied for two different equipment types, namely packed towers and bubble columns. A comprehensive review of challenges and advantages of pulsed packed bed operation has been given by Silveston and Hanika.\(^{43}\) In the packed column configuration, the gas phase flow rate or the liquid phase flow rate is pulsed at low frequencies (below 20Hz) to create alternate cycles of gas rich and liquid rich conditions. This results in better catalyst wetting and thus improved effective surface area. During the liquid rich cycle, the liquid products formed at the catalyst surface are washed away. Subsequently during the gas rich cycle, a thin film of liquid is formed around the catalyst and fresh gaseous reactants are provided through this thin film to the catalyst surface. Results for pulsed packed bed operations are summarized in Table 1.2.

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Reaction</th>
<th>Pulsed parameter</th>
<th>Cycle period [min]</th>
<th>Split*</th>
<th>Performance enhancement [Max %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urseanu et al.(^{44})</td>
<td>a-methyl styrene (AMS) hydrogenation</td>
<td>Natural pulsed flow</td>
<td>NA</td>
<td>NA</td>
<td>50</td>
</tr>
<tr>
<td>Castellari and Haure(^{48})</td>
<td>AMS hydrogenation</td>
<td>Liquid flow</td>
<td>5-45</td>
<td>0.3-0.5</td>
<td>400</td>
</tr>
<tr>
<td>Khadilkar et al.(^{17})</td>
<td>AMS hydrogenation</td>
<td>Liquid flow</td>
<td>0.1-10</td>
<td>0.1-0.6</td>
<td>60</td>
</tr>
<tr>
<td>Lange et al.(^{45})</td>
<td>Cyclohexane hydrogenation, AMS hydrogenation</td>
<td>Composition</td>
<td>1-30</td>
<td>0.2-0.5</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liquid flow</td>
<td>0.2-0.5</td>
<td>0.25-0.5</td>
<td></td>
</tr>
<tr>
<td>Haure et al.(^{46})</td>
<td>SO(_2) oxidation</td>
<td>Liquid Flow</td>
<td>10-80</td>
<td>0.1-0.5</td>
<td>50</td>
</tr>
</tbody>
</table>

* Fraction of cycle when flow rate is high

Many investigators have reported use of vibrations in bubble column for gas liquid contacting. The first report appeared in 1960, when Harbaum and Houghton\(^{47}\) showed that the rate of absorption of CO\(_2\) in water can be enhanced up to 70% by the application of vibrations in
the frequency range 20-2000 Hz and with amplitudes of 0.01-1.0 mm. Vibrations were generated using an electromagnetic vibrator which functions very similar to a loudspeaker. Hence, sometimes these vibrations are also referred to as sonic vibrations. Although the electromagnetic vibrators can generate high frequencies, the amplitude can not be held constant and it decreases with increasing frequency. They observed that the volumetric mass transfer coefficient \((k_{L}a)\) shows multiple maxima when the frequency was increased. Location of these peaks changed depending on the total height of the liquid in the column. They attributed these mass transfer enhancements to the resonance effects caused by traveling waves reflected from the surface of the liquid. They studied the effect of power input on \(k_{L}a\) and observed a linear dependence of \(k_{L}a\) on the total power input in the range 0-1 W. Harbaum and Houghton\(^{48}\) investigated effects of vibrations on the hydrodynamic parameters including gas hold-up, interfacial area, bubble number density and rise velocities. They observed multiple maxima in gas hold-up, interfacial area and bubble number density with increasing frequency and multiple minima in rise velocity. The enhancements observed in the gas hold-up, interfacial area and bubble number density were 400\%, 100 \% and 100\% respectively.

Bretsznajder and Pasiuk\(^{49}\) studied CO\(_2\) absorption in water, using a mechanical vibration system. With the mechanical vibrations, they were able to achieve higher amplitudes (0.5-10.5 mm) at the expense of lower frequency (0-70 Hz). The key advantage of mechanical vibration is, amplitude can be held constant independent of the frequency of vibration. They also observed multiple maxima in absorption rates as a function of the frequency. Bretsznajder and Pasiuk noted that, under the influence of vibrations, the free surface of the water undergoes considerable agitation. The agitations resulted in entrapment of gas bubbles from the CO\(_2\) rich space above the liquid. The captured bubbles then travel downward into the bulk liquid. Bretsznajder and Pasiuk postulated that CO\(_2\) entrapment from the free surface is the main source of the overall mass
transfer enhancement in the oscillating bubble column. This is the only work to attribute mass transfer enhancement to the surface effect.

Baird and Garstang\(^4\) investigated the absorption of oxygen from air into water in a pulsed bubble column. Equally placed baffles were moved coaxially to impart oscillations to the fluid phase in the column. They found that the gas hold-up, \(\varepsilon\), and mass transfer coefficients, \(k_{L,\alpha}\), were increased up to three times with the fluid oscillations. Recently, Krishna and coworkers\(^{50-58}\) investigated oscillating bubble columns for air-water system. A summary of oscillating bubble column studies reported in literature is shown in Table 1.3.

### 1.3.2 Explaining the Effects of Oscillations on a Bubble Column

As shown in Table 1.3 the effect of oscillations on the overall bubble column performance is generally measured in terms of the volumetric mass transfer coefficient, \(k_{L,\alpha}\), and voidage, \(\varepsilon\), which is discussed in previous section. On a more fundamental level the observations for \(k_{L,\alpha}\) and \(\varepsilon\) can be traced to hydrodynamic quantities including bubble size, bubble rise velocity and interfacial area. These variables are interrelated and they directly affect \(k_{L,\alpha}\) and \(\varepsilon\) as schematically shown in Figure 1.22. In order to understand the results shown in Table 1.3, this section discusses the effect of oscillations on each of these parameters separately.

### Table 1.3 Summary of literature on oscillating bubble columns

<table>
<thead>
<tr>
<th>Researcher</th>
<th>System</th>
<th>(f) (Hz)</th>
<th>(A) (mm)</th>
<th>(U_{og}) (mm/s)</th>
<th>(k_{L,\alpha}) (s(^{-1}))</th>
<th>(k_{L,\alpha}) enhancements*</th>
<th>(\varepsilon) enhancements*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bretsznajder and Pasiuk(^{59})</td>
<td>CO(_2) – water</td>
<td>0 - 70</td>
<td>0.5 – 10.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Harbaum and Houghton(^{48})</td>
<td>CO(_2) - water</td>
<td>20 - 2000</td>
<td>0.01 – 1</td>
<td>14</td>
<td>0.02 – 0.06</td>
<td>1.7</td>
<td>0.05 – 0.25</td>
</tr>
<tr>
<td>Baird and Gerstang(^4)</td>
<td>Air – water (baffled)</td>
<td>1 – 1.35</td>
<td>0 – 94</td>
<td>8 – 25</td>
<td>0.03 – 0.17</td>
<td>3</td>
<td>0.04 – 0.2</td>
</tr>
<tr>
<td>Krishna and Ellenberger(^{53})</td>
<td>Air – water</td>
<td>0 – 120</td>
<td>0 - 25</td>
<td>1 – 15</td>
<td>0.01 – 0.05</td>
<td>4</td>
<td>0.01 – 0.12</td>
</tr>
</tbody>
</table>

* Enhancements in \(k_{L,\alpha}\) (or \(\varepsilon\)) are calculated as \(k_{L,\alpha}\) (or \(\varepsilon\)) with vibrations/\(k_{L,\alpha}\) (or \(\varepsilon\)) without vibrations.
1.3.2.1 Bubble Size

Bubble size plays an important role in determining the rate of mass transfer processes for any gas-liquid system as bubble size determines the interfacial area available for the mass transfer. Bubble size also determines the rise velocity of bubble, which in turn affects the gas hold up. Hydrodynamics of the fluid phase such as the extent of recirculation, flow patterns, homogeneous/heterogeneous regime of operation are also governed by bubble sizes. Hence, it is important to understand the effect of oscillations on this important parameter.

At lower power input in the column, the bubble size prevalent in the column is the same as the formation bubble size at the injector. There are two different ways in which bubbles can be formed at the injector. At low gas flow rates bubbles are formed one at a time at the injector and this process is called bubbling. If the gas velocity through the orifice becomes sufficiently high, bubbles are no longer formed individually and the gas leaves the orifice in the form of a jet, which eventually breaks down into individual bubbles. According to Wallis\textsuperscript{113} the condition for the formation of a gas jet is given as,

\[
\frac{u \sqrt{\rho_G}}{(g \sigma (\rho_L - \rho_G))^{0.25}} > 1.25 \left( \frac{4 \sigma}{g (\rho_L - \rho_G) d_o^2} \right)^{0.5} \tag{1.23}
\]
where $u$ is the linear velocity of the gas through the orifice, $\sigma$ is the surface tension, $g$ is acceleration due to gravity and $d_0$ is orifice diameter. The symbols $\rho_G$ and $\rho_L$ are gas and liquid densities respectively.

Fawkner et al.\cite{60} studied bubble formation at the orifice in pulsed-flow liquids. Pulsations were applied by changing the liquid flow rate through the column using a ball valve. They observed that the bubble size at the orifice goes through multiple minima and maxima as frequency was varied from 0-60 Hz. They related the displacement of the center of the bubble relative to the liquid based on a force balance around the bubble and the superimposed liquid velocity. Distance of the center of the bubble from the injector tip decides the detachment of the bubble from the injector. The theoretical model overpredicted bubble sizes but was able to pinpoint the frequencies at which maxima and minima in bubble sizes were observed.

Krishna et al.\cite{50} showed that the number of bubbles can be greatly enhanced in the frequency range 100-200 Hz. This increase in number of bubbles can cause area increases up to 140 %. Krishna and Ellenberger\cite{52} attributed mass transfer enhancements entirely to the reduction in the bubble size. Contrary to the observation of Fawkner et al.\cite{60}, Krishna and Ellenberger\cite{57} observed that at constant amplitude bubble diameter decreases monotonically as frequency is increased and it levels off at around 100 Hz. The detachment of a bubble at the injector is governed by the force balance around the bubble. The bubble is held at the injector by the surface tension force between the injector tip and the bubble. Buoyancy and momentum of the gas opposes the surface tension force. Application of vibration provides an additional force opposite to the surface tension force promoting the early detachment of the bubble from the injector. CFD simulation of the bubble formation process at the orifice\cite{55} showed that the vibrations help in the early detachment of bubbles from the orifice and thus produce smaller bubbles.
The bubbles size can also change from its original size as it moves up in the column. A bubble can break into smaller daughter bubbles or two bubbles can coalesce to form a larger bubble. The bubble breakage and the coalescence processes occur simultaneously and they compete with each other. When the rate of breakage and the rate of coalescence become equal, the bubble size reaches a steady equilibrium value.

Earlier investigations assumed that the dispersed phase consists of a single bubble size. In reality, there exists an entire range of bubble sizes and this is often described statistically as the bubble size distribution (BSD). Generally, the bubble size distribution is measured in terms of the number density, \( n(d) \), of bubbles. The concept of number density is very similar to concentration and is defined as the number of bubbles of size \( d \) per unit volume of fluid dispersion.

A typical bubble size distribution curve is shown in Figure 1.23. It should be noted that the BSD is a function of axial position in the column owing to the breakage and coalescence processes. The bubble size distribution curve depends on properties of the system including viscosity, surface tension and power input in the system. As shown in Figure 1.23, the BSD is broad near the injector; a wide spectrum of bubble sizes are present. As bubbles move up the column, they simultaneously undergo breakage and coalescence, ultimately reaching an equilibrium size. Hence, at larger distances from the injector the BSD becomes narrower and also mean bubble size decreases. Oscillations provide power input to the system producing an even narrower size distribution and smaller mean bubble diameters as compared to the non-oscillatory case.

Previous attempts in the literature focused on understanding the effects of oscillations on the average bubble size. There has been no study investigating bubble size distribution under oscillating condition. The work presented here (chapter 5) fills this gap.
Figure 1.23 Bubble size distribution evolution with respect to axial position, x: (a) BSD at height $x = H$ with oscillations; (b) BSD at height $x = H$ without oscillations; (c) BSD at the injector, $x = 0$.

1.3.2.2 Rise Velocity

Bubble rise velocity is governed by the force balance around the bubble. In the absence of vibrations there are dominantly two forces acting on a bubble: buoyancy force, which is responsible for the upward movement of the bubble and the drag force, which opposes this
movement. In case of a turbulent flow regime, lift force may also play an important role, but it is neglected for the current discussion. Application of oscillations results in an additional force acting downward, generally known as the Bjerknes force. The Bjerknes force is also known as the kinetic buoyancy force. This force arises due to the interaction between the varying bubble volume and the acceleration of pulsing liquid phase. Vibrations produce an oscillating pressure field in the liquid phase as given by the following equation:

\[ P = P_o + \rho_L h g - \rho_L h \omega^2 A \sin \omega t \]  

(1.24)

where, \( P \) is the instantaneous pressure, \( P_o \) is the external pressure at the top free surface of liquid, \( h \) is the height of the liquid column above the bubble, \( \rho_L \) is the liquid density, \( \omega \) is angular frequency of oscillations and \( A \) is the amplitude of vibration.

The volume of a bubble varies according to the changing pressure and it can be assumed that bubbles pulsate in phase with the pressure. If it is assumed that bubble pulsation is isothermal with the internal pressure following Boyle’s law, then the bubble volume can be given as

\[ V = V_0 + \Delta V_{\max} \sin \omega t \]  

(1.25)

where, \( V \) is the instantaneous bubble volume, \( V_0 \) is the mean bubble volume and \( \Delta V_{\max} \) is the maximum volume change due to oscillating pressure. Using Equation 1.24 and 1.25 and using Boyle’s law, maximum change in volume can be given as

\[ \frac{\Delta V_{\max}}{V_o} = \frac{\rho_L h \omega^2 A}{P_o + \rho_L h g - \rho_L h \omega^2 A} \]  

(1.26)

In general, the buoyancy force, \( F \), is given as weight of the liquid displaced by the gas bubble

\[ F = V(\rho_L - \rho_G)g \]  

(1.27)

Neglecting gas density we can write,
The displacement, $X$, of the fluid phase due to vertical sinusoidal oscillations is given as

$$X = A \sin \omega t$$

(1.29)

The second derivative of displacement $X$ will give the acceleration as

$$\ddot{X} = -A \omega^2 \sin \omega t$$

(1.30)

Now the total acceleration acting on a bubble is the combination of the gravitational acceleration and the acceleration due to oscillations, given as $g - A \omega^2 \sin \omega t$. Using this total acceleration and the instantaneous volume given by equation 1.25, Bjerknes proposed that the instantaneous force acting on a bubble due to kinetic buoyancy can be given as

$$F = (V_0 + \Delta V_{\text{max}} \sin \omega t) \rho_L (g - A \omega^2 \sin \omega t)$$

(1.31)

Note the similarities between equation 1.28 and equation 1.31. The constant volume in equation 1.28 is now replaced by the oscillating instantaneous volume. An additional oscillatory acceleration term is added to the gravitational acceleration term. The instantaneous force can be time averaged over the period of oscillation to get the average force given in equation 1.32 as

$$\langle F \rangle = V_0 \rho_L g - \frac{\omega^2 A \Delta V_{\text{max}} \rho_L}{2}$$

(1.32)

Equation 1.32 contains an additional negative term which reduces the original buoyancy force thus reducing the rise velocity of the bubble. At an appropriate vibration intensity, $\langle F \rangle$ can be forced to zero and thus bubble can be held stationary in the liquid. Buchanan showed that this stagnation point can be achieved when

$$\frac{\Delta V_{\text{max}}}{V_0} = \frac{2g}{\omega^2 A}$$

(1.33)
Using a similar analysis Jameson and Davidson\textsuperscript{63} arrived at the following expression for the stagnation point

\[
\frac{f^4 A^2 \rho_L h}{2g(P_0 + \rho_L gh)} = 1
\]  

(1.34)

If the frequency is increased further beyond stagnation point, then bubbles start moving downward. Buchanan\textsuperscript{62} showed that it is possible to entrain the bubbles at the top liquid surface by this method. These bubbles migrate cyclically from the top surface to the bottom, where they aggregate and move back up the column. Buchanan\textsuperscript{64} proposed that this phenomenon can be used for enhanced mass transfer between gas and liquid.

1.3.2.3 Gas Hold-up

Gas hold-up or voidage, \(\varepsilon\), affects the interfacial area available for the mass transfer. Increased dispersion of gas in the system increases the interfacial area. Gas hold up depends on the superficial gas velocity and the bubble rise velocity as shown in the equation 1.35.

\[
\varepsilon = \frac{\text{Superficial gas velocity}}{\text{Bubble rise velocity}}
\]  

(1.35)

As discussed earlier, oscillations reduce bubble rise velocity by two mechanisms. Oscillations promote bubble breakage producing smaller bubbles, which have slower rise velocities. Second, oscillations impart an additional downward Bjerknes force on the bubble, which further reduces the rise velocity of bubble. According to equation 1.35, the gas hold-up is inversely proportional to the rise velocity. Hence, a decrease in the rise velocity results in an increase in the gas hold-up.

Harbaum and Houghton\textsuperscript{48} have reported gas holdup enhancements up to 500\% (see Table 1.3). They did observe multiple maxima in the hold-up as the frequency is increased. Similar observations were made by Ellenberger and Krishna.\textsuperscript{51} Harbaum and Houghton\textsuperscript{48} observed that the optimum frequencies at which the peak occurs depends on the amplitude of
vibration and the height of the liquid column. This observation suggests that there might be some resonance phenomenon associated with bubbles, which gives rise to multiple maxima. Baird\textsuperscript{65} proposed that the resonance occurring in the bubble columns is similar to the resonance of sound occurring in a hollow tube due to the formation of standing waves. Baird showed that the hold-up maxima corresponds to integral harmonics of the resonance frequency. The theoretical predictions were in qualitative agreement with the data of Harbaum and Haoughton\textsuperscript{48}. Ellenberger et al.\textsuperscript{58} confirmed formation of the standing waves and showed that the gas hold up varies along the length of the column and is higher at the anti-nodes than at the nodes.

Baird and Garstang\textsuperscript{4} correlated the hold-up enhancements as a function of the power input and the gas superficial velocity as

$$\varepsilon = 0.155 P_v^{0.42} U_g^{0.5}$$

(1.36)

where, $P_v$ is the power input per unit volume. Outside this empirical equation, there are no other attempts in literature to explain the gas hold-up under oscillating conditions. The work presented here (Chapter 3) reports the first theory developed from first principles to predict the gas hold-up in an oscillating bubble column.

1.3.2.4 Mass Transfer Coefficient

The overall volumetric mass transfer coefficient depends on two independent terms, $k_L$ and $a$. The mass transfer coefficient, $k_L$, is a function of turbulence intensity or energy input in the system and the diffusivity of the solute into the continuous phase. The interfacial area, $a$, depends on the bubble diameter and the gas hold up.

The relationship between the interfacial area, the gas hold up and the bubble diameter can be derived as follows. The interfacial area is given as

$$a = \frac{\text{Surface area of bubble (for mass transfer)}}{\text{Total volume of dispersion (gas + liquid)}}$$

(1.37)
Surface area of bubble = \( \pi d^2 \) \hfill (1.38)

Volume of bubble = \( (1/6) \pi d^3 \) \hfill (1.39)

\[ \varepsilon = \frac{\text{Volume of gas}}{\text{Total volume}} \rightarrow \text{Total volume} = \frac{\text{Volume of gas}}{\varepsilon} = \frac{N(1/6)\pi d^3}{\varepsilon} \] \hfill (1.40)

where, \( N \) is the total number of bubbles all of diameter \( d \). Substituting Equation 1.38 and 1.40 into Equation 1.37 gives,

\[ a = \frac{N\pi d^2}{\left( \frac{N(1/6)\pi d^3}{\varepsilon} \right)} = \frac{6\varepsilon}{d} \] \hfill (1.41)

Equation 1.41 shows that the interfacial area can be improved either by increasing the gas-hold up or by decreasing the bubble diameter. Oscillations do increase gas hold-up by retarding the bubble rise velocity and oscillations also decrease bubble diameter by promoting bubble breakage.

Results of the mass transfer coefficient measurements in an oscillating bubble column have been already discussed in a previous section (see section 1.3.1.5). There were few quantitative attempts to explain the observed mass transfer enhancement. For a column with oscillating baffles, Baird and Garstang\(^4\) correlated the mass transfer coefficient under pulsing to the power input and the gas superficial velocity as follows,

\[ \frac{P_v^{0.42} U_{0g}^{0.5}}{g} = \] \hfill (1.42)

where, \( P_v \) is the power input per unit volume and \( U_{0g} \) is the gas superficial velocity. Recently Ni and Gao\(^5\) gave a similar expression for the mass transfer coefficient in a baffled reactor

\[ k_{La} a = 0.0256 P_v^{0.42} U_{0g}^{0.37} \] \hfill (1.43)

Only Baird and Garstang\(^4\), Ni and Gao’s\(^5\) have proposed empirical correlation to predict \( k_{La} a \) in an oscillating baffled column. There is no theory available for the prediction of \( k_{La} a \) in
unbaffled oscillating bubble column. Current work (Chapter 3) proposes a theory from first principles to explain $k_{L,a}$ in oscillating bubble column.

### 1.3.3 Monolith Reactor

Monoliths consist of straight parallel channels extruded from ceramic material. These channels are characterized by their cell density as cells per square inch (cpsi). Commercially available monoliths typically have cell densities in the range of 100-1000 cpsi. Monoliths are generally available in different geometrical structures including square channel, round channel and internally finned structures as shown in Figure 1.24. Flow through the straight channels of a monolith offers very small pressure drop compared to conventional packed bed reactors. This advantage can be exploited for gas-solid catalyzed reactions and this technology is well established in the automotive industry where monolith catalytic converters are commonly used in automobiles to treat the exhaust gas stream. Although traditionally monolith reactors are used for gas-solid contacting, recently monoliths are gaining importance as alternatives for carrying out gas-liquid-solid three phase reactions.

![Figure 1.24 Commercially available monolith structure on different geometries. Square channel cordierite structures (1,3,5,6), internally finned channels (2), washcoated steel monolith (4) (source: Kapteijn et al., 2001)](image-url)
1.3.3.1 Advantages of Monolith Reactor

Conventionally, three phase reactions are carried out in either a packed bed or in a slurry reactor. Each reactor has its own advantages and drawbacks. In a slurry reactor, very fine catalyst particles are suspended in liquid with the help of agitation. Small particles are preferred kinetically since they offer minimal internal diffusion resistance. Slurry reactors also offer excellent external mass transfer and heat transfer characteristics. The major disadvantages of this reactor are the need to separate catalyst particles and catalyst attrition. A packed bed reactor avoids problems of catalyst separation and attrition. In a packed bed reactor large particles are needed in order to minimize the pressure drop. A large particle size results in slower kinetics due to internal diffusion limitations. Packed bed reactors also suffer from maldistribution of the gas and the liquid phases. Maldistribution can cause under-utilization of effective catalyst surface area and it can also generate local hot spots.

Use of monoliths can help to overcome most of the drawbacks mentioned above. Monolith reactors provide the following advantages over the conventional reactors:

1) Monolith reactors (MR) eliminate the need for the physical separation of the catalyst. For example, Boger et al.68 explained that the hydrogenation of edible oils using MR eliminates the processes related to removal of the catalyst such as filtration of catalyst and bleaching of remaining traces of nickel. Catalyst losses are reduced since the catalyst is fixed on the monolith walls. Current industrial processes use an inexpensive Ni catalyst which unfortunately is highly toxic. A better non-toxic alternative is desired. Pd is an attractive alternative, however it is expensive. Current slurry reactor technology often consumes large quantities of the catalyst to compensate for losses due to attrition. MR facilitates the use of expensive, nontoxic catalysts (such as Pd) due to reduced catalyst losses. An economic analysis showed that the use of MR can reduce the production cost of hydrogenated edible oil by 40%.68
2) There is a limit on maximum catalyst (solid) loading that can be achieved in a slurry reactor. Higher catalyst loading increases the viscosity of the slurry. This makes uniform mixing more difficult and more energy consuming. However in MR, higher catalyst loading can be achieved simply by using a higher cell density or a longer length monolith.

3) Slurry reactors effectively act as continuous stirred tank reactors, CSTRs (well mixed reactors), but monolith reactors exhibit plug flow behaviour. Hydrodynamics in MR is detailed in section 1.3.2. Plug flow systems are often kinetically favored over CSTRs.

4) Monolith reactors show higher external mass transfer rates as compared to trickle bed reactors. Gas and liquid phases flow in the form of slugs in monolith channels. This slug flow behaviour is responsible for higher mass transfer coefficients in monolith reactor. For a typical range of gas and liquid superficial velocities, the mass transfer coefficient in a MR is 50% higher than that observed in trickle beds.\(^69\)

5) Monolithic reactors are characterized by minimal internal diffusion resistance. Bare monoliths are not optimally suited for the preparation of the catalyst as the surface area is low. Therefore, the monolithic supports are usually washcoated with a layer of high surface area support such as $\gamma$-alumina. This layer is 10 to 150 $\mu$m thick. Internal diffusion resistance mainly depends on the diffusion length and the thin layer support offers minimal diffusion resistance. Because of a smaller diffusion length, the Theile modulus is small and the effectiveness factor is near unity for a monolith\(^70\). This can be contrasted with packed bed reactors where typical dimensions of packings are $\sim$ 1-5 mm resulting in effectiveness factors being much less than unity.

6) Monolith reactors show plug-flow behavior characterized by a sharp residence time distribution as compared to packed bed reactors.\(^71\) In packed bed reactors, liquid accumulates in dead zones in the interstitial gap between pellets, giving deviations from an ideal plug flow
behavior. A better residence time distribution can be achieved in MR which often leads to better selectivity as shown for the selective hydrogenation of benzaldehyde (Nijhuis et al.69).

7) Washcoated monolith reactors have higher geometric surface area than packed bed reactors which allows for high catalyst loading on the surface.

8) Taylor flow, characterized by a train of alternating liquid and gas slugs, exists in the monolith channel. A gas slug separates two consecutive liquid slugs. Therefore, there is practically no mixing between two liquid slugs. Monolith reactors have very low axial dispersion because of this segmented flow.

9) Monolith reactors are very easy to scale up.

Along with the advantages explained above, monolithic reactors suffer from a few drawbacks as listed below:

1) Residence times in monolithic reactors are low because of the high gas and liquid linear velocities. A recycle loop must be used to get desired conversion levels in slow reactions.

2) Monolith reactors have poor heat transfer characteristics. Radial heat transfer can occur only by conduction through the solid walls of the monolith, which are made of ceramic materials. Ceramics are poor conductors of heat, hence radial heat transfer in a MR is almost zero. Heat capacity of the liquid flowing through the reactor is typically high and the residence time in a MR is small. Therefore, the temperature rise during single pass is not substantial. The solution to the problem is to operate the monolith reactor in an adiabatic mode followed by a heat exchange step.

3) Good initial distribution of the gas and the liquid at the entrance of monolith is very crucial and difficult to achieve. Initial maldistribution cannot be corrected along the length of the monolith. To achieve uniform gas-liquid distribution, different methods are reported in literature including the use of a froth reactor, use of staggered monolith blocks13 or
introducing the gas into each channel by separate injector. Usually monolithic reactors are operated in cocurrent downflow mode. The liquid is evenly distributed at the top with the help of a shower. The work reported here overcomes distribution problems in MRs.

1.3.3.2 Hydrodynamics

![Figure 1.25 Schematics of observed flow pattern in two phase flow in channels. (a) bubbly flow (b) slug flow (c) churn turbulent flow (d) annular flow (source: Kreutzer et al., 2005)](source: Kreutzer et al., 2005)

Mass transfer in multiphase systems depends on the hydrodynamics and flow patterns of the system. Depending on the gas and liquid superficial velocities certain flow patterns may prevail in capillary systems. A schematic of flow patterns is shown in Figure 1.25. With increasing superficial gas velocities different flow patterns can be observed in the following order:

a) Bubbly flow: At low superficial gas velocities, gas flows in the form of discrete small bubbles in a continuous liquid phase. Generally gas hold up is very small and there is minimal interaction between bubbles.

b) Slug flow: Slug flow is also termed plug flow, Taylor flow, segmented flow or bubble train flow. When superficial gas velocity is increased, bubbles grow in size and occupy the entire cross section of the capillary. Trains of bubble slugs are separated by liquid slug moving in a perfect plug flow manner. This is the most observed and preferred flow pattern in monoliths.
c) Churn turbulent flow: At higher velocities, the tail of the gas slug becomes unstable. It disintegrates forming number of smaller bubbles near the tail. The flow pattern becomes chaotic and highly turbulent.

d) Annular flow: At very high gas velocity, the gas phase becomes continuous. The gas phase is present in the center of the channel and a thin wavy liquid film flows along the walls.

The flow pattern which actually occurs in the given capillary channel depends on the gas and liquid physical properties (density, viscosity, surface tension) and channel geometry (diameter) as well as the gas and liquid superficial velocities. The flow pattern in the capillary channel is generally determined using flow transition maps (Figure 1.26). Characteristic dimensionless numbers are calculated using knowledge of the physical properties and the superficial velocities. Depending on the value of those dimensionless numbers, a particular flow pattern can identified as indicated in Figure 1.26. The flow patterns named “Slug or Annular” in Figure 1.26 refers to the transition region between slug and annular flow pattern. A number of flow maps are available in literature\textsuperscript{77-80}, but they should be used with care since most are applicable to the specific system on which they were obtained.

Monolith channels show a slug flow pattern under typical operating gas and liquid superficial velocities (Figure 1.27). A gas slug can be visualized as a cylinder extending to the capillary walls with hemispherical caps at both ends. A thin liquid film exists between the gas slug and the solid wall. Using lubrication analysis Aussilous and Quere\textsuperscript{81} showed that

\[
\frac{\delta}{d_{ch}} \sim \frac{\mu u}{\sigma}
\]

where, $\delta$ is the thickness of the liquid film, $d_{ch}$ is the diameter of monolith channel, $\mu$ and $\sigma$ are viscosity and surface tension of liquid, respectively, and $u$ is the liquid slug velocity through the capillary. Equation 1.44 indicates that the film thickness increases proportionally with
increasing slug velocity. A well defined circulatory flow pattern exists inside the liquid slug and hence, it can be safely assumed that the liquid slug is well mixed. The circulatory flow pattern in liquid slugs was confirmed both experimentally and using CFD.\textsuperscript{82-86}

![Flow map showing different flow patterns in capillary channels along with flow transition lines. Here, $Re_{Ls}$ is Reynolds number based on liquid superficial velocity, $Re_{Gs}$ is Reynolds number based on gas superficial velocity and $Ca$ is capillary number. (source: Jayawardena et al., 1997)\textsuperscript{79}}

![Slug flow inside a capillary. (a) Photograph of air-water flow (b) schematic of the slug flow (c) velocity field showing liquid circulation (source: Kapteijn et al., 2001)\textsuperscript{67}]

\textbf{Figure 1.26} Flow map showing different flow patterns in capillary channels along with flow transition lines. Here, $Re_{Ls}$ is Reynolds number based on liquid superficial velocity, $Re_{Gs}$ is Reynolds number based on gas superficial velocity and $Ca$ is capillary number. (source: Jayawardena et al., 1997)\textsuperscript{79}

\textbf{Figure 1.27} Slug flow inside a capillary. (a) Photograph of air-water flow (b) schematic of the slug flow (c) velocity field showing liquid circulation (source: Kapteijn et al., 2001)\textsuperscript{67}
1.3.3.3 Mass Transfer

The presence of three phases makes interfacial transport phenomena a key factor in reactor performance. For solid catalyzed reactions, the internal surface area of the monolith channels is not sufficient for surface reactions to take place. To overcome this limitation, a thin layer (thickness ~ 10-150 µm) of high surface area support is coated onto the monolith walls and an active metal catalyst is dispersed in this support as shown in Figure 1.28. Theoretically, this catalyst layer can offer an internal diffusion resistance for the transport of the reactant species. This diffusion resistance can be quantified in terms of effectiveness factor, \( \eta \). The effectiveness factor of a first order reaction, \( \eta \), can be calculated according to equation:

\[
\eta = \frac{\tanh \phi}{\phi}
\]

(1.45)

where, \( \phi \) is the Thiele modulus given as (for first order reaction)

\[
\Phi^2 = \frac{k \rho_c S_a L}{D_e}
\]

(1.46)

where, \( k \) is the first order reaction rate constant, \( \rho_c \) is catalyst density, \( S_a \) geometric surface area and \( D_e \) is the effective diffusivity. The symbol \( L \) is diffusion length scale. For a monolith, \( L \) is equal to the thickness of the catalyst coating. Since, this catalyst layer is very thin, it can offer a minimal internal diffusion resistance\(^{87,88}\) and often the effectiveness factor is close to unity.

For a kinetically fast reaction, the rate of reaction is controlled by the slowest step, which is often mass transfer of a reacting species. In this case, the rate is determined by how fast the gas species diffuses into the bulk liquid and from the bulk liquid to the solid catalyst. The various mass transfer steps that occur inside the monolith channel are illustrated in Figure 1.29. There are three external mass transfer resistances involved in the transport of a gaseous reactant from the gas phase to the catalyst surface as listed below\(^{90}\).
Figure 1.28 Schematic of cross section of a monolith showing solid monolith wall and washcoat of high surface area catalyst support. (source: Roy et al., 2004) 

Figure 1.29 Different mass transfer steps involved in Taylor flow

1) Gas to liquid mass transfer:

For the diffusion of gaseous reactant from the bubble cap to the liquid slug, the flux is given as,

\[ N_{GL} = k_{GL} a_{GL} (c^* - c_{bulk}) \]  \hspace{1cm} (1.47)

where, \( N \) is the molar flux, \( k \) is the mass transfer coefficient, \( c^* \) represents the saturation concentration. It was shown by CFD simulation\(^8^4\) that a recirculating flow pattern exists inside the liquid slug (see Figure 1.27). It can be assumed that the liquid slug is well mixed and the concentration inside the slug, \( c_{bulk} \), is constant. The symbol, \( a_{GL} \) is the interfacial area between the gas bubble and the liquid slug. It is only the area of the hemispherical bubble end caps and it does not include the area of the cylindrical portion of the gas slug.
Bercic and Pintar\textsuperscript{14} measured gas-liquid mass transfer in a single capillary for a wide range of superficial gas and liquid velocities. For methane-water they proposed

\[ a_{GL} = \pi d_b^2 \]  

(1.48)

where, \( u_{TP} \) is the two phase velocity, taken as \( u_l + u_g \). \( L_{UC} \) is length of the unit cell as illustrated in Figure 1.29 and \( \varepsilon_l \) is liquid hold-up. This correlation was developed for very long bubbles and slugs for which a complete saturation of the liquid film was likely. It should be noted that this correlation is independent of the channel or bubble diameter. This correlation does not contain physical properties of the system and is only valid for methane-water system. To use this correlation for other systems, the correlation can be modified as follows

\[ (k_{GL} a_{GL})_A = (k_{GL} a_{GL})_B \left( \frac{D_B}{D_A} \right)^n \]  

(1.50)

where, \( n = 1 \) for film theory and \( n = 0.5 \) for penetration theory. \( B \) represents the methane-water system and \( A \) refers to the system of interest. The symbol \( D \) is the molecular diffusivity.

van Baten and Krishna\textsuperscript{84} performed CFD simulations for gas absorption in Taylor flow. For short contact time (fast slug velocity) they proposed following correlation based on penetration theory

\[ k_{GL} a_{GL} = \frac{8 \sqrt{2}}{\pi \varepsilon_{UC}} \left( \frac{D u_{TP}}{d_b} \right) \]  

(1.51)

This correlation shows a dependence on bubble diameter, as opposed to the Bercic and Pintar correlation. Irandoust et al.\textsuperscript{91} developed a dimensionless correlation based on the model of mass transfer for a rigid sphere and using penetration theory, giving,

\[ Sh = 0.69 \left( 1 + 0.724 \text{Re}^{0.48} \text{Sc}^{1/3} \right) \]  

(1.52)
here, the Sherwood number $Sh = \frac{k_{GL} d_b}{D}$

2: Liquid to solid wall mass transfer:

Flux for the mass transfer from the bulk liquid to the solid surface can be given as

$$N_{LS} a_{LS} = k_{LS} a_{LS} (c_{bulk} - c_s)$$ \hspace{1cm} (1.53)

here, $a_{LS}$ is the interfacial area between the liquid slug and the solid wall which can be calculated as

$$a_{LS} = \frac{4 L_{slug}}{d_{ch} L_{UC}}$$ \hspace{1cm} (1.54)

The liquid slug with the dissolved gaseous reactant comes in contact with the solid surface. The dissolved gaseous reactant reaches the solid surface primarily by diffusion through a stagnant viscous layer of liquid near the solid surface. Kreutzer et al.\textsuperscript{13} performed CFD simulations for a capillary with a moving wall and showed that the Sherwood number, $Sh$, is a function of the mass Graetz number $Gz = \psi_{slug}/(Re \times Sc)$. $Re$ is Reynolds number and $Sc$ is Schmidt number.

Here, $\psi_{slug}$ is the dimensionless slug length given as $L_{UC}/d_{ch}$.

$$Sh = 20 \left( 1 + 0.003 \left( \frac{\psi_{slug}}{Re \times Sc} \right)^{-0.7} \right)$$ \hspace{1cm} (1.55)

Later Kreutzer et al.\textsuperscript{92} generalized this expression using finite element methods to account for the geometry of the monolith as

$$Sh = \sqrt{\alpha + \frac{\beta}{Gz}}$$ \hspace{1cm} (1.56)

with, $\alpha$ and $\beta$ being functions of slug length and channel diameter

$$\alpha = 40 \left( 1 + 0.28 (L_{slug} / d_{ch})^{-4/3} \right)$$

$$\beta = 90 + 104 (L_{slug} / d_{ch})^{-4/3}$$
van Baten and Krishna\textsuperscript{93} performed CFD simulations to study mass transfer from the liquid to the wall. They studied the influence of bubble rise velocity, unit cell length, gas hold up and channel diameter on the mass transfer coefficient. They correlated their data to the Graetz number as:

\[
Sh = \frac{\beta}{G_{\text{tube}}^\alpha}
\]  \hfill (1.57)

where \(\alpha = 0.61G_{\text{slug}}^{0.025}\), \(\beta = \frac{0.5}{(G_{\text{slug}} / \varepsilon_G)^{0.15}}\), \(G_{\text{slug}} = \frac{L_{\text{slug}} D}{d^2 \epsilon_b}\)

In addition to these simulation studies, there have been experimental efforts to measure the liquid-solid mass transfer coefficient. Hatziantoniou et al.\textsuperscript{94} studied liquid-solid mass transfer in capillary tubes of 2.35 and 3.1 mm diameter. The inner walls of the channel were coated with benzoic acid and water and air were passed cocurrently. The outlet concentration of benzoic acid in water was measured to calculate the mass transfer coefficient. Based on the experimental results they proposed the following correlation for the liquid-solid mass transfer coefficient

\[
Sh = 3.51 \left( \frac{\text{Re.Sc}}{\gamma} \right)^{0.44} \beta^{-0.09}
\]  \hfill (1.58)

where, \(\gamma = L_{\text{ch}} / d_{\text{ch}}\) and \(\beta = L_{\text{slug}} / d_{\text{ch}}\).

Based on a similar dissolution study, Irandoust and Andersson\textsuperscript{95} developed the following correlation for the liquid-solid mass transfer coefficient

\[
Sh = 1.5 \times 10^{-7} (\text{Re})^{1.65} (\text{Sc})^{0.18} (\alpha)^{-2.34}
\]  \hfill (1.59)

here, \(\alpha\) is dimensionless film thickness \(\delta / d_{\text{ch}}\).

Bercic and Pintar\textsuperscript{14} also carried out a benzoic acid dissolution experiment similar to Hatziantoniou et al.\textsuperscript{94} and proposed

\[
k_{\text{LS}} a_{\text{LS}} = \frac{0.069 u_{\text{TP}}^{0.63}}{[\varepsilon_L L_{\text{UC}} - 0.105 L_{\text{UC}} \varepsilon_G]^{0.44}}
\]  \hfill (1.60)
All these correlations are dependent on either the liquid slug length or the unit cell length. However there are no means available to predict these parameters making these correlations unsuitable for scale-up.

3) Gas to solid mass transfer:

Flux for the mass transfer from the gas to the solid surface through the thin liquid film surrounding the cylindrical part of the gas slug can be given as:

\[ N_{GS} a_{GS} = k_{GS} a_{GS} (c^* - c_s) \]  \hspace{1cm} (1.61)

where, \( a_{GS} \) is the area of cylindrical portion of the gas slug in contact with the solid wall,

\[ a_{GS} = \frac{4L_{film}}{d_{ch} L_{UC}} \]  \hspace{1cm} (1.62)

and, \( L_{film} \) is the length of the liquid film surrounding the gas slug. Since the liquid film is very thin, the velocity in the film can be neglected. Using penetration theory the mass transfer coefficient can be given as:

\[ k_{GS} = \frac{D}{\delta} \]  \hspace{1cm} (1.63)

where, \( \delta \) is the film thickness of the liquid surrounding gas bubble. Using lubrication analysis Aussilous and Quere\(^8\) showed that the film thickness is related to the Capillary number \( Ca = \mu u / \sigma \) as follows

\[ \frac{\delta}{d_{ch}/2} = \frac{1.34Ca^{2/3}}{1 + 3.35Ca^{2/3}} \] \hspace{1cm} (1.64)

Irandoust and Andersson\(^1\) proposed a different correlation where

\[ \frac{\delta}{d_{ch}} = 0.18(1 - \exp(-3.1Ca^{0.54})) \] \hspace{1cm} (1.65)

Both of these correlations are valid in the range \( 10^{-3} < Ca < 1.3 \). It should be noted that the film thickness is independent of the gas bubble and liquid slug lengths. A counterintuitive aspect
of these correlations is that they predicts the film thickness will decrease with decreasing slug velocity. This means that the mass transfer coefficient from the gas to the solid wall will increase with decreasing velocity or decreasing pressure drop. This is in contrast to the common notion in chemical engineering that enhancement of mass transfer comes at the cost of an increase in velocity or pressure drop.

For the overall transport process, resistances 1 and 2 are in series and resistance 3 is in parallel to resistances 1 and 2. The total flux of the gaseous reactant from the gas phase to the solid surface is given as

\[ N \cdot a = N_{GS} a_{GS} + N_{LS} a_{LS} \]  

(1.66)

here, \( a \) is the overall interfacial area which includes the area of the bubble cap as well as the area of the cylindrical portion of the bubble slug.

\[ N \cdot a = \left( k_{GS} a_{GS} + \left( \frac{1}{k_{GL} a_{GL}} + \frac{1}{k_{LS} a_{LS}} \right)^{-1} \right) (c^* - c_s) \]  

(1.67)

hence,

\[ k_{ov} a = k_{GS} a_{GS} + \left( \frac{1}{k_{GL} a_{GL}} + \frac{1}{k_{LS} a_{LS}} \right)^{-1} \]  

(1.68)

\( k_{ov} \) is the overall mass transfer coefficient. It has been reported in the literature that the contribution of \( k_{GS} \) towards \( k_{ov} \) is significant and accounts for 60-80% of the overall mass transfer.\(^\text{13,84,96}\)

1.3.3.4 Reactions

Monolith reactors can be used to carry out three phase mass transfer controlled reactions. Mass transfer controlled reactions typically occur when the reaction is kinetically fast and the gas is sparingly soluble in the liquid reactants. Hydrogenation and oxidation reactions are common reactions that fit into this category. A survey of different catalytic three phase reactions, which have been carried out using a monolith reactor, is given in Table 1.4.
Advantages of monolithic reactors over conventional reactors have been discussed. MR can be effectively used to improve reaction performance by: 1) Improved mass transfer rates leading to faster reaction rates; 2) Higher selectivities; and 3) Elimination of the filtration step. Each of these advantages are explained in more detail here.

1) Improved mass transfer rates leading to faster reaction rate:

The most common reaction studied for three phase hydrogenation is the hydrogenation of \(\alpha\)-methylstyrene (AMS). This reaction has a high intrinsic rate with almost no side products\(^{13}\). During the reaction, \(\alpha\)-methylstyrene is hydrogenated to cumene, generally over a Pd, Pt or Ni catalyst on \(\gamma\)-alumina. Kreutzer et al.\(^{13}\) showed that, depending on the operating conditions, overall mass transfer rates between 0.5 and 1.5 s\(^{-1}\) can be achieved in monolith reactors. Nijhuis et al.\(^{69}\) did a direct comparison between a monolith reactor and a trickle bed reactor using a Ni catalyst. They found that the monolith reactor showed an activity of \(9.8 \times 10^{-4}\) mol/g\(_{\text{nickel}}\).s, which was ten times higher than the activity shown in the trickle bed reactor (\(8.4 \times 10^{-5}\) mol/g\(_{\text{nickel}}\).s). For styrene (not alpha-methyl styrene) hydrogenation over Pd on alumina, an overall reaction rate of \(5.2 \times 10^{-2}\) mol/kg\(_{\text{cat}}\).s was obtained by Smits et al.\(^{75}\) using the monolith reactor. It is 50 times higher than the reaction rate of \(1.1 \times 10^{-3}\) mol/kg\(_{\text{cat}}\).s achieved by Mochizuki and Matsui\(^{97}\) in an upflow packed bed reactor under similar temperature conditions. A preliminary study from Corning Inc.\(^{70}\) showed applicability of MRs for olefine and toluene hydrogenation reactions. They showed that an order of magnitude higher conversion can be obtained with MR as compared to packed bed reactor.

The use of monolith reactors for improving the rate of oxidation reactions has also been reported in the literature. Wet air oxidation of waste streams is an emerging technique to meet increasingly stringent environmental regulations. Crynes et al.\(^{73}\) investigated catalytic oxidation of aqueous phenol over copper oxide in monolith reactor and showed that reaction rates up to \(2 \times\)
$10^3$ mol/kg\textsubscript{cat}.s can be obtained depending on the operating conditions. Crynes et al. did not present any comparison with conventional reactors. One more important reaction, the oxidation of cellulose, has two different applications in industry. Cellulose is found in certain waste streams from wood and agricultural processing. The degradation and oxidation of cellulose into carboxylic acids is an important step towards developing a process for the use of biomass as a viable feedstock. Schutt and Abraham\textsuperscript{98} studied the catalytic wet oxidation of cellulose over a Pd catalyst. They obtained a conversion of 85\% in a monolith reactor, while a slurry reactor reached only 15\% conversion. Kawakami et al.\textsuperscript{74} studied the oxidation of glucose by immobilized glucose oxidase. They found that the reaction rate is controlled by internal diffusion. Hence a thinner catalyst layer (higher effectiveness factor) showed a better performance.

2) Higher selectivities:

For complex chemical reactions, such as reactions in series or parallel, selectivity can be equally important. Hydrogenation of a mixture of styrene and 1-octene in toluene is a good example of such systems. Such a mixture may be considered to be representative of a broader group of hydrocarbon mixtures subjected to hydrotreating in petroleum refining. The reaction scheme is illustrated in Figure 1.30. During the hydrogenation of styrene, in the first step the double bond on the side chain of styrene is hydrogenated to give ethylbenzene, which is the desired product. But the reaction may proceed further and the benzene ring may be hydrogenated to form ethylcyclohexane, which is undesired. 1-octene can undergo isomerization forming the desired product, internal octene, or it can undergo saturation to form octane. Thus, the hydrogenation of 1-octene involves parallel reaction by using a monolith reactor, Smits et al.\textsuperscript{75} demonstrated that styrene can be preferably hydrogenated to ethylbenzene with almost 100\% selectivity, while 1-octene can be partially isomerized to internal olefins with 60\% selectivity.
Table 1.4 Chemical reactions carried out in monolithic reactor.

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Reaction</th>
<th>Catalyst</th>
<th>Monolithic reactor type</th>
<th>Compared with</th>
<th>Enhancements</th>
<th>Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenation</td>
<td>$\alpha$-methylstyrene + H$_2$ $\rightarrow$</td>
<td>Pd over $\gamma$ alumina</td>
<td>Regular</td>
<td>Trickle bed</td>
<td>$10^a$</td>
<td>Kreutzer et al. (2001)$^{13}$, Nijhuis et al. (2001)$^{69}$</td>
</tr>
<tr>
<td></td>
<td>Cumene</td>
<td></td>
<td></td>
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<tr>
<td>Hydrogenation</td>
<td>Styrene + H$_2$ $\rightarrow$</td>
<td>Pd over $\gamma$ alumina</td>
<td>Regular downflow</td>
<td>Packed bed</td>
<td>$50^b$</td>
<td>Smits et al. (1996)$^{72}$, Nijhuis et al. (2003)$^{99}$*</td>
</tr>
<tr>
<td></td>
<td>Ethylbenzene</td>
<td></td>
<td></td>
<td>Trickle bed</td>
<td>$16^a$</td>
<td></td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>1-Octene + H$_2$ $\rightarrow$ n-Octane</td>
<td>Pd over $\gamma$ alumina</td>
<td>Regular downflow</td>
<td>–</td>
<td>–</td>
<td>Smits et al. (1996)$^{72}$</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>Benzaldehyde + H$_2$ $\rightarrow$</td>
<td>Ni over $\gamma$ alumina</td>
<td>Regular</td>
<td>–</td>
<td>$2^a$</td>
<td>Nijhuis et al. (2001)$^{69}$, Xiaoding et al. (1996)$^{100}$</td>
</tr>
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<td></td>
<td>Benzyliccohol</td>
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<tr>
<td>Hydrogenation</td>
<td>2-ethyl anthraquinone</td>
<td>Proprietary</td>
<td>–</td>
<td>Slurry</td>
<td>$5^a$</td>
<td>Bengtsson (1990)$^{101}$, Albers et al. (2001)$^{102}$</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>Unsaturated edible oil + H$_2$ $\rightarrow$</td>
<td>Pd on washcoat</td>
<td>Stirrer and loop</td>
<td>Slurry</td>
<td>$0.7^c$</td>
<td>Boger et al. (2004)$^{68}$</td>
</tr>
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<td>Partially saturated product</td>
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<tr>
<td>Hydrogenation</td>
<td>3-hydroxypropanal + H$_2$ $\rightarrow$</td>
<td>Ni/SiO$_2$/Al$_2$O$_3$</td>
<td>Regular</td>
<td>Slurry</td>
<td>$10^d$</td>
<td>Cybulski et al. (1999)$^{103}$*</td>
</tr>
<tr>
<td></td>
<td>1,3-propanediol</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Hydrogenation</td>
<td>Phenylacetylene + H$_2$ $\rightarrow$</td>
<td>Pd on alumina</td>
<td>Regular</td>
<td>–</td>
<td>–</td>
<td>Vergunst et al. (2001)$^{59}$*</td>
</tr>
<tr>
<td></td>
<td>Styrene</td>
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<tr>
<td>Hydrogenation</td>
<td>3-methyl-1-pentyn-3-ol + H$_2$ $\rightarrow$</td>
<td>Pd on silica</td>
<td>Stirrer reactor</td>
<td>Slurry</td>
<td>$1^a$</td>
<td>Hoek et al. (2004)$^{104}$</td>
</tr>
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<td></td>
<td>3-methyl-1-penten-3-ol</td>
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<tr>
<td>Oxidation</td>
<td>Phenol (aqueous) + O$_2$ $\rightarrow$</td>
<td>CuO over $\gamma$ alumina</td>
<td>Froth reactor</td>
<td>–</td>
<td>–</td>
<td>Crynes et al. (1995)$^{73}$</td>
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<tr>
<td></td>
<td>CO$_2$ + H$_2$O</td>
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<tr>
<td>Oxidation</td>
<td>Glucose + 0.5O$_2$ $\rightarrow$</td>
<td>Immobilized glucose oxidase</td>
<td>Regular</td>
<td>Trickle bed</td>
<td>$5^c$</td>
<td>Kawakami et al. (1989)$^{74}$</td>
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<td></td>
<td>Glucono-δ-lactone + H$_2$O</td>
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<td></td>
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<tr>
<td>Oxidation</td>
<td>Cellulose(aq.) + O$_2$ $\rightarrow$</td>
<td>Pd over $\gamma$ alumina</td>
<td>Froth reactor</td>
<td>Stirred tank</td>
<td>$5^c$</td>
<td>Schutt and Abraham (2004)$^{98}$</td>
</tr>
<tr>
<td></td>
<td>Succinic acid + Acetic acid + glucose</td>
<td></td>
<td></td>
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<tr>
<td>Fischer-Tropsch</td>
<td>CO + H$_2$ $\rightarrow$ water + Hydrocarbon</td>
<td>Co, Rh on alumina</td>
<td>Loop reactor</td>
<td>Slurry bubble column</td>
<td>$1.3^d$</td>
<td>de Deugd et al. (2003)$^{105,106}$*</td>
</tr>
<tr>
<td>Esterification</td>
<td>1-octanol + hexanoic acid $\rightarrow$</td>
<td>Zeolite BEA</td>
<td>Internally finned</td>
<td>–</td>
<td>–</td>
<td>Nijhuis et al. (2002)$^{107}$</td>
</tr>
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<td>Hydrodesulphurization</td>
<td>Heavy gas oil + H$_2$ $\rightarrow$</td>
<td>Co/Mo/Al$_2$O$_3$</td>
<td>Regular</td>
<td>Trickle bed</td>
<td>$1.2^d$</td>
<td>van Hasselt (1999)$^{108}$*</td>
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<tr>
<td></td>
<td>H$_2$S + Desulfurized diesel</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Reforming</td>
<td>Methanol + H$_2$O $\rightarrow$ H$_2$ + CO$_2$</td>
<td>CuZnO</td>
<td>Microreactor</td>
<td>–</td>
<td>–</td>
<td>Schuessler et al. (2003)$^{109}$</td>
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<tr>
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</tbody>
</table>
* Modeling studies without any experimental work; Enhancements are calculated as the ratio of performance of MR to the performance of reference reactor. Performances are measured as follows: a – rate [mol/gmetal.s]; b – rate [mol/gcat.s]; c – conversion; d – productivity [mol/m$^3$ reactor.s]; e – mass transfer coefficient [1/s]
Residence time distribution is an important factor affecting selectivities of reactions in series. As the desired intermediate product stays in the reactor for a longer time, it may undergo further reactions producing unwanted products. In monolith reactors, the gas and the liquid move in consecutive plugs resulting in a plug flow type of a behaviour. Hence, monolith reactors have sharper residence time distribution. The formation of dead zones, which cause longer residence time, is highly improbable in monolith reactors. Thus the residence time of the reacting fluid in the monolith reactor can be tuned such that the formation of the undesired product is minimized. For example, the hydrogenation of benzaldehyde to benzylalcohol involves selectivity issues. Benzylalcohol, which is the desired product, can undergo a further reaction forming unwanted toluene. Nijhuis et al.\textsuperscript{69} showed that a monolith reactor gives a selectivity of 99.5% towards benzylalcohol as compared to only 73% obtained from a trickle bed reactor.

Another example of enhanced selectivity due to monolith reactors is the Fischer-Tropsch synthesis (FTS). FTS converts synthesis gas (CO+H\textsubscript{2}) to hydrocarbons to form liquid fuels. In this polymerization process, high molecular weight hydrocarbons are desired. Selectivity towards higher hydrocarbons is greatly affected by the stoichiometric ratio of H\textsubscript{2} and CO. A higher H\textsubscript{2} concentration is undesirable since more light products are formed. Because of the differences in diffusivity of H\textsubscript{2} and CO, for longer diffusion lengths, H\textsubscript{2} is present in excess inside the catalyst
pores. This leads to poor selectivity. Therefore shorter diffusion lengths are preferred. A very thin layer of washcoat can be applied to the walls of the monoliths and the active catalyst is dispersed on this layer. In a modeling study, de Deugd et al.\textsuperscript{105,106} showed that, constant H\textsubscript{2}/CO ratio can be obtained across the washcoat thickness for diffusion length scales (washcoat thickness) up to 60 µm, resulting in better selectivities for heavy hydrocarbons.

3) Elimination of the filtration step:

Hydrogenation of edible oils is a large commercial hydrogenation application. Edible oil is hydrogenated in order to impart desirable characteristics such as higher melting point, improved stability and better (harder) consistency. Conventionally this process is carried out in a slurry reactor. The removal of fine Ni catalyst particles by separation is inefficient and time consuming. The pyrophoric nature of Ni also makes the process a potential safety concern. The separation step also results in undesirable catalyst losses. The use of monolithic reactors for the hydrogenation of edible oil offers mass transfer improvements and MR eliminates the catalyst separation step, which means a major saving in operating and capital cost. Elimination of the filtration step of pyrophoric catalyst also makes this process much safer. Boger et al.\textsuperscript{68} showed that the use of a monolith reactor suppresses the cis to trans isomerization reaction of the products as compared to a slurry reactor loaded with an identical catalyst.

Few of these reactions have found application in actual industrial processes. Akzo-Nobel operates a monolith reactor in the anthraquinone process of hydrogen peroxide production.\textsuperscript{102} This is a two step process and carryover of catalyst from one step to another is undesirable. Air Products has developed a process which uses monoliths for highly exothermic nitroaromatic hydrogenations.\textsuperscript{110} Safety considerations in this reaction require the reaction mixture to be recycled through the reactor hundreds of times. The low pressure drop across the monolith reduces pumping cost considerably.
Chapter 2  Pulsing to Improve Bubble Column Performance: Jetting Gas Rates*

2.1 Introduction

The idea of applying pulsation to bubble columns for the purpose of mass transfer enhancement is quite old, notwithstanding recent efforts. Early experiments by Bretsznajder et al. and Harbaum and Houghton showed large improvements in mass transfer. This effect was attributed to increased bubble hold-up, owing to induced Bjerknes “kinetic buoyancy” according to Baird. Baird also provided corrections to the well-known bubble natural frequency originally derived by Minnaert who found that:

\[ \omega_n = \frac{1}{r_0} \left[ \frac{3yP_e^2}{\rho_L} \right]^{1/2} \]  \hspace{0.5cm} (2.1)

and the Baird correction for finite columns yielded,

\[ \omega_n = \frac{1}{r_0} \left[ \frac{3yP_e^2}{\rho_L} \right]^{1/2} \left[ 1 + \left( \frac{r_0}{R} \right) \left( \frac{4L}{R} - 1 \right) \right]^{-1/2} \]  \hspace{0.5cm} (2.2)

It was previously thought that forced oscillations must match the Minnaert natural frequency to cause unstable bubble breakup. For a 3 mm diameter spherical bubble at near atmospheric pressure, this would require pulsing at approximately 2200 Hz. However, significant improvements have been reported in the range 10-150 Hz, with peaking at certain frequencies. The halting or retardation of rising bubbles has been explained as due to the Bjerknes force acting downward. According to this simple theory a bubble is halted by vibrations if \( M \) is unity, where:

\[ M = \frac{\omega^4 A^2 \rho_l h}{2gP_0} \]  \hspace{0.5cm} (2.3)

Most industrial operations operate at high gas rates, such that jetting occurs at the gas injection port. The following expression in Wallis\textsuperscript{113} shows that jetting occurs when the gas velocity from the orifice is such that:

\[
\frac{v_g \sqrt{\rho_G}}{(g \sigma (\rho_L - \rho_G))^{1/4}} > 1.25 \left[ \frac{\sigma}{g (\rho_L - \rho_G) R_0^2} \right]^{1/2}
\]  

(2.4)

For air in water, an injector 0.75 mm i.d. will jet when gas flow exceeds 14 ml/sec.

![Image](72x386 to 270x558)

(a) No forcing

(b) with forcing

\[f = 16\ Hz, \text{ Cam amplitude } = 1.36\text{mm}\]

Figure 2.1 Photograph of bubble column showing gas dispersion. Photograph is taken at 350 mm above nozzle. \(Q_g = 36.4\ ml/s\) (superficial nozzle gas velocity = 46.3 m/s): (a) No forcing; (b) with forcing, \(f = 16\ Hz, \text{ Cam amplitude } = 1.36\text{mm}\)

Under jetting conditions, large gas slugs form with a wide distribution in sizes. Figure 2.1(a), shows the bubbles created downstream from single stainless steel injector (i.d.= 0.75 mm) which is operating at jet flow conditions. Some large, unstable bubbles are formed in the column proper, but there is also a wide distribution of bubble sizes because there is some bubble break-up at the injector tip. This is typical of unforced steady-state injection at high gas feeds and results from gas jet instability controlled by surface tension and shear. Many of the slugs rise as spherical-cap bubbles. We observed reductions in bubble size when such jetted columns were subjected to pulsing in the range 10-30 Hz as shown in Figure 2.1b. We wished to determine if intensification could improve performance under such maldistribution of bubbles.
2.2 Experimental Methods

The experimental equipment consists of a bubble column with a single air injector. Details can be found in previous work.10

2.2.1 Amplitude Measurements

The natural gum rubber sheet at the base of the column is clamped between 2 stainless steel disks. For the high flow experiments, different disk sizes were used. To create a flexible piston, each disk was 2.73 cm in diameter. The column diameter is 8.9 cm, which effectively allows pulsation of 56.3 cm$^2$ of rubber at the column base. Data for true fluid amplitude ($A^*$) as a function of cam setting, oscillation frequency and membrane thickness are given in Part 11, Tables 2.1 and 2.2.

To create a more rigid piston, the natural gum rubber sheet at the base of the column is clamped between two stainless steel disks each 8.26 cm in diameter. This allows pulsation of only 2.74 cm$^2$ of rubber at the column base, which will behave more like a solid piston. Here the fluid amplitude ($A$) was experimentally verified to be the cam setting.

Table 2.1 Flexible Piston Results (Cam amplitude 1.36 mm, $Q_g = 30.4$ ml/s, superficial nozzle gas velocity = 68.8 m/s)

(a) Membrane thickness 1.59 mm

<table>
<thead>
<tr>
<th>$f$ (Hz)</th>
<th>$A^*$ (mm)</th>
<th>$A^*/A_0$</th>
<th>$\varepsilon^*$</th>
<th>$\varepsilon^*/\varepsilon$</th>
<th>$k_{1a}^*$</th>
<th>$k_{1a}^*/k_{1a}$</th>
<th>Sloshing</th>
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<td>0.74</td>
<td>1</td>
<td>0.0113</td>
<td>1</td>
<td>0.004</td>
<td>1</td>
<td>-</td>
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<tr>
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<td>0.7</td>
<td>0.0122</td>
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<td>2.28</td>
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<td>1.97</td>
<td>0.012</td>
<td>3.00</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>22.5</td>
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(Table cont.)
(b) Membrane thickness 3.18 mm

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<th>$\varepsilon^*$</th>
<th>$\varepsilon^*/\varepsilon$</th>
<th>$k_{La^*}$</th>
<th>$k_{La^*/k_{La}}$</th>
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(c) Membrane thickness 6.35mm

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Table 2.2 Flexible Piston Results (Cam amplitude 0.51mm, $Q_g = 30.4$ ml/s)

(a) Membrane thickness 1.59 mm

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<th>$f$ (Hz)</th>
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<th>$\varepsilon^*$</th>
<th>$\varepsilon^*/\varepsilon$</th>
<th>$k_{La^*}$</th>
<th>$k_{La^*/k_{La}}$</th>
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(Table cont.)
2.2.2 Voidage (Gas Hold-Up) Measurements

The gas hold up was determined by the manometric method. Two taps are used, one 11 cm from the rubber sheet and the other 77 cm above the rubber sheet. The manometer fluid is Meriam Red 295 with a specific gravity of 2.95. A pressure balance on each leg of the manometer allows voidage ($\varepsilon$) to be determined using,

$$\varepsilon = \left( \frac{\rho_m - \rho_l}{\rho_l} \right) \frac{\Delta h}{H}$$  \hspace{1cm} (2.5)

The height differential in Meriam Red 295, $\Delta h$, was determined using a cathetometer which provided an accuracy of plus or minus 0.01 mm. Here $H$ is the distance between the two taps.

2.2.3 Mass Transfer Measurements

A key aspect of the forcing technology is to improve mass transfer. The generation of large bubble numbers, and consequently large surface area, using low energy input may allow
agitator replacement with savings. To investigate improvements in mass transfer, we measured the mass transfer coefficient \(k_{l,a}\) as a function of frequency at several air flow rates and amplitudes. The same equipment and equations as Part 1\textsuperscript{114} were again used, and for initially clean solutions \((C_0 = 0)\), the solution as before is:

\[
\frac{C(t)}{C^*} = 1 - \exp\left(-k_{l,a}t\right)
\]  

(2.6)

The only unknown here is \(k_{l,a}\), which is determined by minimizing the sum of the square of the difference between measured and predicted normalized concentration measurements. The standard regression solver in Excel was used. Concentration measurements were collected every 0.33 seconds and then every 10 data points were averaged and stored.

2.3 Results and Discussion

We tested the two types of pistons mentioned earlier: a flexible piston and a more rigid design. The former sustains considerable dynamics owing to elasticity, while the latter acts more like a solid piston.

2.3.1 Mass Transfer and Voidage Measurements - Flexible Piston

In this part, gas pressure hence gas flow is sufficiently high to mitigate the suck-back phenomenon seen in our previous work\textsuperscript{114}. For example, at a cam amplitude of 1.36 mm, suck back occurred at a nozzle gas velocities of about 30 m/s. Above these velocities, jet flow is observed at the injector with little or no flow reversal in the injector tube. Also, for the flexible piston, dynamics arise as discussed in Knopf et al.\textsuperscript{114} and there is a system resonance in fluid amplitude.

At high gas flow rate and under appropriate forcing conditions, dramatic bubble breakage can be obtained as shown in Figure 2.1b. The jetting mode at the injector is manifested by the production of large bubbles in the immediate vicinity of the injector. However, downstream of
the injector (as shown in Figure 2.1b) the bubbles are considerably smaller and more uniform with a tight size distribution, indicating that the large bubbles were broken. The large bubbles start to breakup within approximately two column diameters of the injector and at low frequencies (of order 10 Hz).

![Graph](image)

**Figure 2.2** $k_{La^*}/k_{La}$, $A^*/A_0$ and $\varepsilon^*/\varepsilon$ as a function of frequency; Cam amplitude = 1.36 mm, $Q_g = 30.4$ ml/s (superficial nozzle gas velocity = 68.8 m/s), Membrane thickness = 3.18 mm.

Experiments were performed to measure the effect of vibration frequency, vibration amplitude and gas flowrate on both the volumetric mass transfer coefficient and the gas hold-up. For these experiments, a single stainless steel injector (i.d. = 0.75mm; o.d. = 1.5mm; vertical length = 38mm) was used. Tables 2.1 and 2.2 and Figure 2.2 and Figure 2.3 summarize results for a high gas flowrate of 30.4 ml/s (superficial nozzle gas velocity of 68.8 m/s). Cam amplitudes of both 1.36mm (Table 2.1) and 0.51 mm (Table 2.2) were tested with rubber sheets of 3 different thicknesses: 1.59 mm (1/16”); 3.18 mm (1/8”); 6.35 mm (1/4”). We again use an asterisk to denote the vibrated case.
Membrane thickness = 3.18 mm, Cam A = 0.51 mm, $Q_g = 30.4$ ml/s

**Figure 2.3** $k_{La}/k_{La}$, $A^*/A_0$ and $\varepsilon^*/\varepsilon$ as a function of frequency; Cam amplitude = 0.51 mm, $Q_g = 30.4$ ml/s, Membrane thickness = 3.18 mm.

We have used the nomenclature that $A^*$ is the fluid amplitude as a function of frequency, while $A_0$ is the fluid amplitude as frequency tends to zero. In Tables 2.1 and 2.2 we have marked (in bold) the frequency for maximum amplitude enhancement ($A^*/A_0$), for each of the three membranes tested. Also noted, in bold, are the maximum in mass transfer enhancement ($k_{La}^*/k_{La}$) and voidage enhancement ($\varepsilon^*/\varepsilon$), for each membrane. The observed maximums in $k_{La}^*$ and $\varepsilon^*$ for the flexible piston are in general agreement with the observed maximums in amplitude. For example, Figure 2.2 plots the data from Table 2.1b as ($A^*/A_0$), and the new data for jetting conditions for ($k_{La}^*/k_{La}$) and ($\varepsilon^*/\varepsilon$) versus frequency all showing a symmetric maximum at 17.5 Hz. Figure 2.2 shows maximum mass transfer enhancement of about 225% while Figure 2.3 (data from Table 2.2b), with a lower cam amplitude setting, shows smaller mass transfer enhancements. At both cam settings, voidage enhancements are generally not as large as observed for mass transfer. Referring to the dynamics of the piston system shown in Table 2.3 of Knopf et al.\textsuperscript{114}, we see at these amplitudes the natural frequencies were estimated to be 17.99 Hz for the cam amplitude of 1.36 mm, and 20.37 Hz for the cam amplitude of 0.51 mm.
Figure 2.4 Volumetric mass transfer coefficient as a function of frequency; Cam amplitude = 1.36mm, Membrane thickness = 3.18 mm: (a) Absolute $k_{La^*}$; (b) Enhancement ($k_{La^*}/k_{La}$)
Figure 2.5 Volumetric mass transfer coefficient as a function of frequency; Cam amplitude = 0.51 mm, Membrane thickness = 3.18 mm: (a) Absolute $k_{La^*}$; (b) Enhancement ($k_{La^*}/k_{La}$)
In Tables 2.1 and 2.2 we have also indicated whether sloshing at the top interface was observed. As will be discussed in a later section, sloshing indicates an unstable region of BCR operation. This surface instability may be linked to the observed increase in performance.

To help clarify these findings we examined the effect of gas rate using the 3.18 mm (1/8") rubber sheet at the two cam settings of 1.36 and 0.51 mm. The nozzle gas velocities used were 33.9 m/s, 45.3 m/s, 56.6 m/s and 68.8 m/s (or 15ml/s, 20ml/s, 25ml/s, and 30.4 ml/s gas flowrates). For all tested flowrates, the $k_{La}^*$ values go through a steep symmetric maximum at about 17.5 Hz at the two cam settings. This maximum appears independent of nozzle gas velocities at the tested cam amplitude settings (Figure 2.4 and Figure 2.5). At 17.5 Hz, mass transfer enhancements exceeding 200% were found for all tested flowrates at the higher cam setting (Figure 2.4b), and mass transfer enhancements exceeding 100% were found for tested flowrates at the lower cam setting (Figure 2.5b). Voidage measurements versus frequency at two different flowrates and 2 cam settings (Figure 2.6 and Figure 2.7) show a maximum at 17.5 Hz, however, the voidage enhancements are again not as large as observed for mass transfer.

The trends shown in Figure 2.2 to Figure 2.7 lead to speculation that the flexible piston enhanced mass transfer results may correlate with voidage or amplitude. In Figure 2.8 both $(k_{La}^*/k_{La})/(A^*/A_0)$ versus frequency and $(k_{La}^*/k_{La})/(\varepsilon^*/\varepsilon)$ versus frequency are plotted. The fact $(k_{La}^*/k_{La})/(A^*/A_0) = 1$ (versus frequency) provides strong evidence that bubble breakup and enhanced mass transfer is amplitude driven when using the flexible piston at high gas velocities.

The evidence seems to show that the enhancement at the natural frequency of the membrane-water system arises from the increase in the liquid amplitude under conditions of resonance. Also, Figure 2.5b, Figure 2.6b and Figure 2.7b, suggest that gas rate is not an important factor when results are normalized with respect to non-vibrating conditions. This suggests $k_{La}^*$ for pulsing has the same gas velocity dependence as the steady case, $k_{La}$.  

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Figure 2.6 Gas hold-up as a function of frequency; Cam amplitude = 1.36mm, Membrane thickness = 3.18 mm: (a) Absolute $\varepsilon^*$; (b) Enhancement $\varepsilon^*/\varepsilon$.
Figure 2.7 Gas hold-up as a function of frequency; Cam amplitude = 0.51 mm, Membrane thickness = 3.18 mm: (a) Absolute $\varepsilon^*$; (b) Enhancement $\varepsilon^*/\varepsilon$
Figure 2.8 Comparison of flexible piston normalized mass transfer coefficient, gas hold-up and water amplitude; Cam amplitude = 1.36mm, Membrane thickness = 3.18 mm: (a) \( \left( \frac{k_{La}^*}{k_{La}} \right) / \left( \frac{A^*}{A_0} \right) \) as a function of frequency; (b) \( \left( \frac{k_{La}^*}{k_{La}} \right) / \left( \frac{\varepsilon^*}{\varepsilon} \right) \) as a function of frequency
2.3.2 Mass Transfer and Voidage Measurements - Solid Piston

The extensive dynamics caused by the elastic piston produced unique effects. It became apparent that the elasticity of the membrane piston produced resonant behavior at certain frequencies. We wondered if pure oscillations, using a more rigid piston, would produce different results. To create a solid piston, the natural gum rubber sheet (3.18 mm) at the base of the column is clamped between two larger stainless steel disks each 8.26 cm in diameter. The column diameter is 8.9 cm, which allows a maximum exposure of 2.74 cm$^2$ of rubber at the column base. This combination produces a nearly solid piston behavior so that the cam amplitude setting is the same as the fluid amplitude ($A$). The mass transfer enhancements for different fixed amplitudes of the solid piston at the maximum flowrate of 30.4 ml/s are given in Table 2.3 and plotted in Figure 2.9.

Table 2.3 Solid Piston Results (Membrane 3.18 mm, $Q_g = 30.4$ ml/s)

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<th>f (Hz)</th>
<th>$k_i a^*$</th>
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(Table cont.)
e) Piston amplitude 0.46 mm

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Figure 2.9 Enhancement ($k_L a^*/k_L a$) as a function of frequency for solid piston with different cam amplitudes. $Q_g = 30.4$ ml/s, Membrane thickness = 3.18 mm.

The solid piston produced quite different results, relative to the flexible piston. Enhancements in mass transfer in excess of 500% were observed using 2.46 mm amplitude and frequencies as low as 17.5 Hz. Enhancements in excess of 400% are possible with amplitudes as low as 1.23 mm and frequencies as low as 20 Hz. This improvement exceeds any seen so far in the literature. Sigmoidal behavior, as $k_L a^*$ was plotted versus frequency, was observed reaching clearly defined asymptotes.

Figure 2.9 for the solid piston and Figure 2.8a for the flexible piston can be compared directly. For the solid piston no elastic resonance occurred therefore $A/A_0 = 1$ for all frequencies. There is little agreement between these Figures, especially as the amplitude and frequency are
increased. We suspect that the method of pulsing, flexible versus solid piston, may produces different flow patterns in the column, especially at higher frequencies and amplitudes.

It is possible to make some general comments about the behavior manifest in Figure 2.9. At constant amplitude, as the frequency increases, bubble breakage increases. This will usually occur with second order kinetics, meaning two bubbles form from one large one. More breakage occurs as frequency increases until a critical bubble size occurs. Beyond this point, bubbles no longer break and they retain this maximum stable size. The new surfaces created during breakage cause big increases in $k_La^*$, and after the critical bubble size is reached, no further increase is possible. This possibly explains the mass transfer coefficient values reaching a plateau. This plateau phenomenon was not observed with the flexible piston because of the dynamic phase shift effects caused by the rubber membrane - the fluid amplitude reached a maximum and quickly dropped off.

We also observed column foaming and sloshing at some conditions (Table 2.3). Here with the solid piston at high amplitudes and frequencies, smaller bubbles are moved so violently that the surfaces are cleansed (removing surfactant film) and allowing recoalescence, thereby reducing voidage. During the run up period, enhancement occurred mainly from increased “$a$”, but also owing to surface renewal by giving birth to new, smaller bubbles. This process continues as frequency and/or amplitude is increased until a critical, maximum stable bubble size is attained. Increases in frequency or amplitude beyond this serves only to cleanse the bubble surface, and at some point, bubble coalescence can arise, which serves to reduce voidage. The penetration of the boundary layer around the moving bubbles can be linked to the energy dissipation in the system, which increases with frequency and amplitude. It is also possible that small bubbles are retarded and move downward, owing to the Bjerknes effect, and this may give rise to foaming and increased hold-up.

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2.3.3 Applying the Benjamin and Ursell\textsuperscript{3} Stability Theory to Bubble Breakage

We searched for an explanation for these somewhat curious results. It may be possible that the observed bubble breakup and enhanced mass transfer can be connected to the observed instability at the top interface.\textsuperscript{116} When the free surface shows instability, as indicated by sloshing (Tables 2.1 and 2.2) and sloshing and/or foaming (Table 2.3), column performance is greatly enhanced. The bubble breakup may be due to a “free-surface” instability on the almost horizontal interfaces of the large and very “flat” bottom interfaces on bubbles formed at the jetting injector, many of which took a spherical cap shape. It seems plausible that large, spherical cap bubbles can sustain interfacial oscillations in the same manner as the top interface. The flat bottom of the bubbles will behave just as any flat interface subjected to vibrations, except the flat surface is rising at a substantial rate.

Benjamin and Ursell\textsuperscript{3} studied the unstable wave motion of the free surface (e.g., the air-water interface) of an inviscid liquid column subjected to vibrations at the base of the column. If a similar free surface instability is also created on the flat interfaces of large bubbles, then there is an engine to cause bubbles to break. Benjamin and Ursell\textsuperscript{3} show, under the assumptions of small vibrational amplitude on an inviscid fluid, the stability of the free surface is given by a series of Mathieu equations, which can sustain unstable behaviors at certain pulsing amplitudes and frequencies:

\[
\frac{d^2 a_m}{dT^2} + \left( p_m - 2q_m \cos(2T) \right) a_m = 0 \tag{2.7}
\]

where,

\[
p_m = \left( \frac{4k_m \tanh(k_m h_w)}{\omega^2} \right) \left( g + \frac{k_m^2 \sigma}{\rho_L} \right) \tag{2.8}
\]

\[
q_m = 2k_m A \tanh(k_m h_w) \tag{2.9}
\]
and \( a_m \) is the surface fluid amplitude which is a function of time; \( k_m \) is the characteristic eigenvalue; \( \omega \) is the forcing frequency (radians/s); \( A \) is the forcing amplitude (cm); \( h_w \) is the height of the water (cm), \( \rho_L \) is the water density = 1 g/cm\(^3\); \( g \) is the acceleration due to gravity = 981 cm/s\(^2\); \( \sigma \) is the water surface tension = 72.5 dynes/cm; and \( T \) is \( \frac{1}{2} \omega t \), where \( t \) is the time in s.

For a vessel of cylindrical shape and radius \( R \), \( k_m \) is an abbreviated form of \( k_{l,m} \) where \( J_l'(k_{l,m}R) = 0 \). Here \( m \) denotes the \( m^{th} \) zero of the derivative of the \( l^{th} \) order Bessel function, and \( m = 1, 2, 3 \ldots \) with \( l = 0, 1, 2 \ldots \). These eigenvalues are based on the condition of zero velocity at the vessel wall, where \( r = R \).

The interesting results arising from Benjamin and Ursell analysis led to a map of regions for stable and unstable behavior, using the dimensionless parameters \( p \), \( q \), which are proportional to the inverse square forcing frequency and forcing amplitude, respectively.

In Figure 2.10 (following Dodge\(^{117}\)) we have plotted the solid piston data from Table 2.3 overlaid on the stability regions of Benjamin and Ursell\(^3\). Each frequency produces a constant \( p \) value and each fixed amplitude produces a constant \( q \) value. In Figure 2.10 we have used \( (k_{Bn} R) = 11.706 \), which is the \( 4^{th} \) zero of the derivative of the first order (hence, \( l = 1 \)) Bessel function. There are countably infinite values of \( p_m \) and \( q_m \) for \( l \) varying \( l = 0, 1, 2 \ldots \) and \( m = 1, 2, 3 \ldots \). The harmonics for \( m = 4, l = 1 \), were the lowest to yield \( p, q \) values in the unstable region for our particular column size (8.9 cm i.d.), so the calculations are based on the \( k_{l,4} \) eigenvalue.

Our experiments showed surface instability closely followed that predicted by Benjamin and Ursell. There was good agreement between the regions of instability (free surface sloshing and/or foaming) predicted in Figure 2.10 and the experimental data of Table 2.3, except for the smallest tested amplitude of 0.46 mm. For example at a constant amplitude of 1.23 mm, Figure 2.10 shows 0-15 Hz to be stable but 17.5-30 Hz to be unstable and this was exactly as observed.
in the experiments shown in Table 2.3c. At the very small amplitude of 0.46mm, Figure 2.10 shows instability should occur at 20 Hz, but this was not experimentally observed. Such differences can be attributed to the effect of viscous damping, which are unaccounted for in this theory. Such damping, as estimated in Benjamin and Ursell’s original work, shrinks the area of instability.

![Figure 2.10 Mathieu’s half frequency stability chart for $l = 1, m = 4$ mode showing stable and unstable regions. Darkened data points represent unstable experimental responses, open points represent stable responses (see Table 2.3).](image)

One could use the Benjamin and Ursell theory to predict the proper operating regions to gain large mass transfer and voidage enhancements. However, an even easier approach may be to simply vary the frequency, gradually increasing at a chosen cam setting and wait for the surface to become unstable. There are several frequency ranges which produce instability on the free surface, however, the first range (15-25 Hz in our experiments) is expected to have a strong performance enhancement in the column. In short, observation of the top surface gives fundamental information regarding instability several column diameters beneath the surface. We observed breakage to commence within approximately two column diameters of the injector, and continue close beneath the unstable top surface.
The question of instability imposed on the flat bottom surface or the top curved interface\textsuperscript{118} of a rising spherical cap bubble is an intriguing one. High speed photographs of the fast rising spherical caps in a swarm of other bubbles was not possible in the present work. However, we propose that the Mathieu equation in the Benjamin and Ursell theory is the correct means to forecast behavior, provided the spherical cap radius can be found, by calculation or observation. For example, if the spherical cap bubble sustains a radius half the column diameter, then $k_m$ is doubled and this at least doubles $p_m$ and $q_m$, moving deeper into the unstable region.

\subsection*{2.3.4 Power Dissipation under Pulsing Conditions}

The power dissipation per unit mass of liquid has been widely used to correlate rates of mass transfer and mixing. For example, in an early and quite successful application, Baird and Rice\textsuperscript{119} used the power input by the gas phase, undergoing a pressure drop equal to the hydrostatic head, to correlate axial dispersion coefficient. Hence, the power provided by the gas injection, which is the product of velocity and force, is divided by liquid mass to yield:

$$ P_m = \frac{A_c U_{0g} (\rho_L (1 - \varepsilon) h_0 g)}{A_c h_0 \rho_L (1 - \varepsilon)} = U_{0g} g $$

(2.10)

A correlating function for power input per unit mass of liquid by the vibrating piston can be expressed in the dimensionally consistent framework as:

$$ P_m = \frac{A^2 \omega^3}{2} $$

which is based on the time average of mass times acceleration (force) multiplied by the time average velocity. A physical model for $P_m$ can be developed using the friction factor for circular tubes, as follows:

$$ P_m = 2 \frac{V(t)^3 f_f}{D_c} $$
where $Dc$ is column diameter, and $f_f$ is the Fanning friction factor. For example, if the flow is laminar over most of the cycle and $V(t) = A \omega \sin(\omega t)$, then the time average power/mass is calculated using:

$$P_m = \frac{16 A^2 \omega^2 \nu}{Dc^2}$$

where $\nu$ is kinematic viscosity. For turbulent friction factors, finding the time average for a cycle is troublesome and not straightforward. For this reason, we elect to use the simple correlating function $A^2 \omega^3 / 2$ to bring our data together, as illustrated in Figure 2.11, using the following equation for total power:

$$P_m^* = g U_{og} + \frac{A^2 \omega^3}{2}$$

In these expressions, $A$ denotes the liquid amplitude (half stroke length) which may also be a function of frequency for the flexible membrane piston, so in that case $A$ is to be represented by $A^*$ given in Tables 1 and 2 in Knopf et al.\textsuperscript{114}. In the calculation of mean velocity and acceleration, the RMS for the sinusoidal variations was taken over one period which produced the square root of two in the denominator of each term.

It is difficult to correlate data which sustains maxima, but there have been attempts using power input to do just that.\textsuperscript{4,120} Baird and Garstang\textsuperscript{4} showed for pulsed columns with baffles that,

$$k_l a^* \propto \left( \frac{P_m^*}{\nu} \right)^{0.42} \left( U_{og} \right)^{0.5}$$

(2.12)

Similarly for columns with oscillating baffles Oliveira and Ni\textsuperscript{121} found that,

$$k_l a^* \propto \left( \frac{P_m^*}{\nu} \right)^{0.4} \left( U_{og} \right)^{0.37}$$

(2.13)

Utilizing these results, our solid piston data (Table 2.3) for volumetric mass transfer coefficient is plotted versus ($\text{Power/Unit Mass})^{0.4}$ in Figure 2.11. There is good agreement between this data and the correlations in equations (2.12) and (2.13).
Baird and Garstang\textsuperscript{4} also found for their pulsed column that the voidage could be expressed as,

\[ \varepsilon^* \propto \left( \frac{P^*}{m^*} \right)^{0.42} \left( U_{og} \right)^{0.5} \]  \hspace{1cm} (2.14)

Taking the ratio of equation (2.12) and equation (2.14),

\[ k_L a^* \propto \varepsilon^* \]  \hspace{1cm} (2.15)

where Baird and Garstang\textsuperscript{4} found \( k_L a^* = 0.75 \varepsilon^* \). Plotting our solid piston volumetric mass transfer coefficient versus voidage data in Figure 12 we found \( k_L a^* = 0.82 \varepsilon^* \) which is in agreement with this early work. This interesting result implies that,

\[ k_L^* \propto d \]  \hspace{1cm} (2.16)

since spherical bubbles give:

\[ a = \frac{6}{d} \varepsilon^* \]  \hspace{1cm} (2.17)

Equation (2.16) is contrary to Higbie’s penetration theory which suggests that \( k_L \) is proportional as:
Examination of equation (2.18) shows that $k_L$ actually depends on both the rise velocity and bubble diameter. If the bubble rise velocity is slowing due to oscillations\textsuperscript{56} or contamination of the interface causes immobility of the bubble film, then $k_L^*$ becomes constant or slowly decreasing as observed by Harbaum and Houghton\textsuperscript{48}.

In Figure 2.13 the flexible piston volumetric mass transfer coefficient versus voidage data (Tables 2.1 and 2.2) is presented; here $k_L a^* = 0.55 \varepsilon^*$. Although this value differs from the solid piston, it is in agreement with the results of Krishna and Ellenberger\textsuperscript{53} who found $k_L a^* = 0.5 \varepsilon^*$.

![Figure 2.12 Volumetric mass transfer coefficient as a function of gas hold-up for solid piston.](image-url)

\[ k_L \propto \sqrt{\frac{V_b}{d}} \] (2.18)
Figure 2.13 Volumetric mass transfer coefficient as a function of gas hold-up for flexible piston.

We speculate that the dependence of volumetric mass transfer coefficient on voidage may depend on many factors including the mechanism of vibration. Baird and Garstang\textsuperscript{4} used a column with baffles which may be more aligned with our solid piston. Krishna and Ellenberger\textsuperscript{53} used an air dampener below their vibration source which may have acted similar to our flexible elastic membrane, which introduced visco-elasticity into the system. The difference between harsh and damped vibrations imposed on the system seems to be significant.

2.4 Conclusions

Active forcing to create bubble breakage produces distinctly different mechanisms under low gas flowrate (Knopf et al.\textsuperscript{114}) and high gas flowrate (this work). Under appropriate forcing (pulsing) conditions and with low gas flowrate, bubble breakup involves both shearing in the injector and high velocity water slug impact of bubbles near the injector tip. At high gas flowrate, active forcing breaks bubbles in the column proper.

For high gas flowrates, the method of forcing, flexible piston or solid type piston significantly affects bubble breakage dynamics. The flexible piston imparts the single resonant
frequency of the membrane-water column system. The elasticity produces resonant amplitude much larger than expected from a simple solid piston motion. This causes high breakage rates in the frequency range surrounding that resonant frequency.

The solid piston behaves differently, and, since the system does not sustain elastic resonance, a peak amplitude does not arise. Therefore some other explanation must be found for the breakage that occurred. This may be attributable to hydrodynamic instability at the flat bottoms of rising (large) spherical caps. The observed instability of the top column surface will extend at least several column diameters before it is damped. For the solid piston case, both hydrodynamic instability of the bottom interface of spherical caps, and break up by the penetration of the unstable top interface into the rising bubbles contributes to breakup as a whole. For the flexible piston, in addition to the elastic resonance, the interface instability of the Benjamin and Ursell type will also be present. However, the elastic piston resonance seemed to produce less top surface instability, probably owing to inherent damping by the elastic membrane. It is interesting that the predicted bubble size according to Hinze’s theory of breakage is proportional to \(1/(P_m)^{0.4}\), the same functional dependence we found for the solid piston. We conclude that the enhancements arise from two inextricably linked sources, power input and hydrodynamic instability.

2.5 Nomenclature

\(a\)  
gas-liquid interfacial area per unit volume of liquid, cm\(^2/cm^3\)

\(a_m\)  
surface fluid amplitude, cm

\(A\)  
water amplitude for solid piston (constant), mm

\(A_0\)  
water amplitude as frequency approaches zero, mm

\(A^*\)  
water amplitude at particular forcing frequency for flexible piston, mm

\(A_c\)  
column cross sectional area, cm\(^2\)

\(C\)  
oxygen concentration, gmol/cm\(^3\)
\( C^* \) oxygen saturation concentration, \( \text{gmol/cm}^3 \)

\( D \) diffusion coefficient, \( \text{cm}^2/\text{s} \)

\( D_c \) column diameter, cm

\( d \) diameter of bubble, cm

\( F \) force, dyne

\( f \) frequency, Hz

\( f_f \) Fanning friction factor, cm

\( g \) acceleration due to gravity, \( \text{cm/s}^2 \)

\( H \) distance between two taps, cm

\( h \) mean depth of bubble, cm

\( h_0 \) height of the water above injector tip under non-oscillating condition, cm

\( \Delta h \) height difference between level of manometric fluid, cm

\( h_w \) height of water in the column, cm

\( k_L \) liquid phase mass transfer coefficient, \( \text{m/s} \)

\( k_L a \) liquid phase volumetric mass transfer coefficient, \( \text{s}^{-1} \)

\( k_L a^* \) liquid phase volumetric mass transfer coefficient vibrated case, \( \text{s}^{-1} \)

\( k_m \) characteristic eigenvalue, dimensionless

\( L \) mean depth of bubble below surface, cm

\( M \) \( \frac{\omega^4 A^2 \rho_l h}{2 g P_0} \), dimensionless

\( m \) mass, g

\( P_0 \) pressure inside bubble, dyne/cm\(^2\)

\( P_m \) power per unit mass without forcing, \( \text{cm}^2/\text{s}^3 \)

\( P_m^* \) power per unit mass with forcing, \( \text{cm}^2/\text{s}^3 \)

\( p_m \) as in equation (2.8), dimensionless

\( q_m \) as in equation (2.9), dimensionless

\( Q_g \) gas volumetric flow rate, \( \text{cm}^3/\text{s} \)
\( r_0 \) bubble radius, cm
\( R \) radius of column, cm
\( R_0 \) orifice radius, cm
\( t \) time, s
\( T \) dimensionless time = \( \omega t / 2 \), dimensionless
\( U_{og} \) superficial gas velocity, cm/s
\( V \) velocity, cm/s
\( V_b \) bubble rise velocity, cm/s
\( V_g \) nozzle gas velocity, cm/s

**Greek letters**
\( \varepsilon \) gas holdup, dimensionless
\( \varepsilon^* \) gas holdup vibrated case, dimensionless
\( \gamma \) specific heats ratio of gas (=1.4 for air), dimensionless
\( \nu \) kinematic viscosity, \( \text{cm}^2/\text{s} \)
\( \rho_G \) gas density, g/cm\(^3\)
\( \rho_L \) liquid density, g/cm\(^3\)
\( \rho_m \) manometric fluid density, g/cm\(^3\)
\( \sigma \) surface tension, dynes/cm
\( \omega \) frequency of oscillation, rad/s
\( \omega_n \) bubble system natural resonance frequency, rad/s
Chapter 3  A New Theory to Explain Transport in Pulsed-flow Bubble Columns: the Bjerknes Effect†

3.1 Introduction

Recent data\textsuperscript{114,123} taken from pulsed bubble column reactors (BCR) showed several interesting and unexpected properties relative to the enhanced behavior of mass transfer coefficient and column voidage (hold-up). For both mass transfer and voidage, peaking occurred when a flexible piston was used to impart pulsations, but sigmoidal responses arose when a solid piston was used to pulse the liquid phase. The former response characteristics were explained as a result of elastic dynamics arising from the flexible piston. However, the response from the solid piston was only quantified by correlation using power per unit mass, with passing reference to possible effects arising from Bjerknes forces.

We have now uncovered a simplified, one-dimensional theory to predict the curious effects using the solid piston. New data have been produced to test the theory, with a range of superficial gas velocities.

3.2 Theory

An expression to compute the time average force on a bubble in a vertically vibrating liquid column was derived by Buchanan et al.\textsuperscript{62} some time ago. These authors were more interested in the “entrainment” of bubbles from the top unstable interface of a vibrating column of water, and they provided approximate verification for this entrainment as a function of frequency and amplitude. This was followed by work describing mass transfer into reacting solutions under vibrating conditions\textsuperscript{64}. Later, Jameson\textsuperscript{63} and Lemcoff and Jameson\textsuperscript{124} studied the so-called resonant bubble contactor in mass transfer applications. A vibrating slurry reactor was also studied\textsuperscript{125}. None of these led to a general theory to explain the enhanced transport observed.

A general expression for the time-averaged force on a submerged bubble (after Bjerknes\textsuperscript{6}) is given by:

\[
\langle F \rangle = \rho_L V_o g - \frac{A \omega^2}{2} \Delta V_{\text{max}}
\]  

(3.1)

where the second term is the induced Bjerknes “kinetic buoyancy” force. A bubble experiences a force in an accelerating liquid in the direction of the acceleration, and is the product of the mass of liquid displaced and the imposed acceleration. In vertical pulsation, the bubble volume is greater at the top of the stroke (smaller hydraulic head) than at the bottom, so the net difference of this kinetic buoyancy acts downward against gravity. When the two buoyancy forces are equal, so that \( \langle F \rangle = 0 \), the bubble is held stationary, that is, it oscillates around a fixed position.

The term \( \Delta V_{\text{max}} \) represents the maximum volume amplitude of the bubble around the mean of \( V_o \). Buchanan et al.\textsuperscript{62} derived the following expression to calculate \( \Delta V_{\text{max}} \):

\[
\frac{\Delta V_{\text{max}}}{V_o} = \frac{\rho_L h \omega^2 A}{P_o + \rho_L h g - \rho_L h \omega^2 A}
\]  

(3.2)

where \( h \) is the height above the bubble, and \( P_o \) is the pressure at the top interface. When \( P_o \) is atmospheric or larger, so that under most conditions \( P_o > (\rho_L h g - \rho_L h \omega^2 A) \), hence we shall take:

\[
\frac{\Delta V_{\text{max}}}{V_o} \approx \frac{\rho_L h \omega^2 A}{P_o}
\]  

(3.3)

Here, liquid amplitude \( A \) has been assumed to be independent of vertical position. Earlier, it was shown experimentally that amplitude of liquid pulsation is essentially the same as the cam amplitude.\textsuperscript{123} When equation (3.3) is inserted into equation (3.1), we find:

\[
\langle F \rangle = \rho_L V_o g \left( 1 - \frac{1}{2} \frac{\rho_L h A^2 \omega^4}{g P_o} \right) = \rho_L V_o g (1 - Bj(h))
\]  

(3.4)

where,
which takes a value of unity to cause the bubbles to stop rising. The effect on the time-averaged bubble rise velocity can be inferred from an average force balance including drag:

\[
\langle F \rangle = \frac{1}{2} \rho_L U^2 C_D (\pi R^2)
\]  

(3.6)

### 3.2.1 Predicting Voidage

We wish to predict column voidage arising from the effects of pulsation. The retardation of rise velocity is key. In the present work, we shall use the drag expression after Kunii and Levenspiel\(^7\):

\[
C_D = \frac{10}{\sqrt{Re}}
\]  

(3.7)

which is valid for \( Re < 500 \).

Inserting this into equation (3.6), and using equation (3.4) for an assumed spherical bubble yields:

\[
\frac{U}{d} = \left( \frac{2g}{15\sqrt{\nu}} \right)^{2/3} \left[ 1 - Bj(h) \right]^{2/3}
\]  

(3.8)

where, \( d \) denotes bubble diameter. This expression shows as \( Bj(h) \to 1 \), then \( U \to 0 \), as required.

For batch systems of the type we have used\(^1,2\), and for dilute gas hold-up, we can write:

\[
\varepsilon = \frac{U_{og}}{U}
\]  

(3.9)

which connects gas voidage to gas superficial velocity \( U_{og} \) and gas rise velocity \( U \). Inserting the rise velocity from equation (3.8) gives an expression to calculate voidage at a position \( h \) from the top interface:
\[ c(h) = \frac{U_{og}}{d \left[ \frac{2g}{15\sqrt{\nu}} (1 - Bj(h)) \right]^{2/3}} \] 

(3.10)

It can be seen in this expression that a singularity arises when \( Bj(h) = 1 \). One expects to see a spike in voidage at such points, or bubble clustering\(^{58,126}\). As we shall show, our experiments were operated such that \( Bj(h) < 1 \). Moreover, an average voidage was measured so the above expression must be averaged over the column length. We shall take the bubble size under oscillating conditions to be of the Hinze\(^8\) type, so that

\[ d = k \left( \frac{\sigma}{\rho_L} \right)^{3/5} \frac{P_k}{P_m^{2/5}} \] 

(3.11)

The Hinze formula is based on the bubble breakage process in turbulent flows. In the current work, effects of the bubble to bubble coalescence are neglected. The constant \( k \) was given in the review of Taitel et al.\(^{127}\) for gas-liquid systems as 1.14, and was later determined by experiments to take a value of 1.67 using liquid jets to split bubbles by shearing, as reported by Lewis and Davidson\(^{128}\) (see Table 3.1). The size reported by these authors represented the maximum stable bubble size for the break up of bubbles by turbulent forces. We have made experiments (to be discussed) using high speed photography to find the Sauter mean diameter for the present experimental program, and the value of the fitted \( k \) was found to be 1.70, remarkably close to the value reported by Lewis and Davidson\(^{128}\). We shall use the value 1.70 for \( k \) in the remainder of the development.

As before\(^{114,123}\), we shall take the power per unit mass as:\(^\dagger\)

\[ P_m(t) = g U_{og} - \frac{A^2 \omega^3}{2} \sin(\omega t) \cos(\omega t) \]

Here a maximum for breakage purposes occurs when \( \tan(\omega t) = -1 \), which finally yields the result in equation (3.12)

\(^\dagger\) Equation (3.12) represents the maximum power per unit mass in a cycle, since the transient expression is
which represents the two contributions from, first, gas injection, and second, liquid oscillation.

The clever combination of theory and experiment in the work of Lewis and Davidson\textsuperscript{128} to cause shear induced splitting of bubbles, lends strong support to our contention that bubble breakage in oscillating flow is mainly by shear, and not by eddy effects. Moreover, they showed that the Hinze formula is also applicable to shear breakage, with a different multiplier (1.67) relative to the fitted constant of Hinze (0.725). So, the same power can be used to form eddies (at the tip of impellers, or around baffles) or to cause high shear rates: either can be the source for breaking bubbles, depending on the configuration of equipment.

Inserting the above expression for bubble size and using the power formula above, the local voidage in a plane at distance $h$ from the top interface is found from equation (3.10) to be:

$$
\varepsilon(h) = \frac{U_{ag} \left[ g U_{ag} + \frac{1}{2} A^2 \omega^3 \right]^{2/5}}{1.7 \left( \frac{\sigma}{\rho_L} \right)^{3/5} \left[ \frac{2g}{15\sqrt{\nu}} (1 - Bj(h)) \right]^{2/5}}
$$

To find the average voidage for the column as a whole, we integrate the local value over the total emulsion height $H$ from the gas injector to the top interface:

$$
\langle \varepsilon \rangle = \frac{1}{H} \int_0^H \varepsilon(h) \, dh
$$

which yields

$$
\langle \varepsilon \rangle = \frac{15}{2} \frac{U_{ag} \left[ g U_{ag} + \frac{1}{2} A^2 \omega^3 \right]^{2/5}}{1.7 \left( \frac{\sigma}{\rho_L} \right)^{3/5} \left( \frac{g}{\sqrt{\nu}} \right)^{2/3}} E(Bj)
$$

and

$$
E(Bj) = \frac{3}{Bj} \left[ 1 - (1 - Bj)^{1/3} \right]
$$
where $Bj$ is the $Bj(h)$ evaluated at total liquid column height $H$ and is given as

$$
Bj = \frac{1}{2} \frac{(\rho_L H) A^2 \omega^4}{g \rho_o} \quad (3.15b)
$$

The limits on $E(Bj)$ are as follows:

$$
\lim_{Bj \to 1} E(Bj) \to 3; \quad \lim_{Bj \to 0} E(Bj) \to 1 \quad (3.16)
$$

We shall compare predictions from equation (3.15) in the sections to follow.

### 3.2.2 Predicting Mass Transfer Coefficient

From our previous work\textsuperscript{114,123}, we expect the measured volumetric mass transfer coefficient to be enhanced. There are two sources of enhancement arising from the applied pulsation:

1. Enhancement caused by bubble breakage, which increases area (the Hinze effect),
2. Enhancement arising from bubble retardation, which increases voidage (the Bjerknes effect).

The Bjerknes force also has a third effect, mentioned earlier, which arises when $Bj \to 1$. We shall call this the “flooding effect”, which is similar in many ways to the flooding observed in counter current gas-liquid packed columns. The flooding effect produces a flood line, as we shall see, which is an upper limit to further increases in mass transfer coefficient.

We assume that the penetration theory, with modifications, is the appropriate starting point to predict mass transport. The vibrating interface may affect transport at higher frequency due to changing surface renewal rates, but we have ignored it here. Using penetration theory, for spherical bubbles:

$$
k_i a = \sqrt{\frac{4 D \pi}{\text{tc}}} \left( \frac{6}{d} \right) \quad (3.17)
$$

where, $d$ is the Sauter mean bubble diameter and the contact time is taken to be:

$$
t_c = \frac{d}{U} \quad (3.17a)
$$
Inserting $d/U$ from equation (3.8) and voidage from equation (3.10) yields an expression for local transport coefficient:

$$k_L a = \frac{12}{\sqrt{\pi}} \frac{\sqrt{D} \left( \frac{U_{og}}{d^2} \right)}{(15)^{1/3} \left( 1 - Bj(h) \right)}^{1/3}$$

(3.18)

where again we shall use the Hinze expression in equation (3.11) to calculate bubble size, $d$. To find the average for $k_L a$, we again integrate over the whole volume as:

$$\langle k_L a \rangle = \frac{1}{H} \int_0^H (k_L a) dh$$

(3.19)

which gives

$$\langle k_L a \rangle = \frac{12}{\sqrt{\pi}} \left( \frac{15}{2} \right)^{1/3} \frac{U_{og} \sqrt{D}}{(g/\sqrt{\nu})^{1/3}} G(Bj)$$

(3.20)

where

$$G(Bj) = \frac{3}{2} \left[ 1 - \left( 1 - Bj \right)^{2/3} \right]$$

(3.20a)

with an upper limit of $3/2$ when $Bj = 1$ and lower limit of $1.0$ when $Bj = 0$.

Combining all the constants when $d$ is inserted from equation (3.11) gives:

$$\langle k_L a \rangle = K \frac{U_{og} \sqrt{D} \left( g U_{og} + \frac{1}{2} A^2 \omega^3 \right)^{4/5}}{\left( \frac{\sigma}{\rho_L} \right)^{6/5} \left( \frac{g}{\sqrt{\nu}} \right)^{1/3}} G(Bj)$$

(3.21)

where

$$K = \frac{12}{\sqrt{\pi}} \left( \frac{15}{2} \right)^{1/3}$$

Combining all the constants when $d$ is inserted from equation (3.11) gives:

$$\langle k_L a \rangle = K \frac{U_{og} \sqrt{D} \left( g U_{og} + \frac{1}{2} A^2 \omega^3 \right)^{4/5}}{\left( \frac{\sigma}{\rho_L} \right)^{6/5} \left( \frac{g}{\sqrt{\nu}} \right)^{1/3}} G(Bj)$$

(3.21)

where $K = \frac{12}{\sqrt{\pi}} \left( \frac{15}{2} \right)^{1/3} = 4.58$. The frequency corresponding to:

$$Bj = \frac{1}{2} \frac{(\rho_L H) A^2 \omega^4}{g P_o} = 1$$

(3.22)
for certain values of $A$ and $H$ will be designated as $f_c$, which is the critical value at which bubbles stop rising at the point of gas injection (a distance $H$ from the top interface). For the present work with $H = 78$ cm, the critical frequency $f_c$ is 27.7 and 22.8 Hz for amplitude of 1.66 and 2.46 mm, respectively.

The theoretical results for voidage and mass transfer coefficient, represented by equations (3.15) and (3.21) respectively, rest on the following explicit and implied assumptions:

1. gas concentration is dilute, $\varepsilon << 1$,
2. fluid amplitude is uniform from top to bottom of the column,
3. coalescence rates are small,
4. bubble breakage occurs mainly by shear effects,
5. the expansion and contraction pulsing of bubbles has a small effect on mass transfer (small surface renewal effects).

3.3 Experimental Methods

The equipment used is shown in Figure 3.1. It consists of a Plexiglas® column of 8.9 cm in diameter and 106 cm in height. The base of the column is sealed with a natural gum rubber sheet. The natural gum rubber sheet is clamped between two stainless steel disks. The disks are 8.26 cm in diameter which essentially produces a solid piston at the column base. These disks are directly coupled to an eccentric cam which is driven by a five horsepower variable speed motor. The motor speed is controlled by an Omron Sysdrive 3G 3JV compact inverter controller. The eccentric cam produces a sinusoidal oscillation to the disks at the base of the column. The system is configured for operation from 0 - 30 Hz and amplitudes from 0 to 2.54 mm.

The bubble column reactor was filled with distilled water to a level 78 cm above the injector. Compressed air was injected into the BCR from a single capillary stainless steel injector of 0.75 mm diameter. The gas flow rate was controlled by use of a pressure regulator and a
needle valve. Low gas flow rates \( (U_{og} < 0.5 \text{ cm/s}) \) were measured by a soap bubble meter whereas for high gas flow rates a totalizing dry test meter (Singer DTM-200) was used. Except for the lowest flowrate, jetting conditions prevailed at the injector tip.

\[ \text{Figure 3.1 Pulsed bubble column reactor} \]

The BCR was operated as batch system with respect to liquid phase (water) and continuous up-flow for the gas phase (air). Experiments were performed for a range of gas superficial velocities, namely, 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 cm/s. Frequency was varied from 0 to 30 Hz. Two amplitudes of 1.66 mm and 2.46 mm were investigated.

The gas hold up was determined by the manometric method.\textsuperscript{115} Two taps were used, one 11 cm from the piston and the other 77 cm above the piston. The manometer fluid was Meriam Red 295 with a specific gravity of 2.95. A pressure balance on each leg of the manometer allows voidage \( (\varepsilon) \) to be determined using,
\[ \varepsilon = \left( \frac{\rho_m - \rho_L}{\rho_L} \right) \frac{\Delta x}{X} \]  

(3.23)

The height differential in Meriam Red 295, denoted as \( \Delta x \), was determined using a cathetometer which provided an accuracy of plus or minus 0.01 mm. Here \( X \) is the distance between the two taps.

It was suspected that large errors may be associated with voidage measurements owing to the fact that applied mechanical oscillations cause a sinusoidal pressure field in the column. Baird\textsuperscript{61} showed that under the oscillating conditions, pressure inside the column can be given as,

\[ P(t) = P_o + \rho_L (h + A \sin \omega t) (g - A \omega^2 \sin \omega t) \]  

(3.24)

Hence, a careful error analysis was made for the voidage experiments. Factors contributing towards error in voidage measurement are: error in manometric reading, error in setting amplitude and frequency and error in gas flow rate measurements. At an amplitude of 2.46 mm, all the experiments were repeated three times to quantify the error. Figure 3.2 shows results of voidage measurement experiments at \( A = 2.46 \text{ mm} \) and at various gas superficial velocities. Average values from these three experiments are shown with error bars of length plus or minus one standard deviation. The error is large at high frequencies near the flood line. In fact it was nearly impossible to measure the voidage at or near the flooding conditions, owing to the high magnitude of oscillations in the manometric fluid.

Bubble size distribution (BSD) was measured at different vertical positions in the column. High speed photographs were made using a high speed camera (Photron Fastcam PCI-R2). Pictures were taken through a square water box, size 25 cm with height 86 cm, which surrounded the circular column and allowed the bubble swarm to be viewed more clearly. The images from the camera were analyzed using Image J software, which calculates the area of all the bubbles. Figure 3.3 shows a sample image from the camera and its modified version after the
processing. Determined bubble areas were used to calculate bubble size distribution. Representative bubble size was deduced from the bubble size distribution curve by calculating the Sauter mean diameter- the Sauter mean diameter is the ratio of the third moment to the second moment.

\[ A = 2.46 \text{ mm} \]

![Graph showing gas hold-up as a function of frequency at various \( U_{og}; A = 2.46 \text{ mm} \).](image)

**Figure 3.2** Gas hold-up as a function of frequency at various \( U_{og}; A = 2.46 \text{ mm} \).

![Illustration of image processing during bubble size distribution measurements.](image)

(a) raw image  
(b) processed image using ImageJ software.

**Figure 3.3** Illustration of image processing during bubble size distribution measurements. a) raw image b) processed image using ImageJ software.
Bubble size distribution was measured at four different vertical positions along the column. The amplitude of oscillation and the frequency were held constant at 1.66 mm and 17.5 Hz respectively. Sauter mean diameter decreases as we move up the column ultimately reaching an equilibrium value as shown in Table 3.2. The effect of frequency on bubble size distribution was studied at vertical position, $s = 53.8$ cm. From Figure 3.4 it can be seen that the size distribution is bimodal until frequency exceeds 15 Hz, above which the distributions are normal and unimodal. The peak diameters and the Sauter mean diameters are not the same, although differences between the two values become smaller as the distribution narrows, which is the case for higher frequencies. Figure 3.5 shows the fit for the Hinze multiplier $k$ in equation (3.11) using the Sauter mean diameter determined from the image analysis. The flat line through the diameter 0.6 cm indicates the bubble formation size at the nozzle tip. The fit of the Hinze breakage model was quite satisfactory, using the Sauter mean diameter data. It is seen in Figure 3.5 that when $P_m < 0.5$ W/kg, the birth size of bubbles prevail, while at higher values of power, breakage from turbulence and shear forces\textsuperscript{128} determine bubble size using the Hinze formula with $k = 1.7$.

![Figure 3.4 Bubble size distribution as a function of frequency at a vertical position $s = 53.8$ cm; $A = 1.66$ mm, $U_{og} = 0.16$ cm/s](image-url)
Mass transfer experiments were performed by measuring dissolved oxygen concentration as a function of time. A dissolved oxygen probe from Cole Palmer (Model 300mm) and signal conditioner (Model 01971-00) were used. The oxygen probe was placed 32 cm above the injector. Signals from the oxygen probe were directly recorded in a computer using Labview® instrumentation software. Once oxygen concentration data was obtained, then volumetric mass transfer coefficient was calculated according to the following expression:

\[
\frac{C(t)}{C^*} = 1 - \exp(-k_z a t)
\]

(3.25)

where \(C(t)\) is dissolved oxygen concentration at time \(t\) and \(C^*\) is saturation concentration of oxygen in the water. A more detailed account of mass transfer measurements can be obtained in our previous work.\(^{114}\)

At low frequencies, the top free surface of the water shows a definite pattern of surface waves. As frequency is increased, at certain combinations of amplitude and frequency, the top surface becomes unstable, starts disintegrating\(^{129}\) and the liquid starts sloshing against the walls. This splashing liquid causes entrainment of the gas from the space above. These unstable
conditions can be predicted by applying the inviscid theory of Benjamin and Ursell\textsuperscript{3}. A viscosity correction was provided by Nyborg and Rogers\textsuperscript{126}. Bretsznajker and Pasiuk\textsuperscript{59} observed that this unstable liquid surface contributes significantly to the overall mass transfer. To quantify the contribution from the free surface of water, experiments were performed in which no gas was injected at the bottom of the column. Vibrations were applied ($A = 2.46\text{mm}, f = 17.5\text{Hz}$) and oxygen uptake was measured. In this case the only possible way of oxygen transfer to the liquid is through the unstable top surface of the water. Even after operating for a long period of time (more than 1 hour), no significant dissolved oxygen concentration was observed. Hence it was concluded that there is little mass transfer contribution from the top unstable interface. The mass transfer occurs mainly through gas bubbles dispersed in the liquid phase via the gas injector. We have made estimates for mass transfer through the wavy top interface under the worst case to be no more than seven per cent of the total transfer during an experiment, provided $f < f_c$.

### 3.4 Comparison of Theory and Experiment

Theoretical predictions of voidage and mass transfer coefficient given by equation (3.15) and (3.21), respectively, were compared with experimental results. The kinematic viscosity was taken as $0.01 \text{ cm}^2/\text{s}$ and oxygen diffusivity in water was taken to be $2.5 \times 10^{-5} \text{ cm}^2/\text{s}$.

In Figure 3.6 and Figure 3.7, we confirm the predicted linear dependence of $<k_La>$ on $U_{og}$, and the power/mass dependence as $P_m^{0.8}$, respectively. Earlier work by Harbaum and Houghton\textsuperscript{48} showed linear dependence on $P_m$, which is very similar to the exponent of 0.8 used in this work (see Table 3.3). Baird and Garstang\textsuperscript{4}, Ni and Gao\textsuperscript{5} gave dependence on $P_m$ to the power of 0.42, for rather different methods of imposing pulsations in the presence of baffles. They also showed that $<k_La>$ depends on $U_{og}$ to the power of 0.5 and 0.37, respectively. Krishna and Ellenberger\textsuperscript{53} observed linear dependence of $<k_La>$ on $U_{og}$, which matches with this work.

In our earlier work\textsuperscript{123}, we reported that $<k_La> \propto P_m^{0.4}$ based on $<k_La>$ measurements at a single
superficial gas velocity of 0.5 cm/s. The earlier experiments did not include effects arising from the slowing down of bubbles owing to Bjerknes kinetic buoyancy. This, and the single velocity used, distorted the curve fit, which was based on quite scattered data.

Figure 3.6 Illustrating the linear dependence on $U_{og}$ according to theory, equation (3.21).

Figure 3.7 Illustrating $<k_{La}>$ dependence on $P_m^{0.8}$ according to theory, equation (3.21).
The current theory for $<k_La>$ predicted a squared inverse dependence on bubble size, as shown in equation (3.20). For the Hinze bubble size given by Eq. (3.11), this means $<k_La>$ is forecast to depend on $P_m^{0.8}$, which appears to be confirmed by our new experiments for varying $U_{og}$, $A$ and $\omega=2\pi f$. Similarly, Figure 3.8 and Figure 3.9 shows linear dependence of $\varepsilon$ on $U_{og}$ and also the voidage dependence on $P_m^{0.4}$.

![Figure 3.8 Illustrating the linear dependence on $U_{og}$ according to theory, equation (3.15).](image)

![Figure 3.9 Illustrating voidage dependence on $P_m^{0.4}$ according to theory, equation (3.15).](image)
In Figure 3.10, we illustrate \( <k_{La} > \) predictions from our theory, using our theoretical constant of 4.58, in comparison with experiments at various \( U_{og} \) for amplitudes of 2.46 mm and 1.66 mm, respectively. Figure 3.10 also illustrates the “flooding line” which is the horizontal line formed at the intersection of \( f_c \) (when \( Bj = 1 \)) with the theoretical curve. The line represents the upper asymptote for \( <k_{La} > \) when bubbles are stopped by Bjerknes forces at the nozzle tip.

The derived constant \( (K) \) for \( <k_{La} > \) was stated before as 4.58 while the curve fit yielded 4.45. A total of 81 experimental points were used to fit K. But the best fitted value of \( K \), which is remarkably close to the theoretical value, only approximates pinpointing the flood condition.

![Figure 3.10 Comparison between theoretical predictions and experimental data for mass transfer coefficients at various \( U_{og} \). Solid line shows theoretically predicted curve according to equation (3.21) with \( K = 4.58 \). Open Triangle show data taken from Ma \(^{10}\); (a) \( A = 1.66 \) mm, (b) \( A = 2.46 \) mm.](image.png)
We have also made a comparison by modifying the Hinze expression, so that \( d \to d_c \) as input power gets very large. We have taken the critical bubble size, in the lower limit, to follow Brodkey’s law\(^{130}\):

\[
d_c = \left[ \frac{0.4 \sigma}{(\rho_L - \rho_G) g} \right]^{1/2}
\]

The critical bubble size is the size small enough to maintain sphericity and thus prevent agglomeration owing to turbulent eddies. It would seem adding such a constant to the Hinze expression would be a reasonable proposition, to prevent the rather physically unrealizable state of zero bubble size as \( P_m \to \infty \). The addition of \( d_c \) to the expression for \( d \) in equation (3.11) gave slightly better curve fits, but was not deemed worth the additional complication of one additional parameter. It may be called upon in future.

Figure 3.11 compares the theoretical curve given by equation (3.15) and the experimental data for voidage measurements. The predicted multiplier for voidage in equation (3.15) was 2.25 while the data best fit gave 3.82. Hence, we use the value of 2.25 for the theoretical curve in
Figure 3.11, where the dashed curve is for the best fit. It is quite remarkable that the present theory, which includes several bold assumptions, can track the data so well.

Figure 3.11 Comparison between theoretical predictions and experimental data for gas hold-up at various $U_{og}$. Solid line shows theoretically predicted curve according to equation (3.15) with $K = 2.25$. Dashed line indicates a best fit with premultiplier $K = 3.82$. Open triangle show data taken from Ma.10 (a) $A = 1.66$ mm, (b) $A = 2.46$ mm.
3.5 Comments and Conclusions

A rather simple, one-dimensional theory, based on the Bjerknes kinetic buoyancy force and the Hinze bubble breakage formula, led to good comparisons with a large number of experiments for voidage and mass transfer coefficient. An upper limit is pinpointed when bubbles are stopped from rising upward at the injection point, hence flooding occurs. The theory is strictly applicable to dilute gas systems of low viscosity liquids (such as water). It is also shown that applied pulsations produce more uniform bubble size distributions. An extension to viscous systems is currently being studied, along with the effects of a periodic velocity profile depending on local radial position.

3.6 Nomenclature

\( a \) interfacial area per unit volume, \( \text{cm}^2/\text{cm}^3 \)

\( A \) amplitude of imposed liquid pulsation, cm

\( C \) dissolved oxygen concentration, \( \text{gmol/cm}^3 \)

\( C^* \) equilibrium value of dissolved oxygen, \( \text{gmol/cm}^3 \)

\( C_D \) drag coefficient, dimensionless

\( d \) bubble diameter, cm

\( d_c \) critical bubble diameter, cm

\( D \) molecular diffusion coefficient, \( \text{cm}^2/\text{s} \)

\( E(Bj) = \frac{3}{Bj} \left[ 1 - (1 - Bj)^{1/3} \right] \), dimensionless

\( <F> \) time average force, dyne

\( f \) frequency, Hz

\( f_c \) critical frequency when \( Bj = 1 \), Hz

\( g \) acceleration from gravity, \( \text{cm/s}^2 \)
\[ G(Bj) = \frac{3}{2} \left[ 1 - (1 - Bj)^{2/3} \right], \text{ dimensionless} \]

\[ h \quad \text{distance from top interface to bubble, cm} \]

\[ H \quad \text{distance from top interface to gas injector, cm} \]

\[ k \quad \text{pre-multiplier from equation 3.11, dimensionless} \]

\[ k_{La} \quad \text{volumetric mass transfer coefficient, 1/s} \]

\[ <k_{La}> \quad \text{average volumetric mass transfer coefficient under pulsing, 1/s} \]

\[ Bj(h) \quad \text{local Bjerknes number, } \frac{1}{2} \left( \frac{\rho_l \cdot h}{g \cdot P_o} \right) \cdot A^2 \cdot \omega^4, \text{ dimensionless} \]

\[ Bj \quad \text{Bjerknes number at position } H, \frac{1}{2} \left( \frac{\rho_l \cdot H}{g \cdot P_o} \right) \cdot A^2 \cdot \omega^4, \text{ dimensionless} \]

\[ P \quad \text{pressure, dyne/cm}^2 \]

\[ P_o \quad \text{pressure at top interface, dyne/cm}^2 \]

\[ P_m \quad \text{power input per unit mass, W/kg or cm}^2/\text{s}^3 \]

\[ R \quad \text{bubble radius, cm} \]

\[ Re \quad \text{bubble Reynolds number, } \frac{d \cdot U}{\nu}, \text{ dimensionless} \]

\[ s \quad \text{vertical position in the column, cm} \]

\[ t \quad \text{time, s} \]

\[ t_c \quad \text{contact time for mass transfer, d/U, s} \]

\[ U_{og} \quad \text{superficial gas velocity, cm/s} \]

\[ U \quad \text{time average bubble rise velocity, cm/s} \]

\[ V_o \quad \text{mean bubble volume, cm}^3 \]

\[ X \quad \text{distance between the two taps for manometer, cm} \]

\[ \Delta \nu \quad \text{height difference between two arms of the manometer, cm} \]
Greek letters

$\varepsilon(h)$  local voidage in a plane at $h$

$<\varepsilon>$  average voidage over column

$\nu$  kinematic liquid viscosity, cm$^2$/s

$\rho_L$  liquid density, g/cm$^3$

$\rho_G$  gas density, g/cm$^3$

$\rho_m$  manometer fluid density, g/cm$^3$

$\sigma$  surface tension, dyne/cm

$\omega$  frequency, radians/s
Chapter 4  Mass Transfer in a Viscous Bubble Column with Forced Oscillations

4.1 Introduction

Use of oscillations for improving performance of chemical engineering operations is not new and can be dated back to at least 1938. In that year, Martinelli and Boelter\(^1\) found that heat transfer in a natural convection mode from a tube to water can be increased by up to 400% using vibrations. Since then, vibrations have been used in a variety of chemical engineering operations ranging from mineral washing to fluidization. In a classical review paper, Baird\(^2\) presented the scope of various applications of vibrations for the chemical processing industry. In general, frequencies ranging from 1-10\(^5\) Hz can be utilized for chemical engineering applications. Particularly, frequencies in the range 1-500 Hz can be utilized for gas-liquid contacting. Various generators such as pistons, bellows, air pulsers, electromagnetic vibrators and loudspeakers can deliver the necessary frequency of vibration.

Many investigators have reported application of vibrations in bubble columns for gas liquid contacting. The first report appeared in 1960, when Harbaum and Houghton\(^47\) showed that the rate of absorption of CO\(_2\) in water can be enhanced up to 70% by the application of sonic vibrations in the frequency range 20-2000 Hz and the amplitude range of 0.01-1.0 mm. They observed that the mass transfer coefficient showed multiple maxima when frequency was increased. They attributed this behavior to the bubble resonance phenomenon. Further detailed investigations by Harbaum and Houghton\(^48\) revealed the effects of vibrations on other hydrodynamic parameters such as the gas hold-up, interfacial area, bubble size and rise velocities. Bretsznajder and Pasiuk\(^59\) studied a similar system of CO\(_2\) absorption in water, but using a mechanical vibration system as opposed to the sonic vibrations used by Harbaum and Houghton. With the mechanical vibrations, they were able to achieve higher amplitudes (0.5-
10.5 mm) at the expense of a lower frequency range (0-70 Hz). They observed similar multiple maxima in absorption rates as a function of the frequency. Baird and Garstang\(^4\) investigated the absorption of oxygen from air into water in a pulsed bubble column containing fixed baffles. They found that the gas hold up and the mass transfer coefficients were increased up to three times with the help of vibrations. Recently, Krishna and coworkers\(^{50-58}\) have rejuvenated interest in the oscillating bubble column reactor. They studied the influence of vibrations on the air-water system. Vibrations were imparted using an electromagnetic vibrator. They reported enhancements of up to 4 times in the mass transfer coefficient under oscillating conditions as compared to the non-pulsed case. Knopf et al.\(^{114,123}\) showed that the application of low amplitude (0.5-2.5 mm) and low frequency (0-25 Hz) vibrations can be used to achieve mass transfer enhancements up to 500% and gas hold-up enhancements up to 200%. A summary of oscillating bubble column studies reported in the literature is shown in Table 4.1.

### Table 4.1 Summary of literature on oscillating bubble columns

<table>
<thead>
<tr>
<th>Researcher</th>
<th>System</th>
<th>(f) (Hz)</th>
<th>(A) (mm)</th>
<th>(U_{avg}) (mm/s)</th>
<th>(k_La) (s(^{-1}))</th>
<th>(k_La) Enhancement</th>
<th>(\varepsilon) Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bretsznajder and Pasiuk(^59)</td>
<td>CO(_2) – water</td>
<td>0 - 70</td>
<td>0.5 – 10.5</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Harbaum and Houghton(^48)</td>
<td>CO(_2) – water</td>
<td>20 - 2000</td>
<td>0.01 – 1</td>
<td>14</td>
<td>0.02 – 0.06</td>
<td>1.7</td>
<td>0.05 – 0.25</td>
</tr>
<tr>
<td>Baird and Gerstang(^4)</td>
<td>Air – water (baffled)</td>
<td>1 – 1.35</td>
<td>0 – 94</td>
<td>8 – 25</td>
<td>0.03 – 0.17</td>
<td>3</td>
<td>0.04 – 0.2</td>
</tr>
<tr>
<td>Krishna and Ellenberger(^23)</td>
<td>Air – water</td>
<td>0 – 120</td>
<td>0.01 – 0.05</td>
<td>1 – 15</td>
<td>0.01 – 0.05</td>
<td>4</td>
<td>0.01 – 0.12</td>
</tr>
<tr>
<td>Knopf et al.(^{114,123,131})</td>
<td>Air – water</td>
<td>0 – 25</td>
<td>0.5 – 2.5</td>
<td>0.1 – 1.5</td>
<td>0.001- 0.036</td>
<td>5</td>
<td>0.005- 0.06</td>
</tr>
</tbody>
</table>

All of the previous studies dealt with aqueous systems. There were few attempts to investigate the effects of physical properties of the fluid on the performance of a bubble column with oscillations. The present work reports the effects of viscosity and superficial gas velocity on
the mass transfer coefficient in an oscillating bubble column. Different concentrations of aqueous solution of carboxymethylcellulose (CMC) were prepared to get different viscosities of liquids. The mass transfer coefficient was measured by oxygen uptake experiments.

Most of the available literature has reported experimental findings along with correlations but there have been few attempts to derive a general theory to explain the experimental findings. Baird and Garstang, Ni and Gao’s used an empirical correlation to predict $k_{L}a$ in an oscillating baffled column. They correlated $k_{L}a$ with power input and superficial gas velocity. In our previous work, we derived a comprehensive theory to explain the mass transfer and the gas hold-up enhancements in a bubble column under the influence of oscillations. It is the purpose of the current work to extend that theory to take into account the effects of viscosity of the pulsed liquid phase.

4.2 Experimental Methods

The equipment used to carry out this work is shown in Figure 4.1 and is the same as used in our previous work. It consists of a Plexiglas® column of 8.9 cm diameter and 106 cm in height. The base of the column is sealed with a natural gum rubber sheet. The natural gum rubber sheet is clamped between two stainless steel disks. The disks are 8.26 cm in diameter which essentially produces a solid piston at the column base. These disks are directly coupled to an eccentric cam which is driven by a five horsepower variable speed motor. The motor speed is controlled by an Omron Sysdrive 3G 3JV compact inverter controller. The eccentric cam produces a sinusoidal oscillation to the disks at the base of the column. The system is configured for operation from 0 - 30 Hz and amplitudes from 0 to 2.5 mm.

The bubble column reactor was filled with liquid to a level 78 cm above the injector. Compressed air was injected into the BCR from a single capillary stainless steel injector of 0.75 mm diameter. The gas flow rate was controlled by a pressure regulator and a needle valve.
flow rate was measured by a totalizing dry test meter (Singer DTM-200). Jetting conditions prevailed at the injector tip for the entire range of gas flow rates under consideration, so the initial bubble size was widely distributed.

![Figure 4.1 Oscillating bubble column reactor.](image)

The BCR was operated as batch system with respect to liquid phase (water or aqueous CMC solution) and continuous up-flow for the gas phase (air). Experiments were performed for a range of gas superficial velocities, namely, 0.5-1.5 cm/s. Frequency was varied from 0-25 Hz. Two amplitudes of 1.66 and 2.46 mm were investigated.

Mass transfer experiments were performed by measuring dissolved oxygen concentration as a function of time. A dissolved oxygen probe from Cole Palmer (Model 300mm) and signal conditioner (Model 01971-00) were used. The oxygen probe was placed 32 cm above the injector. Signals from the oxygen probe were directly recorded in a computer using Labview® instrumentation software. Once the oxygen concentration data was obtained, then the volumetric mass transfer coefficient was calculated according to the following expression:
\[ \frac{C(t)}{C^*} = 1 - \exp(-k_L a t) \] (4.1)

where \( C(t) \) is dissolved oxygen concentration at time \( t \) and \( C^* \) is the saturation concentration of oxygen in pure water. A more detailed account of the mass transfer measurements can be found in our previous work.\(^{114}\)

Experiments were performed with three liquids of different viscosity. Distilled water (viscosity = 1 cP) was used as the lowest viscosity solution. Two different concentrations (2 and 3 wt\%) of aqueous solution of CMC were prepared by dissolving a low viscosity carboxymethylcellulose sodium salt (Sigma-Aldrich) in distilled water. The 2 wt % solution gave a viscosity of 11 cP and the 3 wt% solution gave a viscosity of 62 cP at 25° C. Viscosity was measured using a AR1000 Rheometer (TA Instruments). A cone-and-plate geometry was used with a cone diameter of 40 mm, a gap of 27 \( \mu \)m and a cone angle of 0°59’54”. Viscosity and shear stress were measured for shear rates ranging from 10 – 100 s\(^{-1}\). A solvent trap was used around the sample to prevent any change in concentration of CMC solution due to the evaporative loss of water during the measurement run. Generally, low viscosity CMC solutions behave as a Newtonian fluid. This fact was confirmed by plotting shear stress data versus shear rate on a log-log scale (Figure 4.2) to assess the power-law index. The value of the power-law index was found to be 0.97 and 0.94 for 2 and 3wt% CMC solutions, respectively. An index slightly less than 1 suggests the existence of some shear thinning. But since the value of the exponent is very close to unity, for the purpose of the present work it was assumed that these CMC solutions behaved as Newtonian fluids.

The Bubble Size Distribution (BSD) was measured for pure water. High speed photographs were made using a high speed camera (Photron Fastcam PCI-R2). Pictures were taken through a square water box, size 25 cm with height 86 cm, which surrounded the circular
column and allowed the bubble swarm to be viewed more clearly. The images from the camera were analyzed using Image J software, which calculates the area of all the bubbles. Bubble areas so determined were used to calculate bubble size distribution. A representative bubble size was deduced from the bubble size distribution by calculating the Sauter mean diameter. The Sauter mean diameter is the ratio of the third moment to the second moment. More details about the bubble size measurements can be found in our previous work.\(^\text{132}\)

![Figure 4.2 Plot of shear stress vs shear rate showing an exponent of 0.94 for 3% CMC solution.](image)

4.3 Experimental Results

The volumetric mass transfer coefficient was measured as a function of frequency at two different amplitudes of 1.66 and 2.46 mm. Three solutions of different viscosities, namely, 1, 11 and 62 cP were investigated. Gas superficial velocity was varied from 0.5 to 1.5 cm/s.

Figure 4.3 shows representative mass transfer coefficient results at a pulsed-flow amplitude of 1.66 mm for the CMC solution of viscosity 11 cP, at different superficial gas velocities, plotted against frequency. At a constant superficial gas velocity, \(k_{L\alpha}\) increases with the increasing frequency, ultimately reaching a plateau at around 17.5 Hz. From the graph it can be
seen that the mass transfer enhancement up to 300% is obtained as compared to the non-oscillating case. If the frequency is held constant, then the increasing superficial gas velocity gives an increase in $k_{L}a$ values.

Figure 4.3 Volumetric mass transfer coefficient vs frequency at different superficial gas velocities. $A = 1.66$ mm, $\mu = 11$ cP

Figure 4.4 shows effect of viscosity on $k_{L}a$ in an oscillating bubble column. The volumetric mass transfer coefficient for different viscosity solutions is plotted against frequency at a constant superficial gas velocity of 0.5 cm/s. It can be seen from the graph that, at a constant viscosity, $k_{L}a$ increases with increasing frequency and ultimately reaches a plateau. This behavior is observed for all the viscosities. The shape of the curve for mass transfer coefficient vs frequency remains unchanged for viscous systems, but the absolute value of the mass transfer coefficient decreases as a function of increasing viscosity.

4.4 Theory

We wish to develop a theory to explain the mass transfer enhancements observed in an oscillating bubble column. We seek to explain the behavior of $k_{L}a$ as a function of operating
parameters such as frequency and amplitude of vibration, gas superficial velocity and physical properties, namely viscosity, surface tension and diffusivity. The volumetric mass transfer coefficient is a lumped parameter and depends on other fundamental hydrodynamic parameters such as the bubble size, bubble rise velocity etc. It is an important step to understand the effects of oscillations on these fundamental parameters. This will serve as a building block for a unified theory to predict mass transfer coefficient. If these effects are modeled individually, then the individual models can be combined to obtain a final expression to estimate $k_{La}$.

![Graph showing the effect of viscosity on volumetric mass transfer coefficient](image)

**Figure 4.4 Effect of viscosity on volumetric mass transfer coefficient.** $A = 1.66$ mm, $U_{og} = 0.5$ cm/s.

There are chiefly three effects associated with the oscillations in viscous bubble column. The first observable effect of imposed oscillations is the slowing down of the bubble rise velocity. Second, forced oscillations caused breakage and the formation of smaller bubbles. Third, viscosity affects the mass transfer coefficient owing to the dependence of diffusivity on viscosity, via the Stokes-Einstein effect. These three phenomena are discussed in detail in the following sections.
4.4.1 Bubble Rise Velocity: the Bjerknes Effect

The rise velocity of a single bubble is governed by the force balance controlling its movement. In the absence of vibrations, there are two main forces acting on a bubble in steady rise: the buoyancy force, responsible for the upward movement of the bubble, and the drag force, which opposes this upward movement. The application of forced oscillations gives rise to an additional force acting downward, generally known as the Bjerknes force. This force is also known as the kinetic buoyancy force. It arises owing to the interaction between the pulsing bubble volume and the acceleration of the oscillating liquid phase. Forces acting on a bubble under the influence of vibration can be visualized as shown in Figure 4.5.

![Figure 4.5 Force balance around a bubble under the application of vibrations.](diagram)

The vibrations produce an oscillating pressure field in the liquid phase as shown by the following equation:

\[ P = P_0 + \rho_L h g - \rho_L h \omega^2 A \sin \omega t \]  

(4.2)
where, \( P_o \) is the external pressure acting on the top liquid surface and \( h \) is the height of the liquid column above the bubble. The volume of a bubble varies according to the changing pressure and it will be assumed that bubbles pulsate in phase with the pressure oscillations (the experiments reported by Jameson and Davidson\(^{133} \) found this to be off the mark). For an isothermal bubble pulsation, following Boyle’s law, the bubble volume can be given as\(^{62} \):

\[
V = V_o + \Delta V_{\text{max}} \sin \omega t
\]  
(4.3)

where, \( V_o \) is mean bubble volume and \( \Delta V_{\text{max}} \) is the maximum volume change owing to pressure pulsation. Using Equation (4.2) and (4.3) and Boyle’s law, the maximum change in volume can be determined to be\(^{62} \):

\[
\frac{\Delta V_{\text{max}}}{V_o} = \frac{\rho_l h \omega^2 A}{P_o + \rho_l h g - \rho_l h \omega^2 A}
\]  
(4.4)

When \( P_o \) is atmospheric or larger, so that under most conditions \( P_o > (\rho_l h g - \rho_l h \omega^2 A) \), hence we shall take:

\[
\frac{\Delta V_{\text{max}}}{V_o} \approx \frac{\rho_l h \omega^2 A}{P_o}
\]  
(4.5)

In general, the buoyancy force is given as

\[
F_b = \text{Volume of bubble} \times \text{density difference} \times \text{acceleration}
\]  
(4.6)

\[
F_b = V(\rho_l - \rho_g)g
\]  
(4.7)

Neglecting gas density we can write,

\[
F_b = V \rho_l g
\]  
(4.8)

Apart from the acceleration due to the gravity, there is additional acceleration acting on the bubble under oscillating conditions. The displacement of the fluid phase owing to vertical sinusoidal oscillations is given as

\[
X = A \sin \omega t
\]  
(4.9)
The second derivative of the displacement $X$ will give the acceleration as

$$\ddot{X} = -A\omega^2 \sin \omega t \hspace{1cm} (4.10)$$

Now the total acceleration acting on a bubble is the combination of the gravitational acceleration and the acceleration arising from oscillations, which can be seen to be $g - A\omega^2 \sin \omega t$. Using this total acceleration and the instantaneous volume given by equation 4.3, Bjerknes proposed that the instantaneous force acting on a bubble due to kinetic buoyancy can be expressed using equation (4.6) as

$$F = (V_0 + \Delta V_{\text{max}} \sin \omega t) \rho_L (g - A\omega^2 \sin \omega t) \hspace{1cm} (4.11)$$

This instantaneous force can be time averaged over the period of oscillation to get the average force $<F>$

$$<F> = V_0 \rho_L g - \frac{\omega^2 A \Delta V_{\text{max}} \rho_L}{2} \hspace{1cm} (4.12)$$

Substituting the expression for $\Delta V_{\text{max}}$ of from Equation 4.5, gives

$$<F> = \rho_L V_0 g \left( 1 - \frac{1}{2} \frac{\rho_L h A^2 \omega^4}{g P_o} \right) = \rho_L V_0 g (1 - Bj(h)) \hspace{1cm} (4.13)$$

where, $Bj$ is the dimensionless Bjerknes number defined as:

$$Bj(h) = \frac{1}{2} \frac{\rho_L h A^2 \omega^4}{g P_o} \hspace{1cm} (4.14)$$

Note that the Bjerknes number is the ratio of the net downward force $\rho_L V_0 (\rho_L h A^2 \omega^4 / 2P_o)$ to the net upward force $\rho_L V_0 g$.

Equation (4.13) contains an additional negative term which reduces the original buoyancy force causing reduced rise velocity of a bubble. At appropriate vibration intensity, $<F>$ can be forced to zero and hence a bubble can be held stationary in the liquid. Since the Bjerknes number, $Bj$, is the ratio of the net downward force to the net upward force, hence the stagnation
point can be achieved when these forces become equal and $Bj$ takes a value of 1. We will call this frequency, $f_c$, and it is the value which corresponds to a flooding point, whereby bubbles no longer rise in a uniform fashion.

Buchanan et al.\textsuperscript{62} did a similar analysis without the assumption of $P_o > (\rho_L h g - \rho_L h \omega^2 A)$ made in equation (4.5). They gave the condition for the stagnation point as:

$$\omega^2 A = g + \sqrt{\frac{2gP_o}{\rho_L h} + 3g^2}$$  \hspace{1cm} (4.15)

Jameson and Davidson\textsuperscript{133} also found the condition for the stagnation point to be $Bj = 1$ based on a rather different approach. This theory is based on an inviscid flow model using potential flow theory. Their theory also predicted that the bubble vertical motion was in phase with liquid pulsing and that the bubble displacement was predicted to be three times the liquid displacement. But their experimental work revealed that there was a phase difference and also that the displacement difference between bubble and liquid was not three, but diminished as viscosity became larger.

We did visual experiments to measure the critical frequency ($f_c$) at the stagnation point for different viscosity solutions. Results are presented in Table 4.2. Experiments from Jameson and Davidson\textsuperscript{133} are also included for comparison purposes, where we note that the liquid height above the bubble in our work was nearly twice that of Jameson and Davidson. This of course means, for a constant value of $Bj$, that the value of critical frequency to cause stagnation or levitation will be nearly 20% larger for their experiments, as the results in Table 4.2 show. It can also be seen that at the stagnation point, experimentally observed values of $Bj$ are greater than 1 and these values decrease with higher viscosity solutions. These results are in agreement with Jameson and Davidson. The observed dependence of $f_c$ on viscosity can not be predicted from
the current theoretical condition of $Bj = 1$. In a companion paper, Jameson$^{63}$ developed a theory for the motion of a bubble in a vertically oscillating viscous liquid. His analysis indicated that the stagnation or levitation point is independent of viscosity of the fluid.

If the frequency is increased further beyond the critical frequency, then bubbles start moving downward. Buchanan et al.$^{62}$ showed that it is possible to entrain the bubbles from the top liquid surface by this method. These bubbles migrate cyclically from the top surface to the column base, where they gradually aggregate and then move back up the column as a loosely cohesive gas slug.

Table 4.2 Comparison of experimental $Bj$ values at stagnation point for different viscosity fluids.

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Liquid</th>
<th>Viscosity $\mu$ cP</th>
<th>Density $\rho_L$ g/cm$^3$</th>
<th>Height $h$ cm</th>
<th>Amplitude $A$ mm</th>
<th>Frequency $f_c$ Hz</th>
<th>$Bj$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work ($h=78$ cm)</td>
<td>Water</td>
<td>1</td>
<td>1</td>
<td>78</td>
<td>2.46</td>
<td>27.1</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>2 wt% CMC</td>
<td>11</td>
<td>1</td>
<td>78</td>
<td>2.46</td>
<td>24</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>3 wt% CMC</td>
<td>62</td>
<td>1</td>
<td>78</td>
<td>2.46</td>
<td>23.4</td>
<td>1.11</td>
</tr>
<tr>
<td>Jameson and Davidson$^{133}$</td>
<td>Water</td>
<td>1</td>
<td>1</td>
<td>41.8</td>
<td>1.69</td>
<td>32.9</td>
<td>2.82</td>
</tr>
<tr>
<td></td>
<td>Dilute glycerol</td>
<td>18.1</td>
<td>1.17</td>
<td>42.6</td>
<td>2.14</td>
<td>32.1</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>Concentrated glycerol</td>
<td>74.3</td>
<td>1.21</td>
<td>38.7</td>
<td>2.12</td>
<td>31.8</td>
<td>1.41</td>
</tr>
</tbody>
</table>

Taking a time-averaged force balance around a bubble, we find:

$$Bouyancy\ force = Drag\ force$$

(4.16)

$$\rho_L V_o g(1 - Bj(h)) = \frac{1}{2} \rho_L U^2 C_D (\pi R^2)$$

(4.17)

Here, the buoyancy force contains both the static buoyancy and the Bjerknes force (kinetic buoyancy). The symbol $U$ is used to denote rise velocity and $C_D$ is the drag coefficient. In this work, we shall use the drag expression after Kunii and Levenspiel$^7$

$$C_D = \frac{10}{\sqrt{Re}}$$

(4.18)

which is valid for $Re < 500$. Inserting this into Equation 4.17 yields
\[
\frac{U}{d} = \left(\frac{2g}{15\sqrt{\nu}}\right)^{2/3} \left[1 - Bj(h)\right]^{2/3}
\]

where \(d\) denotes mean bubble diameter. This expression shows as \(Bj(h) \to 1\), then \(U \to 0\), as required. The expression in equation (4.19) becomes more accurate as \(Bj\) gets closer to unity, or as \(U \sim 0\), since then \(Re < 500\).

### 4.4.2 Bubble Size

Vibrations cause enhanced bubble breakage rates, thus forming many smaller bubbles. This produces higher interfacial areas, which then leads to mass transfer improvements. Figure 4.6 shows a photograph of an operating bubble column. When the column is operated without the application of oscillations, there is a small number of bubbles present in the column. The bubble diameter is large and the bubble size distribution is very broad. Under the application of vibration, the bubble column produces a larger number of bubbles with smaller diameter. The bubble size distribution becomes more uniform. This improvement owing to bubble breakage can be attributed to the higher power input arising from the impressed pulsations of liquid.

![Figure 4.6 Photograph of bubble column showing improved bubble breakage due to oscillations.](image)

(a) No oscillations  
(b) With oscillations

**Figure 4.6** Photograph of bubble column showing improved bubble breakage due to oscillations. Photograph is taken at 350 mm above nozzle. \(Q_g = 0.6 \text{ cm/s}\): (a) No oscillations; (b) with oscillations, \(f = 16 \text{ Hz, } A = 1.36\text{mm}\)
In a classical paper, Hinze\textsuperscript{8} proposed a correlation based on the Kolmogorov principle of isotropic turbulence to predict bubble diameter as a function of power per unit mass and the cohesive properties of a fluid including surface tension and density:

\[
d = k \left( \frac{\sigma}{\rho_L} \right)^{3/5} \left( \frac{P}{P^2/m} \right)^{2/5}
\]

where \( P_m \) is the power input per unit mass. This portrays a balance between the forces of destruction and cohesion. The diameter was intended to be the maximum stable size, which is difficult to assess in metric terms. We shall replace this with an easily measured quantity, namely, the Sauter mean diameter. For an oscillating bubble column, the total power input is a combination of the power input from gas injection and the power input from applied oscillation, which has been taken to be the maximum, for breakage purposes, of the product of impressed acceleration and velocity, which is the nominal value for power per unit mass\textsuperscript{19}:

\[
P_m = \left( g U_{og} + \frac{1}{2} A^2 \omega^3 \right)
\]

The constant of proportionality \( k \) in equation (4.20) depends on the mechanism of bubble breakage. Originally Hinze proposed a value of 0.725 for \( k \) in turbulent systems. Based on new experiments, Taitel et al.\textsuperscript{127} later modified this constant to get a value of 1.14. For shear bubble breakage by liquid jets, Lewis and Davidson\textsuperscript{128} reported that \( k \) should be 1.67.

We measured Sauter mean bubble diameter in oscillating bubble column at various frequencies and amplitudes of vibrations. From Figure 4.7, it can be seen that when the Sauter mean bubble diameter \( d \) is plotted against power input it tracks very nicely the Hinze formula with a fitted constant of proportionality \( k = 1.7 \). This value is very close to the value of \( k = 1.67 \) calculated by Lewis and Davidson\textsuperscript{128} for shear bubble breakage. The Hinze formula predicts unrealistically higher bubble sizes at very small power input (<0.5 W/kg). At small power input,
bubble breakage is negligible and the average bubble diameter is governed by the formation or birth bubble size near the tip of the injector, as we illustrate in Figure 4.7. A detailed study of bubble size distributions in oscillating bubble column can be found in our previous work.132

![Graph showing Sauter mean bubble diameter vs power input](image)

**Figure 4.7 Sauter mean bubble diameter (measured at vertical position, s = 53.8 cm) vs power input showing Hinze type of bubble breakage.**

### 4.4.3 Viscosity Effects

It can be seen from Equation (4.19) that viscosity affects bubble rise velocity. But the most important effect of viscosity with respect to mass transfer is the dependence of molecular diffusivity on viscosity. The Stokes-Einstein equation provides a useful relationship between the diffusivity and the viscosity, so for constant density we have:

\[
\frac{D_1\nu_1}{T_1} = \frac{D_2\nu_2}{T_2}
\]

(4.22)

At constant temperature this gives:

\[
\frac{D_1}{D_2} = \frac{\nu_2}{\nu_1}
\]

(4.23)

Equation 4.23 shows that increasing viscosity leads to a decrease in molecular diffusivity.

According to penetration theory, the mass transfer coefficient depends on diffusivity as
Thus, an increase in viscosity causes a decrease in diffusivity which results in decreased mass transfer coefficient.

### 4.4.4 Voidage Prediction

It is important to get an expression for predicting voidage, since this expression will be needed for the interfacial area which is part of the volumetric mass transfer coefficient. The dependence of voidage on superficial gas velocity has been reported to take the form\(^{134}\)

\[
\varepsilon \propto U_{og}^n \tag{4.25}
\]

The values of \(n\) depend on the flow regime in the column. For bubbly flow, \(n\) is reported to range from 0.7 to 1.2.\(^{134-136}\) Based on equation (4.25), voidage can be calculated from the ratio of the gas superficial velocity to the bubble rise velocity.

\[
\varepsilon = \left(\frac{U_{og}}{U}\right)^n \tag{4.26}
\]

where, \(U_{og}\) is the gas superficial velocity and \(U\) is the rise velocity. Previously, we have taken \(n = 1.\)\(^{131}\) Inserting the rise velocity from Equation (4.19), the following equation can be obtained where voidage is a function of height in the column

\[
\varepsilon(h) = \frac{U_{og}^n}{d^n \left[ \frac{2g}{15\sqrt{D}} (1 - Bj(h)) \right]^{2n/3}} \tag{4.27}
\]

Using the Hinze formula for bubble diameter (Equation 4.20), we get

\[
\varepsilon(h) = \frac{U_{og}^n \rho_m^{2n/5}}{1.7^n \left( \frac{\sigma}{\rho_L} \right)^{3n/5} \left[ \frac{2g}{15\sqrt{D}} (1 - Bj(h)) \right]^{2n/3}} \tag{4.28}
\]

This equation can be used in the prediction of mass transfer coefficient.
4.4.5 Mass Transfer Coefficient Prediction

Penetration theory is used as the basis for predicting mass transfer coefficient. For a spherical bubble, one can write

\[ k_L a = \frac{4 D}{\pi t_c} \left( \frac{6}{d} \right) \]  

(4.29)

where \( d \) is the Sauter mean bubble diameter and the contact time for the mobile interface is taken to be:

\[ t_c = \frac{d}{U} \]  

(4.30)

The vibrating interface may affect transport at higher frequency, but we have ignored it here. Inserting \( d/U \) from equation (4.19) and voidage from equation (4.27) yields an expression for local transport coefficient:

\[ k_L a(h) = \frac{12}{\sqrt{\pi}} \frac{\sqrt{D}}{d^{n+1}} \left[ \frac{2g}{15\sqrt{d}} \right]^{(2n-1)/3} \left[ (1 - Bj(h)) \right] \]  

(4.31)

This expression for \( k_L a \) is a function of height \( h \). To find the averaged \( k_L a \), integrate it over the whole volume as:

\[ \langle k_L a \rangle = \frac{1}{H} \int_0^H (k_L a) dh \]  

(4.32)

which gives

\[ \langle k_L a \rangle = \frac{12}{\sqrt{\pi}} \left( \frac{15}{2} \right)^{(2n-1)/3} \frac{U_{og} \sqrt{D}}{d^{n+1}} G(n, Bj) \]  

(4.33)

where

\[ G(n, Bj) = \frac{3}{2} \left[ \frac{1 - (1 - Bj)^{2(2-n)/3}}{Bj(2-n)} \right] \]  

(4.34)
When \( d \) is inserted from equation (4.20), we find the average coefficient to be:

\[
\langle k_L a \rangle = 6.77 \left( \frac{15}{2} \right)^{(2n-1)/3} U_{og}^n \sqrt{\frac{D_o v_0}{\nu}} \frac{p_m^{2(n+1)/5}}{G(n, Bj)} \tag{4.35}
\]

Diffusivity can now be replaced with the Stokes-Einstein relationship (Equation 4.23) to get:

\[
\langle k_L a \rangle = 6.77 \left( \frac{15}{2} \right)^{(2n-1)/3} U_{og}^n \sqrt{\frac{D_o v_0}{\nu}} \frac{p_m^{2(n+1)/5}}{G(n, Bj)} \tag{4.36}
\]

Here, \( D_o \) and \( v_0 \) are the diffusivity and the kinematic viscosity of a reference fluid which will be taken as that of a pure water. Rearranging the terms in Equation (4.36) we get

\[
\langle k_L a \rangle = \frac{6.77 \left( \frac{15}{2} \right)^{(2n-1)/3}}{1.7^{n+1}} U_{og}^n \nu^{(n-2)/3} \sqrt{\frac{D_o v_0}{\nu}} \frac{p_m^{2(n+1)/5}}{G(n, Bj)} \tag{4.37}
\]

This is the final generalized expression for predicting volumetric mass transfer coefficient for a variety of circumstances.

It should be noted that the theoretical results for voidage and mass transfer coefficient, rest on the following explicit and implied assumptions:

1. gas concentration is dilute, \( \epsilon << 1 \),
2. fluid amplitude is uniform from top to bottom of the column,
3. coalescence rates are small,
4. bubble breakage occurs mainly by shear effects,
5. the expansion and contraction pulsing of bubbles has a small effect on mass transfer (small surface renewal effects)
6. the nominal power per unit mass can be taken as shown in equation (4.21).
4.4.6 Comparison of Theory and Experiment

The theoretical expression for the volumetric mass transfer coefficient contains a single unknown parameter which can be fitted, namely, the parameter $n$, which needs to be found. A log-log plot of experimental values of $k_La$ against superficial gas velocity, $U_{og}$, indicates that the $n$ should take a value of 1 (see Figure 4.8) for the present work.

![Figure 4.8 Illustrating the dependence of $k_La$ on $U_{og}$ showing $n = 1$.](image)

Equation (4.37) suggests that for $n = 1$, $k_La$ should be proportional to $P_m^{0.8}$. This is confirmed from Figure 4.9 where $k_La$ is plotted against $P_m$, keeping superficial gas velocity constant.

Equation (4.37) takes the following form for $n = 1$:

$$\langle k_La \rangle = 4.58 \frac{U_{og} \nu^{-1/3} \sqrt{D_0 \nu_0} P_m^{4/5}}{g^{1/3} \left( \frac{\sigma}{\rho_L} \right)^{6/5}} G(Bj)$$

(4.38)

where,

$$G(Bj) = \frac{3}{2} \left[ \frac{1-(1-Bj)^{2/3}}{Bj} \right]$$

(4.39)
From equation (4.38) it can be seen that $<k_La>$ should decrease with increasing viscosity. When $k_La$ data at different viscosities are plotted on log-log scale it suggests an exponent of $-1/3$ for viscosity (Figure 4.10), which is the value dictated by theory.

![Figure 4.9 Illustrating $<k_La>$ dependence on $P_m^{0.8}$.](image)

![Figure 4.10 Illustrating $<k_La>$ dependence on $\nu^{-1/3}$.](image)
Earlier work by Harbaum and Houghton\textsuperscript{48} showed a linear dependence of $k_L a$ on $P_m$, which is very similar to the exponent of 0.8 found in this work. Baird and Garstang\textsuperscript{4} and Ni and Gao\textsuperscript{5} gave a dependence on $P_m$ to the power of 0.42, for rather different methods of imposing pulsations in the presence of baffles. They also showed that $\langle k_L a \rangle$ depends on $U_{og}$ to the power of 0.5 and 0.37, respectively. Krishna and Ellenberger\textsuperscript{53} observed linear dependence of $\langle k_L a \rangle$ on $U_{og}$, which matches with this work. In our earlier work\textsuperscript{123}, we reported that $\langle k_L a \rangle \propto P_m^{0.4}$ based on $\langle k_L a \rangle$ measurements at a single superficial gas velocity of 0.5 cm/s. The earlier experiments did not include effects arising from the slowing down of bubbles owing to Bjerknes kinetic buoyancy. This, and the single velocity used, distorted the curve fit, which was based on quite scattered data.

There is no earlier literature available illustrating $k_L a$ dependence on viscosity (CMC solution) in a pulsed-flow bubble column. Some literature is available on dependence of mass transfer coefficient on the viscosity of fluids in regular, unforced bubble column reactors. Buchholz et al.\textsuperscript{137} have reported $k_L a$ data in a bubble column for various viscosities. He studied oxygen mass transfer in a viscous bubble column with CMC solutions (1-1.7 wt%). Henzler\textsuperscript{138} correlated most of the data of Buchholz et al. by the equation

$$\frac{k_L a \left( \frac{\nu}{g} \right)^{1/3}}{U_{og}^{1/2} S_e^{1/3}} = 0.06 \left[ \frac{U_{og}}{(g \nu)^{1/3}} \right]^{-0.9} \tag{4.40}$$

Deckwer et al.\textsuperscript{139} analyzed this equation, assuming oxygen diffusivity in CMC solutions does not change (which is at variance with the present work) and deduced

$$k_L a \propto U_{og}^{0.1} \nu^{-0.87} \tag{4.41}$$

According to Deckwer et al., data correlated by Henzler\textsuperscript{138} for a staged bubble column shows

$$k_L a \propto U_{og}^{0.6} \nu^{-1.03} \tag{4.42}$$

Deckwer et al. also analyzed a correlation proposed by Nakanoh and Yoshida\textsuperscript{140} to show
\[ k_La \propto U_{og} \nu^{-0.28} \]  

(4.43)

It can be seen, there is a wide variation in the bubble column literature regarding the dependence of \( k_La \) on viscosity. The dependence shown in Equation (4.43) is very close to the observation in the present work. Equations (4.41) and (4.42) strongly over-predict the dependence on viscosity.

After establishing the exponent dependence of \( k_La \) on the individual operating parameters (\( U_{og} \), \( P_m \) and \( \nu \)), it will be important to compare the experimental \( k_La \) data with the overall prediction based on theory. To facilitate the plotting of all the available data at the different gas superficial velocities and at different viscosities, Equation (4.38) was rearranged as follows

\[
\frac{\langle k_La \rangle \nu^{1/3} \nu_{fg}^{1/3}}{U_{og}} = 4.58 \sqrt{\frac{D_0}{u_0} P_m^{4/5}} \left( \frac{\sigma}{\rho_L} \right)^{6/5} G(Bj) \]  

(4.44)

Note that the right hand side is a function only of vibration parameters, frequency and amplitude and constant physical properties of the fluid (there is a small effect of gas velocity within \( P_m \) as seen in equation (4.21), but generally this is swamped by the pulsing contribution in the power term).

Figure 4.11 shows all the available \( k_La \) data plotted against the theoretical prediction for both the applied amplitudes, 1.66 and 2.46 mm. It can be seen that the theoretical predictions are in quite good agreement with the experimental data. It should be noted that the constant of multiplication, 4.58, is obtained from first principles and no fitting exercise was used. Considering that no parameter fitting was done and the data was collected for a wide range of operating conditions including various superficial gas velocities and a range of viscosities, it can be concluded that the proposed theory does a reasonable job predicting behavior under pulsed-flow conditions. The theory may be suitable for design purposes, since estimates from theory are seen to be conservative.
Figure 4.11 also illustrates the “flooding line” which is the horizontal line formed at the intersection of critical frequency, \( f_c \) (when \( Bj = 1 \)) with the theoretical curve. This line represents the upper asymptote for \( \langle k_La \rangle \) when bubbles are stopped by Bjerknes forces at the nozzle tip. When compared to experimental data, theory only approximates pinpointing the flood condition. As we have seen in Table 4.2, the value of the dimensionless Bjerknes number, \( Bj \), at the stagnation point is always greater than unity for our work and also that of Jameson and Davidson. It is also clear from Table 4.2 that as viscosity increases, the stagnation frequency gives a value of \( Bj \) which gradually approaches unity.

\[
A = 1.66 \text{ mm}
\]

![Diagram showing comparison between theoretical prediction and experimental data for mass transfer coefficient. Solid line shows theoretically predicted curve according to equation (4.44). (a) \( A = 1.66 \text{ mm} \), (b) \( A = 2.46 \text{ mm} \).](image)

(Figure cont.)
4.5 Comments and Conclusions

Mass transfer measurements were performed on a pulsed-flow bubble column with solutions of different viscosities. Increased viscosity resulted in decreasing the mass transfer coefficient, but pulsations are shown to enhance transfer relative to the unforced case for higher viscosity. An improvement in the mass transfer coefficient was observed with the application of oscillations for all cases considered. A simple, one-dimensional theory was developed to explain the dependence of the mass transfer coefficient on the operating parameters such as the frequency and amplitude of vibration, the gas superficial velocity and the viscosity of the fluid. The theory takes into account three effects: the reduction in the rise velocity owing to the Bjerknes force, the generation of smaller bubbles arising from enhanced bubble breakage (the Hinze effect) and, finally, the decrease in the molecular diffusivity owing to the increased viscosity, according to the Stokes-Einstein relationship. The theoretical predictions compared very well with a large number of experimental data.
We are currently considering the effects on mass transfer owing to bubble volume pulsation, which is not accounted for in the present effort. At the frequencies used here, we suspect such effects to be small.

### 4.6 Nomenclature

- \( a \) interfacial area per unit volume, cm\(^2\)/cm\(^3\)
- \( A \) amplitude of imposed liquid pulsation, cm
- \( Bj(h) \) local Bjerknes number, 
  \[
  \frac{1}{2} \frac{(\rho_L h) A^2 \omega^4}{g P_o}, \text{ dimensionless}
  \]
- \( Bj \) Bjerknes number at position \( H \), 
  \[
  \frac{1}{2} \frac{(\rho_L H) A^2 \omega^4}{g P_o}, \text{ dimensionless}
  \]
- \( C \) dissolved oxygen concentration, gmol/cm\(^3\)
- \( C^* \) equilibrium value of dissolved oxygen, gmol/cm\(^3\)
- \( C_D \) drag coefficient, dimensionless
- \( d \) Sauter mean bubble diameter, cm
- \( D \) molecular diffusion coefficient, cm\(^2\)/s
- \( F_b \) buoyancy force, dyne
- \( <F> \) time average force, dyne
- \( f \) frequency, Hz
- \( f_c \) critical frequency when \( Bj = 1 \), Hz
- \( g \) acceleration from gravity, cm/s\(^2\)
- \( G(Bj) \) 
  \[
  \frac{3}{2} \left[ 1 - \left(1 - \frac{Bj}{Bj^2} \right)^{2/3} \right], \text{ dimensionless}
  \]
- \( h \) bubble distance from top interface, cm
- \( H \) distance from top interface to gas injector, cm
- \( k \) pre-multiplier from equation 4.20, dimensionless
- \( k_{L,a} \) volumetric mass transfer coefficient, 1/s
- \( <k_{L,a}> \) average volumetric mass transfer coefficient under pulsing, 1/s
- \( n \) exponent in equation 4.25, dimensionless
\( P \) pressure, dyne/cm\(^2\)
\( P_o \) pressure at top interface, dyne/cm\(^2\)
\( P_m \) power input per unit mass, W/kg or cm\(^2\)/s\(^3\)
\( R \) bubble radius, cm
\( Re \) bubble Reynolds number, \( \frac{dU}{D} \), dimensionless
\( s \) distance from injector, cm
\( Sc \) Schmidt number, \( \frac{\mu}{\rho U D} \), dimensionless
\( t \) time, s
\( t_c \) contact time for mass transfer, d/U, s
\( T \) temperature, K
\( U_{og} \) superficial gas velocity, cm/s
\( U \) time average bubble rise velocity, cm/s
\( V \) bubble volume, cm\(^3\)
\( V_o \) mean bubble volume, cm\(^3\)
\( \Delta V_{max} \) maximum difference in bubble volume due to pulsation, cm\(^3\)
\( X \) displacement, cm

**Greek letters**
\( \varepsilon(h) \) local voidage in a plane at h
\( \mu \) dynamic liquid viscosity, cP
\( \nu \) kinematic liquid viscosity, cm\(^2\)/s
\( \rho_L \) liquid density, g/cm\(^3\)
\( \rho_G \) gas density, g/cm\(^3\)
\( \sigma \) surface tension, dyne/cm
\( \omega \) frequency, radians/s
Chapter 5  Bubble Size Distribution for A Bubble Column Reactor Undergoing Forced Oscillations

5.1  Introduction

The bubble column reactor is a widely used gas-liquid contactor because of its simple design and low maintenance cost. It is used in variety of applications including physical absorption of gases, as well as to carry out gas-liquid reactions such as hydrogenation, oxidation etc.\textsuperscript{141} It is also used for fermentation processes. Performance of the bubble column reactor is limited by its low mass transfer coefficient. The mass transfer coefficient can be enhanced at the expense of higher energy input which is generally achieved by vigorous stirring. As an alternative, forced oscillations can also be used to increase the mass transfer coefficient\textsuperscript{114,123}. In pulsed-flow bubble columns, vertical oscillations are imparted to the fluid phase to improve the column performance.

Harbaum and Houghton\textsuperscript{47} reported the effect of sonic vibrations on the rate of absorption of carbon dioxide in bubble columns back in 1960. Since then many investigators have studied bubble column performance under pulsating conditions\textsuperscript{4,48,49,53,56}. The main focus of these investigations was the study of mass transfer and gas hold up enhancements. The mass transfer coefficient is a lumped parameter and it depends on other fundamental hydrodynamic parameters such as bubble size distribution, rise velocity etc. Hence, it is important to understand the effect of vibrations on the bubble size distribution.

Fawkner et al. (1990)\textsuperscript{60} studied bubble formation at the orifice in pulsed-flow liquids. They observed that the bubble size at the orifice goes through multiple minima and maxima as frequency was varied from 0-60 Hz. Krishna et al.\textsuperscript{50} showed that the number of bubbles can be greatly enhanced in the frequency range 100-200 Hz. This increase in number of bubbles can cause area increase up to 140 %. Krishna and Ellenberger\textsuperscript{52} attributed mass transfer
enhancements entirely to the reduction in the bubble size. Contrary to the observations of Fawkner et al.⁶⁰, Krishna and Ellenberger⁵⁷ observed that bubble diameter decreases as frequency is increased and it levels off at around 100Hz. CFD simulation of the bubble formation process at the orifice⁵⁵ showed that vibrations help in early detachment of bubbles from the orifice and thus produce smaller bubbles. Our group⁴,⁷ also found high rates of breakage within the gas injection tube at low gas rates, owing to an observed suck-back of liquid into the tube during downstroke. Many photographs of this phenomenon were published².

In the past, attempts were made to measure the average bubble size in the oscillating bubble column. In reality, there exists an entire range of bubbles sizes and this is often described statistically as a bubble size distribution. The objective of the present work is to study the effect of forced vibrations on the bubble size distribution. The Sauter mean bubble diameter is calculated from the BSD data and has been correlated with power per unit mass¹³¹. Population balance modeling (PBM) is used to simulate the bubble breakage and the coalescence processes to obtain the evolution of BSD.

5.2 Experimental Methods

The equipment used to carry out the present experiments is shown in Figure 5.1 and is the same as used in our previous work²,³,¹³¹. It consists of a Plexiglas® column of 8.9 cm in diameter and 106 cm in height. The base of the column is sealed with a natural gum rubber sheet. The natural gum rubber sheet is clamped between two stainless steel disks. The disks are 8.26 cm in diameter which essentially produces a solid piston at the column base. These disks are directly coupled to an eccentric cam which is driven by a five horsepower variable speed motor. The motor speed is controlled by an Omron Sysdrive 3G 3JV compact inverter controller. The eccentric cam produces a sinusoidal oscillation to the disks at the base of the column. The system is configured for operation from 0-30 Hz and amplitudes from 0 to 2.54 mm.
The bubble column reactor was filled with distilled water to a level 78 cm above the injector. Compressed air was injected into the BCR from a single capillary stainless steel injector of 0.75 mm diameter. The gas flow rate was controlled by a pressure regulator and a needle valve. Gas flow rate was measured by a soap bubble meter.

The BCR was operated as batch system with respect to liquid phase (water) and continuous up-flow for the gas phase (air). Experiments were performed for a range of gas superficial velocities, namely, 0.017-0.17 cm/s. Frequency and amplitude were varied from 0-20 Hz and 0.46-2.46 mm respectively.

BSD was measured by visual photographic technique. Bubble column operation was recorded at different vertical positions in the column using a high-speed camera (Photron Fastcam PCI-R2) assembly. A rectangular observation box, size 25 cm with height 86 cm, was built around the column to minimize the distortion due to curvature effects. The observation box was filled with tap water.
Pictures were taken at 250 frames per second. The size of the observation window was approximately 6.5 cm x 6.15 cm. From a pool of 500 images, five were randomly selected and were analyzed to get the bubble size distribution. It was confirmed that increasing the sample size does not affect the bubble size distribution. Sample images were analyzed using the image analysis software, ImageJ. Raw images obtained from the camera were processed to obtain the final image ready for analysis, as shown in Figure 5.2. The projected area of each bubble was measured. The bubble diameter was calculated from the projected area assuming perfectly spherical geometry. The entire bubble volume range was divided into classes and the total number of bubbles in each volume class was calculated to get the BSD.

![Figure 5.2 Illustration of image processing during bubble size distribution measurements. a) raw image b) processed image using ImageJ software.](image_url)

5.3 Experimental Results and Discussion

5.3.1 Effect of Height

The bubble size distribution was measured at four different heights along the axis of the column. Previous work indicated the mass transfer coefficient plateaued near 17.5 Hz. Hence, initially the amplitude and the frequency of oscillations were held constant at 1.66 mm and 17.5 Hz, respectively. Two superficial gas velocities of 0.017 and 0.17 cm/s were investigated.
Figure 5.3 shows the plot of Sauter mean diameter as a function of height at low gas flow rate \( U_{ag} = 0.017 \text{ cm/s} \). Sauter mean diameter, \( d_{32} \), is defined as the ratio of the third moment to the second moment calculated from the bubble size distribution. For the case of low gas flow rate it was observed that the bubble size distribution does not change as the bubbles move up the column. This means that no bubble breakage occurs inside the column proper. The bubble retains its identity when it was formed at the injector. Thus at low flow rates, the bubble size reduction can entirely be attributed to the bubble breakage inside the injector, the suck-back breakage.

Knopf et al\(^{114}\) have already reported that at low superficial gas velocities (up to 0.083 cm/s), reduction in the bubble size on the application of oscillations is mainly due to the bubble breakage at the injector. Gas and Liquid phases inside the injector undergo expulsion and suck-back cycles causing the bubbles to break inside the injector. Similar observations were given by Krishna and Ellenberger\(^{52}\). They reported that the decrease in the bubble size occurs at the injector and no further decrease was observed further in the column proper.

For a higher superficial gas velocity (0.17 cm/s), momentum of the gas flowing through the injector is large enough to overcome the expulsion – suck back forces. A continuous jet of gas comes out from the injector hole, which then breaks-off from the nozzle tip to form distinct bubbles. A plot of Sauter mean diameter vs height (Figure 5.4) shows that the bubble size decreases with increasing height. It starts with a larger bubble size near the injector and then it decreases exponentially reaching an equilibrium size.

There are two competing processes which govern bubble size in any dispersed system. Bubbles undergo breakage because of the turbulent or shear forces acting on a bubble. At the same time, bubbles collide with each other and coalesce to form larger bubbles. The bubble size distribution reaches an equilibrium value when the rates of these two processes, breakage and coalescence, become equal.
Figure 5.3 Effect of height on Sauter mean diameter at low gas flow rate; \( A = 1.66 \text{ mm}, U_{og} = 0.017 \text{ cm/s}, f = 17.5 \text{ Hz} \)

Figure 5.4 Effect of height on Sauter mean diameter at high gas flow rate; \( A = 1.66 \text{ mm}, U_{og} = 0.17 \text{ cm/s}, f = 17.5 \text{ Hz} \).
The evolution of the bubble size distribution with respect to height is shown in Figure 5.5. Data is plotted as volume fraction/\( \Delta d \) versus diameter so that the area under the curve is always unity. A broad distribution of bubble sizes was observed near the sparger. As the bubbles move up the column, they undergo breakage, forming bubbles of more uniform sizes. Thus, BSD curve becomes more uniform and Gaussian shaped with a narrow variance. BSD curves at the height of 25.0 cm, 37.7 cm, 53.8 cm and 67.2 cm were similar indicating that equilibrium size is reached. A small variance indicates that a homogeneous gas-liquid dispersion was obtained due to the vibrations. Ellenberger and Krishna\textsuperscript{55} reported that the vibrations help in maintaining a homogeneous flow regime in the bubble column. Similar effects were reported by Waghmare et al.\textsuperscript{131}

![Figure 5.5 Effect of Height on Bubble size distribution; \( A = 1.66 \text{ mm} \), \( f=17.5 \text{ Hz} \), \( U_{og} = 0.17 \text{ cm/s} \).](image)

### 5.3.2 Effect of Gas Flow Rate

The bubble size distribution was measured at five different gas flow rates, namely, 1, 2, 4, 8 and 10 ml/s. This corresponds to gas superficial velocities of 0.017, 0.033, 0.067, 0.133 and 0.167 cm/s. Frequency and amplitude were held constant at 17.5 Hz and 1.66mm, respectively.
Two different heights above the injector, 10.6 cm and 53.8 cm were considered. Size distribution observed at height 10.6 cm is the indicator of formation bubble size and BSD at 53.8 cm is expected to illustrate the equilibrium bubble size distribution.

In the region near the injector (height = 10.6 cm), the effect of gas flow rate on the Sauter mean diameter dominates. As the gas flow rate is increased, the bubble diameter increases. This shows that near the injector, the bubble diameter depends on gas hole velocity through the injector. From the log-log plot of the bubble diameter vs. the gas flow rate (Figure 5.6) it was found that

\[ d_{32} \propto Q_g^{2/5} \]  

(5.1)

where, \( Q_g \) is the volumetric flow rate.

![Figure 5.6 Effect of gas flow rate on Sauter mean diameter; \( A =1.66\text{mm}, f =17.5\text{Hz}, H =10.6\text{cm} \)](image)

Wallis\textsuperscript{113} gave the following expression for the volume of a bubble at detachment in an inviscid fluid:

\[ v = 1.138 \frac{Q_g^{6/5}}{g^{3/5}} \]  

(5.2)
This equation suggests that for spherical bubbles, \( d \propto Q_g^{2/5} \), which is matching with our experimental observations. Figure 5.7 shows a plot of bubble volume formed near the injector as a function of gas flow rate. The points represent experimentally observed values and the solid line shows theoretical predictions based on the above equation but with different fitted multiplier which takes a value of 0.65 instead of 1.138.

![Figure 5.7 Effect of gas flow rate on the formation bubble volume near the injector: experimental observation versus theoretical prediction.](image)

The bubble size distribution was also measured at a height of 53.8 cm. As seen from Figure 5.8, the Sauter mean diameter initially increases with increasing gas flow rate. For higher gas flow rates it reaches a plateau and remains constant. This behavior is different than at the 10.6 cm height, where bubble diameter increased monotonically as a function of gas flow rate. This again supports the claim that at low flow rates, all the breakage occurs inside the injector and bubble diameter does not change in the column proper. Thus, for low gas flow rates, bubble diameter is dependent on gas flow rates and hence it increases with increasing gas flow rate. But
at high flow rate, the bubble breakage occurs mainly within the column and, hence, bubble diameter is independent of the gas flow rate.

![Graph showing the effect of gas flow rate on Sauter mean diameter.]

**Figure 5.8 Effect of gas flow rate on Sauter mean diameter; \(A = 1.66\text{mm}, f = 17.5\text{Hz}, H = 53.8\text{cm}.\)**

### 5.3.3 Effect of Frequency

The effect of frequency on the bubble size distribution was studied at 4 different frequencies (10, 15, 17.5, 20 Hz) as shown in Figure 5.9. A constant liquid pulsing amplitude of 1.66 mm and a constant gas flow rate of 10 ml/s were maintained. Pictures were taken at 53.8 cm height from the injector. At low frequencies, the bubble size distribution is much broader and the Sauter mean diameter is large. As the frequency is increased, bubble breakage increases and the distribution becomes bell shaped and its variance decreases. With increasing frequency, the peak of the bell shape curve shifts leftward indicating smaller mean bubble diameters.

### 5.3.4 Effect of Amplitude

The frequency of oscillation was held constant at 17.5 Hz and the amplitude was varied from 0.46 mm to 2.46 mm using values of 0.46, 0.84, 1.23, 1.66 and 2.46 mm. The gas flow rate was maintained at 10 ml/s and pictures were taken at a height of 53.8 cm.
Figure 5.9 Effect of frequency on BSD; $U_{og} = 0.17$ cm/s, $A = 1.66$ mm, $H = 53.8$ cm

Figure 5.10 Effect of amplitude on Sauter mean diameter; $U_{og} = 0.17$ cm/s, $f = 17.5$ Hz, $H = 53.8$ cm

At low amplitudes of 0.46 mm and 0.84 mm, the bubble size distribution remains almost independent of the amplitude as it can be seen from Figure 5.10. It suggests that these amplitudes were too small to cause any bubble breakage because the power is too low and so bubble diameter is governed by formation size. It will be shown later, that a critical power input is
needed before bubbles start breaking in the column. A further increase in the amplitude caused a rapid reduction in bubble sizes. Figure 5.11 shows BSD curves at different amplitudes. Increase in the amplitude clearly gives a narrow distribution.

![BSD Curves at Different Amplitudes](image)

**Figure 5.11** Effect of amplitude on bubble size distribution; $U_{og} = 0.17$ cm/s, $f = 17.5$ Hz, $H = 53.8$ cm

5.3.5 Effect of Power Input

The effect of the frequency and amplitude on the BSD are coupled as the power input. Power input is the more fundamental parameter which affects the BSD. The power input is a strong function of both the amplitude and the frequency and it also depends on the superficial gas velocity as given by the following expression\textsuperscript{123,131}:

$$P_m = \left( g U_{og} + \frac{1}{2} A^2 \omega^3 \right)$$ \hspace{1cm} (5.3)

Hinze\textsuperscript{8} proposed a correlation to predict bubble size as a function of power input per unit mass. According to Hinze, the maximum stable bubble size under the turbulent flow conditions is given as:
\[
d = k \left( \frac{\sigma}{\rho_L} \right)^{3/5} \frac{p_l}{P_m^{2/5}}
\]

(5.4)

where \( k \) is a premultiplier given as 0.725 by Hinze. When our experimental data for Sauter mean diameter was fitted against the above equation, we earlier\textsuperscript{131} found that best fitted value of \( k \) was 1.70. This value is remarkably close to the value of 1.67 reported by Lewis and Davidson\textsuperscript{128} for bubble breakage by shear flow.

Figure 5.12 shows the fit for the Hinze multiplier \( k \) in Equation 5.4 using the Sauter mean diameter. The flat line through the diameter 0.6 cm indicates the bubble formation size at the nozzle tip. The fit of the Hinze breakage model was quite satisfactory, using the Sauter mean diameter data. It is seen in Figure 5.12 that when \( Pm < 0.8 \text{ m}^2/\text{s}^3 \), the birth size of bubbles prevail, while at higher values of power, breakage from turbulence and shear forces\textsuperscript{131} determine bubble size using the Hinze formula with \( k = 1.70 \).

![Figure 5.12](image)

**Figure 5.12** Sauter mean bubble diameter (measured at vertical position, \( H = 53.8 \text{ cm} \)) versus power input showing Hinze type of bubble breakage.
5.4 Population Balance Modeling

5.4.1 Population Balance Equations

It is possible to theoretically model the evolution of bubble size distribution using population balance modeling (PBM). The gas phase can be discretized into number of size classes, each class $i$ representing a bubble volume of $v_i$. In the present work, classes were assigned such that the volume of class $i+1$ is twice the volume of the previous class $i$, ($v_{i+1} = 2 v_i$).

The population balance equation for a class $i$ can be expressed as

$$\frac{\partial}{\partial t} n_i + \nabla \cdot (u_i n_i) = S_i \tag{5.5}$$

Here, $n_i$ is the number density of class $i$. The number density for class $i$ can be defined as

$$n_i = \frac{\text{number of bubbles in the size class } i}{\text{Volume of fluid dispersion}} \tag{5.6}$$

Also in equation 5.5, $u_i$ is the rise velocity of bubble of diameter $d_i$. For an oscillating system $u_i$ is not only a function of the bubble diameter and the physical properties of the fluid but it also depends on the vibration frequency and the amplitude due to the “kinetic buoyancy” Bjerknes force. In the present work, rise velocities of bubbles under the oscillating conditions were experimentally measured and a modified Kunii and Levenspiel drag model was used to fit the data. As shown by Waghmare et al., the bubble rise velocity can be calculated from a force balance around a bubble as follows

$$\rho V_o g (1 - Bj(h)) = \frac{1}{2} \rho_L u^2 C_o (\pi R^2) \tag{5.7}$$

where, the left hand side of equation 5.7 shows buoyancy force minus the Bjerknes force and right hand side is the drag force. Here $Bj(h)$ is the local Bjerknes number given as

$$Bj(h) = \frac{1}{2} \frac{(\rho_L h) A^2 \omega^4}{g \rho_o} \tag{5.8}$$
and $h$ is the height of the liquid column above the point of interest. When the dimensionless number $Bj(h)$ goes to unity, bubble rise velocity tends to zero, that is, the bubble oscillates at a point. For example, at $h=78$ cm, $Bj(h)$ becomes unity when $f = 27.7$ Hz for the amplitude of 1.66 mm$^{131}$. In the above equation, $C_D$ represents the drag coefficient. A modified form of the drag coefficient proposed by Kunii and Levenspiel$^7$ is used here.

\begin{equation}
C_D = K_D + \frac{10}{\sqrt{\text{Re}}} \tag{5.9}
\end{equation}

where, $K_D$ is an adjustable parameter which was tuned to fit our experimental data. It was found that the value of $K_D = 0.85$ gives a good fit. Using equation 5.9 in equation 5.8 gives a polynomial in $u$ (equation 5.10) which was solved numerically using MATLAB. This polynomial has only one real root.

\begin{equation}
K_D \sqrt{\frac{d \rho_l}{\mu}} u^2 + 10u^{3/2} - \frac{4 \rho_l^{1/2} g (1-M(h))}{\sqrt{\mu}} = 0 \tag{5.10}
\end{equation}

Figure 5.13 shows a comparison between the experimentally observed bubble rise velocities and the model predictions using equation 5.10. It can be seen that the model predictions are in reasonable agreement with the experimental data.

In equation 5.5, $S_i$ is the source term for bubble class $i$ and it depends on breakage and coalescence processes as follows:

\begin{equation}
S_i = [B_B - D_B + B_C - D_C]_i \tag{5.11}
\end{equation}

Where $B_B$ denotes the birth of a particular size bubble due to bubble breakage, $D_B$ is the death due to breakage, $B_C$ is the birth due to coalescence and $D_C$ is the death due to coalescence. Hagesaether$^{142}$ et al. gave the following expression for these terms. Here, it is assumed that bubbles from the smallest class ($i = 1$) do not break and bubbles from the largest class ($i = N$) do not coalesce.
Figure 5.13 Comparison of experimentally observed bubble rise velocity and predictions using modified Kunii and Levenspiel\textsuperscript{7} drag law.

\[
B_g(i) = \sum_{k=i+1}^{N} \Omega_g(k,i) + \sum_{k=1, k \neq N}^{i} y_{b_i,k} \Omega_g(i+1,k) + \sum_{k=1, k \neq 1}^{i-1} (1-y_{b_i,k}) \Omega_g(i,k) \text{ for } i = 1, \ldots, N \tag{5.12}
\]

where, \( y_{b_i,k} = 2^{1+k-i} \) for \( k < i \) and

\[
D_g(i) = \sum_{k=1}^{i-1} \Omega_g(i,k), \ i = 2, \ldots, N \tag{5.13}
\]

\[
B_c(i) = \sum_{j=1, j \neq N}^{i-1} y_{c_i,j} \Omega_c(i,j) + \sum_{j=1}^{i-1} (1-y_{c_i,j}) \Omega_c(i-1,j), \ i = 2, \ldots, N \tag{5.14}
\]

where, \( y_{c_i,j} = 1 - 2^{j-i} \) for \( i \geq j \) and

\[
D_c(i) = \sum_{j=1}^{N-1} \Omega_c(i,j) + \Omega_c(i,i), \ i = 1, \ldots, N-1 \tag{5.15}
\]

The symbol \( \Omega_g(i,k) \) is the rate of breakage of bubble of size \( d_i \) to form a bubble of size \( d_k \) and \( \Omega_c(i,j) \) is the rate of coalescence of bubbles of size \( d_i \) and \( d_j \). The first term on the right hand side of Equation 5.12 indicates the rate of formation of bubble of size \( d_i \) due to the breakage of any larger bubble of size \( d_k \) such that \( k > i \). Hence, this term is summed over \( k = i+1 \) to \( k = N \).
The next two terms arise due to the redistribution of bubbles. When a bubble in size class \( i \) breaks, its volume is distributed into two daughter bubbles such that:

\[
v_i = v_i + v_m \tag{5.16}
\]

For example, consider fictitious size classes 1,2,3,4 etc. with corresponding volumes 1,2,4,8 etc. and that a bubble in size class \( v_i = 8 \) breaks into \( v_j = 7 \) and \( v_m = 1 \). The volume \( v_m \) can be directly assigned to size class 1, but \( v_j \) must be redistributed to size classes 8 and 4 to conserve the volume. Here 14% of the volume of the bubble is assigned to size class 4 and 86% to size class 8. In general, \( v_j \) is redistributed among \( v_{i-1} \) and \( v_i \) according to the volume balance constraint as follows:

\[
v_i = y b_{i,k} v_{i-1} + (1 - y b_{i,k}) v_j \tag{5.17}
\]

where, \( y b_{i,k} = 2^{1-k+i} \) for \( k<i \).

Similarly for the coalescence process when bubble of volume \( v_i \) (larger of the two bubbles) and \( v_j \) coalesce they form a bubble of volume \( v_k \) such that \( v_i < v_k < v_{i+1} \). Volume \( v_k \) is redistributed between \( v_i \) and \( v_{i+1} \) as follows:

\[
v_k = v_i + v_j = y c_{i,j} v_i + (1 - y c_{i,j}) v_{i+1} \tag{5.18}
\]

Here, we take \( y c_{i,j} = 1 - 2^{-j+i} \) for \( i \geq j \). Further details regarding the derivation of \( y b_{i,k} \) and \( y c_{i,j} \) can be found in the paper of Hagesaether et al.\textsuperscript{142}.

### 5.4.2 Breakage Model

In order to solve equations 5.12 and 5.13, an expression for the breakage rate \( \Omega_B(i,k) \) is needed. Two breakup models were considered in this study. A model proposed by Luo and Svendsen\textsuperscript{143} (LS model) and a second model proposed by Martinez-Bazan et al.\textsuperscript{144,145} (MB model) were considered. These two models were chosen because the basic physical approach of these two models is significantly different. The LS model is based on an idea that the bubble
breakage occurs due to the bombardment of eddies, having different sizes and different energies, with the bubble. This collision may or may not result in bubble breakage depending on the size and the energy of the colliding eddy. The total breakage rate is the product of the collision frequency and the collision efficiency. The MB model, on the other hand, assumes that the breakage rate is proportional to the difference between the non-inertial forces which produce bubble deformation and the surface tension forces responsible for confinement. These two models give rise to different breakage rates and, more notably, radically different daughter size distributions. The MB model closely follows the logic of the formula derived by Hinze\textsuperscript{17}, which shows the maximum stable bubble size is a balance between surface tension and turbulence forces.

5.4.2.1 Luo-Svendsen Model (LS Model)

Bubble breakage rate from the Luo and Svendsen\textsuperscript{143} model can be expressed as:

$$\Omega_p(i,k) = 0.923(1-\alpha)n_i\left(\frac{\varepsilon}{d_i^2}\right)^{1/3}\int_{\xi_{\text{min}}}^{1} \frac{(1+\xi)^2}{\xi^{11/3}} \exp\left(-\frac{5.87c_f\sigma}{\rho_L \varepsilon^{2/3} d_i^{5/3} \xi^{11/3}}\right) d\xi$$

(5.19)

The term $\xi$ is the dimensionless eddy size given as the ratio of eddy size to bubble size, $d_i$. In equation 5.19 integration is performed from $\xi = \xi_{\text{min}}$ to $\xi = 1$. For the upper limit, it is assumed that breakage of a bubble of diameter $d$ can only be accomplished by an eddy of size $d$ or smaller. The lower limit $\xi_{\text{min}}$ is a function of energy dissipation rate. The term $\varepsilon$ is the energy dissipation rate which is assumed to be the same as the power input per unit mass ($P_m$). Finally, $c_f$ denotes the increase coefficient of surface area given as:

$$c_f = \left(\frac{v_k}{v_i}\right)^{2/3} + \left(1 - \frac{v_k}{v_i}\right)^{2/3} - 1$$

(5.20)

Equation 5.19 shows that the breakage rate increases with the increasing energy dissipation rate and with the increasing number density.
5.4.2.2 Martinez-Bazan Model (MB Model)

A general breakage rate \( \Omega_b(i,k) \) can be expressed as

\[
\Omega_b(i,k) = q \times b(i) \times P_b(i,k)
\] (5.21)

where \( q \) is number of daughter bubbles produced by the breakup of a parent bubble. In the present case, for binary bubble breakup, \( q = 2 \). The term \( b(i) \) is the total rate of breakage for a parent bubble of size \( d_i \) and \( P_b(i,k) \) is the probability of formation of bubble of size \( d_k \) due to the breakup of bubble of size \( d_i \). According to Martinez-Bazan et al.\textsuperscript{144}

\[
b(i) = K_g n_i \sqrt{\beta (\varepsilon d_i)^{2/3} - 12 \sigma/(\rho_L d_i)}
\] (5.22)

where \( K_g \) is the proportionality constant and experimentally its value was found to be 0.25 by Martinez-Bazan et al.\textsuperscript{144} The constant \( \beta = 8.2 \). In equation 5.22, when the surface tension forces become equal to the turbulent forces the breakage rate becomes zero. This serves as the basis for the critical bubble diameter in the MB model. In fact, when \( b(i) = 0 \) in equation (5.22), it is seen that the Hinze formula is recovered exactly, except for a multiplying constant of 1.26 instead of 0.725.

According to Martinez-Bazan et al.\textsuperscript{145} the probability of the formation of a daughter bubble of size \( d_k \) from the breakage of a parent bubble of size \( d_i \) can be expressed as

\[
P_b(i,k) = \frac{[D_k^{*2/3} - D_{cr}^{*5/3}][(1 - D_k^{*3})^{2/3} - D_{cr}^{*5/3}]}{[D_{cr}^{*2/3} - D_{cr}^{*5/3}][(1 - D_{cr}^{*3})^{2/3} - D_{cr}^{*5/3}]} dD^*
\] (5.23)

where, \( D^* \) is the dimensionless bubble diameter, \( d/d_i \) such that:

\[
D_k^* = \frac{d_k}{d_i}
\] and
\[ D_{cr}^* = \frac{d_{cr}}{d_i}, \text{where the critical bubble diameter is } d_{cr} = \left( \frac{12\sigma}{\beta \rho_L} \right)^{3/5} e^{-2/5} \]

\[ D_{min}^* = \frac{d_{min}}{d_i}, \text{and } d_{min} = \left( \frac{12\sigma}{\beta \rho_L d_i} \right)^{3/2} e^{-1} \]

\[ D_{max}^* = \frac{d_{max}}{d_i}, \text{and } d_{max} = d_i \left( 1 - \left( \frac{d_{min}}{d_i} \right)^3 \right)^{1/3} \]

### 5.4.3 Coalescence Model

The coalescence model can be chosen independent of the breakage model. Here the coalescence model of Luo\(^{11}\) is used with both the LS breakage and MB breakage models. The coalescence rate \( \Omega_c (i, j) \) can be expressed as the product of collision frequency \( \omega_c (i, j) \) and coalescence probability \( P_c (i, j) \). Only the collision frequency due to turbulence was considered by Luo:

\[
\omega_c (i, j) = 0.089 \pi n_i n_j (d_i + d_j)^2 e^{1/3} (d_i^{2/3} + d_j^{2/3})^{1/2}
\]

(5.24)

According to coalescence theory, when two bubbles collide the shared interface begins to drain or thin. If the bubbles remain in contact long enough for this interface to reach a critical rupture thickness the bubbles will coalesce, otherwise the bubbles will move apart. Based on this theory, Luo expressed coalescence probability as follows:

\[
P_c (i, j) = \exp \left( -C \frac{[0.75(1 + D_j^{*2})(1 + D_j^{*3})]^{1/2}}{(\rho_G / \rho_L + 0.5)^{1/2} (1 + D_j^{*})^3} We_{ij}^{1/2} \right)
\]

(5.25)

where, \( C \) is the proportionality constant and its value was taken as 1. Here, \( D_j^{*} \) is dimensionless bubble diameter given as \( d_j/d_i \). \( We_{ij} \) is Weber number given as

\[
We_{ij} = \frac{\rho_L d_i \bar{u}_{ij}^2}{\sigma}, \quad \bar{u}_{ij} = (\bar{u}_i^2 + \bar{u}_j^2)^{1/2}, \quad \bar{u}_i = 1.43 (\epsilon d_i)^{1/3}
\]

(5.26)
This model could be modified to eliminate the so-called critical rupture thickness of the film thinning process, by using a thinning model based on the added Hamaker force\textsuperscript{146} which allows the film to progress to zero thickness to calculate coalescence time. For pure air-water systems, this reduces coalescence time by about 10%.

### 5.4.4 Solution Method

For present work, it was assumed that the column operates at the time averaged periodic steady state. Spatial effects in the radial direction were ignored. With these assumptions, equation 5.5 becomes

\[
    u_i \frac{d}{dx} n_i = S_i
\]

(5.27)

A MATLAB code employing backward differencing scheme,

\[
    n_i\big|_{x-\Delta x} = n_i\big|_x + \frac{\Delta x}{u_i} S_i
\]

(5.28)

was used to obtain the evolution of bubble size distribution.

### 5.5 Simulation Results and Discussion

PBM simulations were performed for an oscillatory bubble column at three different frequencies (15, 17.5, 20 Hz) with constant amplitude (1.66 mm) and constant superficial gas velocity (0.17 cm/s). In the previous experimental section it was shown that a critical power input of 0.8 m\(^2\)/s\(^3\) is necessary for the vibration induced bubble breakup to occur in the column. For the amplitude of 1.66 mm and the gas superficial velocity of 0.17 cm/s, a value of $f = 13$ Hz or greater is needed to provide the necessary critical power. Hence, frequencies of 15, 17.5 and 20 Hz were considered in this simulation. These frequencies correspond to power input of 1.16, 1.85 and 2.75 m\(^2\)/s\(^3\) respectively. Experimental BSD at a height ($H$) of 10.6 cm above the injector was provided as a boundary condition needed to solve the one dimensional differential-integral equation, equation 5.28.
The objective of the simulation was to predict the evolution of BSD and the Sauter mean diameter as a function of power input and compare these results to the experimental values. A single fitted parameter for each model was used to tune the simulation results with the experimental data. For the Luo and Svendsen breakage model, the breakage rate (equation 5.19) was multiplied by a premultiplicative factor of 0.04 to fit our data. In the Martinez-Bazan breakage function (eq. 5.22), a value of $K_g = 0.55$ was used. Figure 5.14 shows a plot of Sauter mean diameter vs height for the three chosen frequencies and using the two different breakage models. The triangles represent experimentally measured values of Sauter mean diameters and the solid line indicates predictions from the simulation. The LS model and MB model show similar predictions for Sauter mean diameter over the frequency range 15-20 Hz. However the MB model indicates an equilibrium bubble size is being approached near the top of the column, while the LS model continues to reduce the average mean diameter.

More important are the results from the evolution of the BSD as shown in Figure 5.15. Figure 5.15 shows the simulation results again at the three different frequencies and using both breakage models. Examining the results at a given frequency, the LS model shows an increase in number of bubbles at and below 0.4 cm diameter as the height increases. For the MB model, there is a gradual shifting of an almost normal distribution from 0.8 cm to 0.2 cm bubble diameter as height increases. At a given height, the LS model shows increasing bubble numbers below 0.4 cm as the applied frequency increases. For the MB model there is a narrowing of the distribution as the frequency increases. This drastic difference in predicted bubble size distribution can be traced directly to the assumptions used in developing each model. LS model favors a single bubble breaking into a large and a small bubble. Here, surface free energy between the two daughter bubbles is minimized. The MB model favors a single bubble breaking into two equal size bubbles.
Figure 5.14 Comparison between predicted and observed values of Sauter mean diameter as a function of height $A = 1.66$ mm, $U_{0g} = 0.17$ cm/s.
Figure 5.15 Evolution of bubble size distribution at different heights in the column. $A = 1.66$ mm, $U_{0g} = 0.17$ cm/s.
For the LS model the daughter probability distribution function is given by:

\[
P_b(i, k) = \frac{2 \int_{\hat{\xi}_m}^{1} (1 + \xi)^2 \xi^{-11/3} e^{-\chi_{cr}} d\xi}{\int_{0}^{\hat{\xi}_m} \int_{0}^{\hat{\xi}_m} (1 + \xi)^2 \xi^{-11/3} e^{-\chi_{cr}} d\xi d\hat{f}_{BV}}
\]

(5.29)

where, \( \chi_{cr} \) is given as:

\[
\chi_{cr} = \frac{5.87 c_f \sigma}{\rho_L \varepsilon^{2/3} d_i^{5/3} \xi^{11/3}}
\]

(5.30)

Equation 5.29 is plotted in Figure 5.16a as a function of energy input and different parent bubble diameters. As seen from the Figure 5.16a, LS breakage gives a U shaped distribution with the smallest probability for the equal size bubble breakage.

The MB model daughter probability distribution function is given by equation 5.23 and plotted in Figure 5.16b. MB breakage gives an inverse U shaped distribution function with highest probability for the formation of equal size daughter bubbles.

Figure 5.16 Illustration of different shape of daughter probability distribution function for both breakage models at different energy dissipation rates and different parent diameters. (a) LS model (b) MB model
In Figure 5.17, we have compared the experimentally observed equilibrium BSD at $H = 67.7$ cm with the simulation results for both the breakage models. Predictions from the MB model match reasonably well with the experimental results; both show a bell shaped BSD centered near the mean diameter. But the predictions from the MB model show broader distribution as compared to the experimental values. The BSD obtained from the LS model is not in agreement with experimental results as contrasted to the experimentally observed narrow, bell shaped curve.

5.6 Conclusions

In this work, effects of low frequency and low amplitude fluid vibrations on the BSD in a bubble column reactor were studied. Experimentally it was found that at low gas flow rates, breakage occurs at the injector and within the injector tube, whereas at high gas flow rates under jetting conditions, bubble breakage takes place within the column proper. If a critical power has been supplied, bubbles undergo breakage as they move up the column. At a certain point in the column, the rate of breakage becomes equal to the rate of the coalescence process. Above this height, the BSD remains at the equilibrium value and the Sauter mean diameter remains
unchanged. The effect of the amplitude and the frequency on BSD is coupled through the power input term. It was shown that the Sauter mean diameter is inversely proportional to the power input and it follows the Hinze breakage formula.

![Graph showing BSD comparison](image)

**Figure 5.17** Comparison between experimentally observed equilibrium BSD and simulation results for two different breakage models at \( H = 67.7 \) cm. (a) \( f = 15 \) Hz; (b) \( f = 17.5 \) Hz; (c) \( f = 20 \) Hz.

(Figure cont.)
To help explain experimental results, population balance modeling simulations were performed using two fundamentally different breakage models, namely the Luo-Svendsen and the Martinez-Bazan model. The MB model reached an equilibrium bubble size within the height of the column which was also observed experimentally. The LS model failed to reach equilibrium at the frequencies studied.

Predictions for these two models differ significantly in the shape of the respective BSD curve. The LS model predicts the generation of a large numbers of small size bubbles which results in a very broad size distribution. The MB model gives preference to equal size bubble breakage. The predictions obtained from the MB model are in agreement with the experimental observations. We speculate that fluid vibrations enhance the production of nearly equal size bubble breakage, mainly owing to shear effects, and results in more uniform BSD and smaller bubbles. This leads to enhanced mass transfer as we have shown in our earlier work\textsuperscript{131}.

5.7 Nomenclature

\begin{itemize}
\item \textbf{A} amplitude of imposed by liquid pulsation, m
\item \textbf{b} total breakage rate, 1/(m\textsuperscript{3}.s)
\end{itemize}
$B_B$  birth due to breakage, $1/(m^3.s)$

$B_C$  birth due to coalescence, $1/(m^3.s)$

$C$  proportionality constant in equation 5.23, dimensionless

$C_D$  drag coefficient, dimensionless

$c_f$  defined in equation 5.18, dimensionless

$d$  bubble diameter, m

$d_{32}$  Sauter mean bubble diameter, m

$D^*$  dimensionless bubble diameter

$D_B$  death due to breakage, $1/(m^3.s)$

$D_C$  death due to coalescence, $1/(m^3.s)$

$f$  frequency, Hz

$g$  acceleration due to gravity, m/s$^2$

$h$  height of the liquid head, m

$H$  vertical distance from the gas injector, m

$k$  pre-multiplier from equation 5.4, dimensionless

$K_g$  pre-multiplier from equation 5.20, dimensionless

$K_D$  constant from equation 5.9, dimensionless

$BJ(h)$  local Bjerknes number, $\frac{1}{2} \left( \frac{\rho_l h A^2 \omega^4}{g P_o} \right)$, dimensionless

$n$  number density of bubbles, $1/m^3$

$P_b$  breakage daughter bubble size distribution, dimensionless

$P_c$  coalescence daughter bubble size distribution, dimensionless

$P_m$  power input per unit mass, $m^2/s^3$

$Q_g$  volumetric gas flow rate, $m^3/s$
\( q \)  number of daughter bubbles formed per breakage event, dimensionless

\( S \)  source term, \(1/(m^3.s)\)

\( t \)  time, s

\( U_{og} \)  superficial gas velocity, m/s

\( u \)  bubble rise velocity, m/s

\( \bar{u} \)  characteristic velocity, m/s

\( v \)  volume of bubble, m\(^3\)

\( We \)  Weber number, dimensionless

\( x \)  spatial variable, m

Greek symbols

\( \alpha \)  gas hold-up, dimensionless

\( \beta \)  constant in equation 5.20, dimensionless

\( \varepsilon \)  energy dissipation rate = \( P_m \), m\(^2/s^3\)

\( \mu \)  liquid viscosity, Pa .s

\( \rho_l \)  liquid density, kg/m\(^3\)

\( \rho_g \)  gas density, kg/m\(^3\)

\( \sigma \)  surface tension, N/m

\( \omega \)  frequency, radians/s

\( \omega_c \)  coalescence collision frequency, \(1/(m^3.s)\)

\( \Omega_B \)  breakage rate, \(1/(m^3.s)\)

\( \xi \)  dimensionless eddy size
Chapter 6  Hydrogenation of Alpha-methyl Styrene in a Piston Oscillating Monolith Reactor

6.1  Introduction

Reactors based on monolithic catalysts have traditionally been utilized in gas phase cleanup (e.g. de-NO\(_x\)) for the automotive industry. More recently, interest has turned to using these reactors in three-phase systems as an alternative to stirred tanks, where the catalyst is present as a slurry, or to trickle bed reactors. Three-phase monolith reactors are sometimes attractive alternatives to stirred tanks for fine chemicals production, with higher reaction rates at lower power input.\(^{103}\) Selectivities with the monolith reactors are typically unaffected; for example, Cybulski et al.\(^{103}\) observed selectivities equal to or better than a stirred tank, in the hydrogenation of 3-hydroxypropanal to 1,3-propanediol. Furthermore, by coating the catalyst on a monolith there is no need to separate catalyst from product.

The primary advantage of monolith over packed bed reactors is in fluid phase transport-limited reactions, where monolith reactors are often several times more efficient on a volume basis.\(^{68}\) As is well known, packed trickle beds suffer from poor catalyst wetting phenomena due to rivulet formation. This behavior leads not only to highly variable concentration gradients in gas to solid transport, but also to variations in residence time distribution. Both phenomena can worsen reaction selectivity, especially in serial reaction pathways.\(^{69,147}\) It appears that monolith reactors offer improvements in both areas, as is also the case for other reactor types with well-defined geometry and simpler gas-liquid hydrodynamics, for example the tubular supported catalytic membrane reactor.\(^{19}\)

At relatively low gas-to-liquid (G/L) volumetric ratios, both gas and liquid flow through a monolith as discrete, alternating slugs, the Taylor regime (Figure 6.1). Plug flow-like behavior exists because gas slugs in Taylor flow force the reactants through the channels with little back
mixing. Because intense mixing takes place in the liquid slug, and because only a thin film
separates the gas slug from the catalyst-coated monolith, the rates of liquid-solid and gas-solid
transport can be high. Some argue that monolith reactors are already sufficiently active for
certain hydrogenations in the Taylor flow regime; however, they are far from ideal at the
more common volumetric rates (G/L >> 1) where trickle beds can operate. At these conditions,
liquid/gas distribution in a monolith is uneven and can result in significant under-
performance of the reactor.

Figure 6.1 Schematic of Taylor Flow behavior in a capillary with alternating slugs of gas
and liquid. \(N_x\) denotes molar flux.

Other design parameters greatly affect monolith reactor performance, for example the
geometry of the gas distributor. Uniform gas bubble dispersion is critical. Significant variations
in hydrodynamic behavior have been noted for different distributor designs. For distributors
placed too close to the first monolith segments, preferential gas flow through the center of the
monolith was observed. Placing the distributor far away led to gas flow along the outer walls of
the reactor.

Although most monolith three-phase reactor research deals with low molecular weight
reactants, viscous effects can affect the hydrodynamics. In MRI studies, a sucrose solution with
twice the viscosity of water led to an increase in the thickness of the liquid film surrounding gas
slugs. Higher viscosities can also lead to more liquid loading in packed beds. A thicker liquid film would decrease mass transfer rates by increasing the diffusion length, $\delta$.

One method to improve hydrodynamics in packed bed reactors is to periodically modulate liquid loading, such that during the gas-rich cycle the gas phase reactant can more easily diffuse to the catalyst surface. The liquid-rich cycle provides liquid phase reactant and flushes product from the surface while also ensuring high rates of heat transfer. Khadilkar et al. and Lange et al. reported enhancements in time averaged conversion of up to 60% and 10% respectively for AMS hydrogenation in a pulsed trickle bed using a Pd/Al$_2$O$_3$ catalyst. Castellari and Haure noted reaction rates can be enhanced up to 400% for the same reaction in a pulsed trickle bed. Pulse behavior within trickle beds is largely governed by column dimensions and superficial gas and liquid velocities. Boelhouwer and co-workers performed an in-depth analysis of pulsing behavior in trickle beds. They concluded that there were inherent impracticalities at relatively high imposed frequencies of 1 Hz and greater, where a shock wave decays rapidly along the length of the bed. For an on-off cycled feed the time between liquid pulses had to be at least 120 s in a bed 3.2 m in length to avoid shock wave coalescence. However, at high superficial gas velocities and short liquid pulsing times, stable pulses up to 1 Hz could be attained over the entire bed length. Apparently, controlling pulse behavior inside a trickle bed is difficult and in most cases practical only over a narrow operating range.

The piston oscillating monolith reactor (POMR) is an extension of previous work on pulsed bubble columns to three-phase reactors with a structured catalyst. Since a key challenge to most three-phase reactors is the transport of gas to the catalyst surface, we believed that the previously observed enhanced gas-liquid mass transfer rates arising from pulsed flow would increase observed rates. Other important aspects of such reactions, such as the surface wetting distribution and the residence time distribution within the monolith channels, might also
be effectively controlled using forced pulsing. The POMR represents a novel way to tune the catalyst pore environment, as opposed to the more traditional methods of varying temperature, pressure, and superficial velocities/agitation rates.

The hydrogenation of α-methylstyrene (AMS) to cumene (Figure 6.2) is often used to investigate the performance of three phase reactor systems, because of its mild reaction conditions (~50-100 °C and ~0.1-0.68 MPa) and fast kinetics. It is typically limited by gas mass transfer. At sufficiently high AMS concentration (>0.5 wt%), the reaction is zero order in AMS and first order in H₂.

![Figure 6.2 Hydrogenation of AMS to cumene.](image)

**Figure 6.2 Hydrogenation of AMS to cumene.**

### 6.2 Experimental

#### 6.2.1 Catalyst Preparation

The Pd/Al₂O₃ catalysts used were prepared via an ion exchange (IX) technique. PdCl₂ was first converted into Pd(NH₃)₄(NO₃)₂ by dissolving in an aqueous solution containing excess aqueous ammonia and NH₄NO₃ at a pH of 11. Excess Cl⁻ was removed from solution by contacting with an ion exchange resin (Amberlite IRA-400, Rohm and Haas). Pseudoboehmite (Versal V-250, UOP) was converted at 500°C in flowing air to γ-Al₂O₃, which was then contacted with the Pd solution at 60°C overnight. The sample was filtered, dried at 80°C and then calcined at 500°C in flowing air. Finally, it was reduced at 130°C in 10% H₂/N₂.

The catalyst powder was washcoated onto cordierite ceramic monoliths with cylindrical channels (200 cpsi, 5 x 5 x 1.2 cm, 1.3 mm hole diameter, 26.5 g bare weight), from an aqueous
slurry (25 wt% solids). The slurry was first ball milled for 90 min after which a stable alumina suspension was obtained. Then 0.1 M HNO₃ was added to bring the pH to 3.5-4. Upon removal from the slurry, compressed air was used to blow out excess slurry and clear any blocked channels.

For pretreatment 1, the as coated monoliths were dried in air at 90°C and then calcined at 500°C in flowing air before being reduced at 130°C in 10% H₂/N₂. For pretreatment 2, a catalyst that had already been used in reaction experiments was then subjected to additional calcination at 500°C in flowing air, then reduction at 130°C in 10% H₂/N₂. As explained below this additional treatment alters the surface structure of the Pd catalyst.

6.2.2 Piston Oscillating Monolith Reactor (POMR) System

The POMR consists of a 1 L stainless steel square vessel in which three catalyst coated monoliths and heat exchangers are alternately stacked in a “sandwich” arrangement (Figure 6.3). This arrangement sits above a gas distributor. At the bottom of the reactor is a flexible Teflon diaphragm connected to a cam/motor arrangement. The diaphragm can be used to impose oscillatory behavior on the reactor system. The frequency (f) can be controlled between 0-50 Hz at a maximum amplitude (A) of 25.4 mm. The diaphragm has a diameter of 17.8 cm. Experiments were performed at frequencies of 0-17.5 Hz and amplitude 2.5 mm. The POMR process flow diagram is shown in Figure 6.4. The reactor is operated in batch mode with respect to the liquid. Hydrogen is continually recycled through the system by a gas booster and additional hydrogen is allowed to enter the system to replace any that is lost due to reaction. The gas booster is a positive displacement pump with its own oscillatory frequency of 0.5 Hz.

6.2.3 Procedure for Reactor Studies

AMS and cyclohexane (both 99+, Sigma-Aldrich) were used. The polymerization inhibitor (15 ppm p-tertbutylcatechol) present in AMS can deactivate hydrogenation
catalysts,\textsuperscript{13,153} so it was removed by contacting the AMS with adsorption grade alumina beads and complete removal verified by GC/MS. Cyclohexane was contacted with molecular sieve to remove traces of water.

Figure 6.3 Schematic of the Piston Oscillating Monolith Reactor (POMR).

Figure 6.4 POMR process flow diagram.
A mixture of 13 mol% AMS/cyclohexane was charged to the reactor, which was brought to temperature (46°C) under 0.1 MPa of H₂, then pressurized to 0.44 MPa H₂. The piston/cam oscillator and gas booster were then started and the gas recirculation flow rate set. Gas superficial velocity was held constant at 18 cm/s. Analysis of 1 mL liquid samples withdrawn at defined intervals was by GC (HP 5890, FID detector) with an Alltech EC-1 capillary column (30 m x 0.25 mm ID). Ethylbenzene was added as an internal standard. Trace side products were identified by GC/MS (HP 5972).

For comparison purposes, a stirred reactor (500 mL Autoclave Engineers Zipperclave, 6.8 cm marine propeller) was also used at the same pressure and temperature. The catalyst was reduced in situ (130°C) and a constant H₂ purge maintained on the system when not in use. A catalyst-coated monolith identical to those used in the POMR was held stationary 3.5 cm below the propeller, with approximately 20 mL fluid volume beneath the monolith.

6.3 Results and Discussion

6.3.1 Catalyst Characterization

For the alumina washcoat, the BET surface area was 290 m²/g. The BJH pore size distribution of the washcoat was also measured, based on the desorption isotherm. The average pore diameter was 10 nm with a FWHM of 4 nm. Pd weight loadings after ion exchange were determined by ICP-AES; results are summarized in Table 6.1. The impregnation from the first Pd ion exchange was only 0.23 wt%. In order to obtain higher Pd loadings the same catalyst underwent sequential exchanges. Each time, the catalyst was dried, calcined, and reduced before being re-introduced to the ion exchange solution. This resulted in a final weight loading of 0.5 wt%. Monolith loading after washcoating is also shown in Table 6.1. Weight loadings were consistently ~4 wt% with coating thicknesses of ~100 µm. Metal dispersion was measured on a Micromeritics 2700 by pulse chemisorption of H₂. The pretreatment 1 catalyst showed a

174
dispersion of 74% and the pretreatment 2 catalyst was 60%. To ensure that 130°C was sufficient to fully reduce the catalyst, the sample was exposed to increased temperatures (150-180 °C) under H₂ flow, but no further increases in dispersion were measured.

Table 6.1 ICP results showing Pd and washcoat loadings.

<table>
<thead>
<tr>
<th>Ion Exchange</th>
<th>Pd wt%</th>
<th>Monolith</th>
<th>Loading</th>
<th>Catalyst wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.38</td>
<td></td>
<td></td>
<td>4.05</td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td></td>
<td></td>
<td>3.92</td>
</tr>
<tr>
<td>4</td>
<td>0.50</td>
<td></td>
<td></td>
<td>3.97</td>
</tr>
</tbody>
</table>

6.3.2 Visualization Studies

Visualization experiments were performed to better understand the hydrodynamics of the POMR. Photographs of the acrylic mock up in operation (air-water) were taken with a high speed camera (Photron Fastcam PCI-R2). In the absence of oscillations, channeling of gas took place at low gas superficial velocities (0.4-6.3 cm/s). The preferential flow of gas through certain channels decreased as superficial gas velocities increased over this range. Using an MRI technique, Gladden et al.⁷² found that at low gas superficial velocities (approximately 0.85-2.5 cm/s), gas flowed through only 70% of monolith channels. From a reaction perspective, this means that only 70% of the catalyst will take part in reaction at any one time. Unequal flow distribution also results in inhomogeneous liquid residence times through the monolith stack, which can give poor selectivities in serial reactions.

Upon application of oscillation, even gas distribution across the monolith cross section was obtained as shown in Figure 6.5. The oscillations induced both rapid gas expulsion and liquid suck back, in different parts of the cycle. During the liquid-rich part of the cycle, the gas velocity decreased due to the downward force of the liquid (Fig. 6.5a). After the onset of the upward stroke, liquid is expelled from the channels; gas flows through almost all channels (Fig. 6.5c).
6.3.3 Reactor Studies

6.3.3.1 Activity

Figure 6.6 shows reactant and product concentrations as a function of time on stream in the POMR at typical pulsing conditions of 8 Hz frequency and 2.5 mm amplitude. The best-fit slope of this line (mol L\(^{-1}\) min\(^{-1}\)) was used to calculate the rate in mmol g\(_{Pd}\)^{-1} s\(^{-1}\). From these rate data it was determined that the rate is independent of AMS concentration at these conditions, consistent with earlier work which also shows the reaction is first order in H\(_2\) concentration.\(^{16,19,154}\) The slopes of the AMS and cumene lines are identical but opposite in sign; this shows there is a good mass balance on the system.

Figure 6.5 One complete cycle of oscillation, air-water in monolith mock-up assembly with oscillation: 121 channels (11x11) each 1.59mm diameter; Amplitude = 2.46 mm; Frequency = 2 Hz; Gas superficial velocity = 6.2 cm/s.
Figure 6.6 Concentration of cumene (product) and AMS (reactant) versus time in the POMR. Conditions: frequency = 8 Hz, piston amplitude = 2.5 mm, 46°C, 0.44 MPa H₂.

Figure 6.6 also shows the catalyst used here does not noticeably deactivate over the time scale of a reactor experiment. However, some catalyst deactivation for the pretreatment 1 catalyst was noted between successive reactor runs. In these reactor experiments, attempts to reproduce rates by re-reducing the catalyst in-situ before each run resulted in partial regeneration only. Rates of hydrogenation varied from 1.5-6.0 mmol g⁻¹ s⁻¹ for the pretreatment 1 catalyst in the POMR. Therefore, thermogravimetric analysis (TGA) of the used pretreatment 1 catalyst sample was performed to investigate the source of deactivation. In Figure 6.7(a) the sample was treated in a manner similar to the in-situ reduction preceding most runs. Regardless of gas chosen, the low-temperature treatment only decreases the starting weight by ~7%. In Figure 6.7(b) it is shown that an oxidative treatment at 500°C removed up to 17% of the initial weight. Because traces of oligomer were observed in the liquid samples by GC/MS, we conclude that the deactivation we observed is caused not by loss of reduction, but rather by the formation of AMS oligomers blocking sites on the catalyst surface, for fresh catalysts. We believe this to also be the cause of previously observed catalyst deactivation for AMS hydrogenation in stirred tanks.²⁰
Figure 6.7 (a) Low temperature TGA of used Pd/Al₂O₃ catalyst in N₂ (0-160 min), air (160-280 min), and H₂ (280-400 min). Ramp of 5°C/min to 120 °C. (b) High temperature TGA in air. Ramp at 5°C/min to 130°C with hold for 2 h, followed by ramp at 5°C/min to 500 °C.
While previous literature\textsuperscript{13,20} has noted that deactivation could be minimized by maintaining a high hydrogen partial pressure between reactor runs, we found that by itself this action was insufficient to fully restore activity in multiple successive runs. In previous work the catalyst was simply replaced when deactivation affected the results.\textsuperscript{13} Our strategy was instead to calcine (500°C, air) and then reduce (130°C, 10\% H\textsubscript{2}/N\textsubscript{2}) the once-used catalyst, one time only, in order to completely regenerate the activity (denoted “pretreatment 2”). Reaction rates for the catalyst after pretreatment 2 were approximately an order of magnitude higher than for pretreatment 1, and cumene selectivity was higher. Therefore, this treatment protocol not only regenerated the catalyst, but also greatly improved its performance in all subsequent runs. The pretreatment 2 catalyst required no additional regeneration steps, even after multiple successive runs.

Figure 6.8 summarizes the differences in activity at different oscillation frequencies for the pretreatment 2 catalyst. Due to the operation of gas booster and the applied piston oscillations, the pressure inside the reactor oscillates, and these pressure oscillations at different frequencies are reported in Table 6.2. The POMR runs labeled as 0.5 Hz were performed with the piston-oscillated diaphragm off. However, this is not a true run at zero frequency since the gas booster is used to introduce and recycle hydrogen, and the booster’s characteristic frequency is 0.5 Hz. It can be considered a gas-pulsed, but not “actively forced” (simultaneous pulsing of both gas and liquid by the diaphragm) run. The other runs used the diaphragm and are labeled with its pulsing frequency. At zero frequency (recycle gas booster off) there was no measurable reaction rate, therefore less than 0.1 mmol g_{Pd}^{-1} s^{-1}.

The results (Figure 6.8) show that low frequency, low amplitude oscillations by active forcing greatly enhance observed reaction rates for this highly gas mass transfer-limited system. The POMR pulsing frequency can be varied over a wider range than previous work in pulsed
trickle beds which showed lower activity and difficulty in controlling the pulsing over a wide range of process variables such as reactor length and superficial velocities.\textsuperscript{17,45,149}

![Graph showing reaction rate vs. frequency for different conditions](image)

**Figure 6.8** Comparison between hydrogenation rates in the POMR and stirred tank for the pretreatment 2 catalyst. Other conditions are same as in Figure 6.6.

<table>
<thead>
<tr>
<th>$f$ (Hz)</th>
<th>$u_L$ (cm s(^{-1}))</th>
<th>Avg. P (MPa)</th>
<th>P. Std. Deviation (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0</td>
<td>0.44</td>
<td>0.05</td>
</tr>
<tr>
<td>8</td>
<td>45</td>
<td>0.46</td>
<td>0.07</td>
</tr>
<tr>
<td>17.5</td>
<td>97</td>
<td>0.43</td>
<td>0.08</td>
</tr>
</tbody>
</table>

AMS hydrogenations with the same type monoliths were carried out in a stirred tank. Results of these runs are compared to the POMR runs in Figure 6.8. Experiments were performed at 400 and 800 rpm. Doubling the agitation rate had the effect of increasing the activity from 5.1 to 8.5 mmol g\(_{\text{Pd}}^{-1}\) s\(^{-1}\) for the pretreatment 2 catalyst. To ensure the results from the monolith supported catalyst in the stirred tank were not a result of poor liquid circulation through the monolith, an additional experiment was carried out with the washcoat removed and run as a slurry at identical temperature and pressure. The observed rate was 6.1 mmol g\(_{\text{Pd}}^{-1}\) s\(^{-1}\) at 400 rpm, showing the activity results with monolith or powdered catalyst do not differ
significantly. This result is also shown in Fig. 8 as the experiment with particle catalyst. To further compare POMR to stirred tank performance, the power per unit volume \((P_v)\) input into the system was calculated for each system. For the POMR, \(P_v\) was calculated based on Equation 6.1\(^{123}\) at 8 and 17.5 Hz. These results were used to find the corresponding agitated tank rpm at identical \(P_v\) based on the correlation of Pandit et al.\(^{155}\) for a stirred tank with marine propeller and no gas sparger (Equation 6.2). The \(P_v\) results are summarized in Table 6.4.

\[
P_v = \rho_L \left( g u_g + \frac{A^2 \omega^3}{2} \right)
\]

(6.1)

\[
P_v = N_c \rho_L N_i^3 d_i^5
\]

(6.2)

At 8 Hz and 2.5 mm amplitude, \(P_v = 1.63 \times 103 \text{ W/m}^3\), which is equivalent to an agitated tank at 520 rpm. For 17.5 Hz, the equivalent \(P_v\) is at 730 rpm. Because the observed rates in the stirred tank at both 400 and 800 rpm are below all observed rates for the POMR, we conclude that the POMR is superior to a stirred tank at similar \(P_v\) and otherwise comparable conditions.

The reason for the regenerative effect of pretreatment 2 is obvious as the heavy oligomers are combusted at sufficiently high temperature. The reason for the greatly enhanced activity is more subtle. Dispersion measurements for the catalyst subject to pretreatment 2 showed a decrease in Pd dispersion from 74% to 60%. Therefore, Pd crystallite size increased relative to a purely reductive pretreatment. It is well known that Pd crystallite size can have an important influence on hydrogenations (i.e. structure sensitivity).\(^{156,157}\) It is therefore likely that the lower initial activity of the higher dispersion catalyst can be explained in these terms.

6.3.3.2 Selectivity

Previous work with the AMS hydrogenation test reaction has focused almost exclusively on activity, because the hydrogenation of AMS with Pd-based catalysts is highly selective under normal operating conditions.\(^{16}\) However, a product breakdown by GC/MS shows several minor
side products. The heavier ones are identified in Figure 6.9 and will be referred to as products 1-5 for simplicity. These are mostly disproportionation products, formed by the serial pathway of cracking followed by alkylation and in some cases hydrogenation. Though not shown in Figure 6.9, there are also positional isomers of these products, a small amount of AMS dimer, and a noticeable light hydrocarbon peak (C₁-C₃) in the GC spectrum. The wt% of light hydrocarbons was similar to the sum of the wt% of the peaks identified in Figure 6.9. Selectivity \( S_x \) for each product in Figure 6.9 was defined on a molar basis (Eq. 6.3).

\[
S_x = \frac{(Mol)_x \times (#C)_x}{\sum(Mol)_x \times (#C)_x} \times 100
\]  

(6.3)

The selectivity to cumene was always >98%, and it is likely that such products would be undetectable with less active catalysts. However, a complete product breakdown is important because it indicates how selectively the catalyst/reactor might behave in more important reactions that are not as simple.

Figure 6.9 AMS hydrogenation side products identified by GC/MS.
A selectivity comparison between the POMR and stirred tank is shown in Figure 6.10. The effect of catalytic pretreatment is also shown. In all cases the POMR with the pretreatment 2 catalyst showed the best overall selectivity, although the effects of pretreatment far outweighed those of reactor type. Products 3-5 were not even formed at detectable limits. Since the pretreatment 2 catalyst has larger Pd crystallites and therefore fewer edge and corner sites that are more active for hydrocracking reactions\textsuperscript{160}, it follows that it would give higher hydrogenation selectivity.

![Figure 6.10 Molar selectivities of different reactor systems. (a) POMR vs. stirred tank (400 rpm), (b) POMR - pretreatment 2 catalyst. Other conditions same as in Figure 6.6.](image-url)
Products 3-5 especially are so complex that they would require longer time on the surface to form. The decrease of these products in the POMR for the pretreatment 1 catalyst suggests that the primary product (cumene) does not remain on the surface for a very long time. This is consistent with actively forced pulsing in the POMR controlling the catalyst surface wetting (indicated by the high speed photographs in Figure 5) and removing the primary product before an undesired reaction occurs.

The increased selectivity may also explain why the pretreatment 2 catalyst also showed superior long-term stability. Along with fewer hydrocracking and alkylation products, there were also fewer oligomers formed. This may also explain why some of the previous literature notes deactivation issues while some do not.

6.3.3.3 Comparison to Previous Work

The hydrogenation of α-methylstyrene is generally mass transfer controlled because of its “fast” intrinsic kinetics. It is important to take into account both rates of mass transfer and the intrinsic kinetics when comparing observed reaction rates to previous work. In monolith channels, there are three external (to the catalyst) mass transfer steps for the transport of hydrogen to the catalyst surface, namely, gas to liquid, liquid to solid and gas to solid, as indicated in Fig. 5.1. Different correlations that have been used to calculate the volumetric mass transfer coefficients for each step are listed in Table 6.3. Gas to liquid and liquid to solid mass transfer occurs in series; these are in parallel with gas to solid mass transfer.

By combining these three steps the overall volumetric mass transfer coefficient \( k_{oa}a \) can be determined as:

\[
k_{oa}a = k_{GS}a_{GS} + \left( \frac{1}{k_{GL}a_{GL}} + \frac{1}{k_{LS}a_{LS}} \right)^{-1}
\]  

(6.7)
Table 6.3 Mass transfer correlations used to calculate mass transfer rates in catalyst monoliths, three-phase reactions.

<table>
<thead>
<tr>
<th>Mass transfer step</th>
<th>Correlation</th>
<th>Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas to liquid through bubble cap</td>
<td>$k_{GL}a_{GL} = \frac{0.111u_{TP}^{1.2}}{\varepsilon_L L_{UC}^{0.55}}$</td>
<td>Bercic and Pintar (1997)$^{14}$</td>
</tr>
<tr>
<td>Liquid to solid</td>
<td>$k_{LS} = \frac{D^H}{d_{ch}} 20\left(1 + 0.003\left(\frac{L_{UC} / d_{ch}}{Re Sc}\right)^{-0.7}\right)$</td>
<td>Kreutzer et al. (2001)$^{13}$</td>
</tr>
<tr>
<td>Gas to solid through liquid film</td>
<td>$k_{GS} = \frac{D}{\delta}$</td>
<td>Irandoust and Andersson (1989)$^{12}$</td>
</tr>
<tr>
<td></td>
<td>$\delta = (d_{ch} - d_h) / 2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\frac{d_h}{d_{ch}} = 0.64 + 0.36\exp(-3.08Cd_{ch}^{0.54})$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a_{GS} = \frac{4(1 - \varepsilon_L)}{d_{ch}}$</td>
<td></td>
</tr>
</tbody>
</table>

Using these equations, the values of the individual volumetric mass transfer coefficients were computed at the conditions of this study. The gas superficial velocity was fixed for all experiments based on the gas recycle rate. However, the liquid superficial velocity is a function of pulse frequency. The velocities are 45 and 97 cm/s at respective frequencies of 8 and 17.5 Hz. These values were calculated based on the volume of fluid displaced by each upward stroke per time and divided by the cross sectional area of the monolith channels. At pulsing conditions, the liquid hold up $\varepsilon_L$ is $u_L / u_L + u_G$, while at no pulsing conditions, the liquid superficial velocity was taken to be zero and the liquid hold up $\varepsilon_L$ as $1 - L_{slug} / L_{ch}$ with $L_{slug}$ taken as $3 d_{ch}$. The results are summarized in Table 6.2.
The overall volumetric mass transfer coefficients obtained from these calculations (Table 6.2) are similar to values reported by Kreutzer et al.\textsuperscript{13} for gas-liquid co-current flow in a monolith catalyst at similar superficial velocities. For a 200 cpsi monolith Kreutzer et al.\textsuperscript{13} reported volumetric mass transfer coefficients between 0.5-1 s\textsuperscript{-1} at gas and liquid superficial velocities varying between 10-40 cm/s. Because the visualization studies showed liquid-dominated flow on the piston down-stroke (half the cycle), a minimum volumetric mass transfer coefficient $k_{ovmin}a$ was estimated as 0.5 $k_{ov}a$.

Using the calculated maximum and minimum values of $k_{ov}a$, it is possible to compute maximum and minimum theoretical observed rates by equating the mass transfer rate to the kinetic rate. We used the rate expression of Meille et al.\textsuperscript{16} as follows:

$$r\left(\text{mol s}^{-1} \text{g}_{\text{Pd}}^{-1}\right) = A_0 \exp\left(-\frac{E_a}{RT}\right) \frac{K_H C_H}{(1+\sqrt{K_H C_H})^2}$$

where $A_0 = 8.5 \times 10^6 \text{ mol g}_{\text{Pd}}^{-1} \text{s}^{-1}$; $E_a = 38.7 \text{ kJ mol}^{-1}$ and $K_H = 1.4 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$. From this expression, the rate constant $k_o (0.055 \text{ m}^3 \text{ g}_{\text{Pd}}^{-1} \text{s}^{-1})$ was calculated by lumping together $A_0$, the exponential term, and $K_H$ to give:

$$r\left(\text{mol s}^{-1} \text{g}_{\text{Pd}}^{-1}\right) = k_o \frac{C_H}{(1+\sqrt{K_H C_H})^2}$$

This rate expression was chosen because the hydrogenation was studied under conditions similar to ours (up to 50$^\circ$C and 0.6 MPa). Also, it gave the highest observed rates from all of the literature reviewed. The internal diffusion resistance was accounted for by calculating the Thiele modulus:

$$\Phi = L \frac{k_o^{-1}}{D_e}$$

where $L$ is the characteristic length scale which is taken as the thickness of the washcoat (100 µm) and $D_e$ is the effective diffusivity of hydrogen ($2.4 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$). The rate constant ($k_o$) has
been multiplied by the catalyst particle density and catalyst active metal loading to obtain $k_0'$ with units of (m$^3$ fluid s$^{-1}$ m$^{-3}$ catalyst). Assuming $C_H$ on the catalyst surface is small, the denominator in Eq. 9 approaches one and the kinetics are effectively first order. The effectiveness factor therefore becomes:

$$\eta = \frac{\tanh(\Phi)}{\Phi}$$  \hspace{1cm} (6.11)

For the present conditions, $\eta \sim 1$. Equating the mass transfer and reaction rates gives:

$$k_{ov} a (C^* - C_{surf}) = \eta r(C_{surf}) \rho_c$$  \hspace{1cm} (6.12)

where $C^*$ is saturation concentration (20.4 mol m$^{-3}$) of H$_2$ in the reaction mixture$^{32}$ and $C_{surf}$ is the reactant concentration at the surface. $\rho_c$ is the catalyst reactor loading expressed as total grams of Pd divided by the liquid volume of all monolith channels (0.553 kg Pd m$^{-3}$). From equation 6.12 it is possible to calculate the concentration of reactant at the external catalyst surface. The observed rate of reaction is then:

$$r_{obs} = \eta r(C_{surf})$$  \hspace{1cm} (6.13)

In all cases, the surface concentration of hydrogen ($C_{surf}$) was <10% of $C^*$, showing that the assumption of effectively first order kinetics for computing the Thiele modulus is valid. The expected observed reaction rates for both minimum and maximum $k_{ova}$ at different frequencies are reported in Table 6.4. The reaction rates calculated at $(k_{ova})_{\text{min}}$ are in broad agreement with the experimentally determined reaction rates, which varied from 16 – 30 mmol g$^{-1}$ Pd s$^{-1}$ at 0.5 to 17.5 Hz in the POMR. This suggests that the effective $k_{ova}$ for the reactor is in fact closer to $(k_{ova})_{\text{min}}$ as shown by the high speed photographs where the liquid rich duration is half the cycle.

Similarly, we computed the expected observed reaction rates using the mass transfer correlations of van Baten and Krishna. These correlations were developed from CFD and model the mass transfer from Taylor bubbles by accounting for the contributions of the “cap” and
“film” regions. Predicted rates of reaction and overall mass transfer coefficients are summarized in Table 5. Results show the predicted rates of reaction are similar to those obtained using the correlations of Table 3 and are in excellent agreement with what was experimentally observed in the POMR for \((k_{ova})_{\text{min}}\).

### Table 6.4 Computed values for POMR studies at different frequencies using the correlations in Table 6.3 and equation 6.1

<table>
<thead>
<tr>
<th>(f)</th>
<th>(P_v)</th>
<th>(k_{ova})</th>
<th>Rate min.</th>
<th>Rate max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hz</td>
<td>W m(^{-3}) x 10(^{-3})</td>
<td>s(^{-1})</td>
<td>mmol g(_{\text{Pd}}) s(^{-1})</td>
<td>mmol g(_{\text{Pd}}) s(^{-1})</td>
</tr>
<tr>
<td>0.5</td>
<td>1.32</td>
<td>0.86</td>
<td>15</td>
<td>29</td>
</tr>
<tr>
<td>8</td>
<td>1.63</td>
<td>1.5</td>
<td>25</td>
<td>49</td>
</tr>
<tr>
<td>17.5</td>
<td>4.53</td>
<td>2.4</td>
<td>40</td>
<td>75</td>
</tr>
</tbody>
</table>

### Table 6.5 Computed values for POMR studies at different frequencies using the correlation of van Baten and Krishna.

<table>
<thead>
<tr>
<th>(f)</th>
<th>(k_{ova})</th>
<th>Rate min.</th>
<th>Rate max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hz</td>
<td>s(^{-1})</td>
<td>mmol g(_{\text{Pd}}) s(^{-1})</td>
<td>mmol g(_{\text{Pd}}) s(^{-1})</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>1.5</td>
<td>26</td>
<td>50</td>
</tr>
<tr>
<td>17.5</td>
<td>1.8</td>
<td>30</td>
<td>58</td>
</tr>
</tbody>
</table>

The AMS hydrogenation reaction has been extensively studied using many different reactor configurations.\(^{13,15-19,21-23}\) It is interesting to compare the performance of the POMR with other reactor systems at similar temperature and H\(_2\) pressure, all using supported Pd/Al\(_2\)O\(_3\) catalysts. In Figure 6.11 the observed reaction rates of several systems are compared. In constructing the graph we only used data where the rate on a metal weight basis could be determined, at relatively high liquid superficial velocities (or as high as reported in the paper). We excluded some data where the catalyst appeared to be of lower intrinsic activity, and only used data at conditions leading to maximum activity for the reactor in question, within the temperature and pressure constraints.
The performance of the POMR is superior except for stirred tank data where all transport resistances were carefully eliminated by operating at high rates of agitation (>1500 rpm) and with powdered catalysts.\textsuperscript{22,36} The POMR is at least an order of magnitude more productive than a conventional monolith reactor, and greatly superior to either conventional or advanced (pulsed, rotating) trickle beds. Only certain membrane and metal mesh microreactors approach the performance of the POMR. For the former there is segregation of liquid and gas phases, which is likely to give small liquid film thicknesses, similar to what we observe for the POMR. For the latter the liquid film thickness is kept small by the geometry of the microreactor.

![Figure 6.11 Comparison of reactor performance for different types of reactors.](image)

The stirred tank data have been included in Fig. 6.11 to show how far the normal operating conditions for this reaction are from those conditions where rates are not transport-limited, and also to demonstrate the considerable spread of intrinsic (not transport-limited) catalyst activities which have been observed. As previously mentioned, our transport-limited data for pretreatment 2 are consistent with the intrinsic kinetics of Mielle et al.,\textsuperscript{22} whose data were used to determine the kinetic constants in Eq. 6.8. Their activity data can be considered as an upper bound for all Pd/Al\textsubscript{2}O\textsubscript{3} catalysts in the AMS hydrogenation. Our transport-limited data for pretreatment 1 are consistent with the intrinsic kinetics of Germain et al.\textsuperscript{36} There are other
reports of intrinsic activities for even less active Pd catalysts, but these catalysts may have been poisoned by either AMS inhibitor or oligomeric reaction products.

### 6.4 Conclusions

The POMR is a viable alternative to stirred tanks, trickle beds, and conventionally operated monoliths. By using actively forced pulsing (piston-cam arrangement) we were able to increase the AMS reaction rate by 84% over an unforced run where the gas flow is pulsed at low frequency (0.5 Hz). The POMR gave rates 200% higher than a stirred tank reactor operated at similar power input, both using the same catalyst monolith. The enhanced activities arise because the POMR alters the surface wetting phenomena, minimizing the liquid film thickness over at least part of a pulse cycle, thereby enhancing rates of external mass transport. High speed photography reveals both gas- and liquid-rich conditions within the monolith stack during pulsing, as well as an even distribution of bubbles in each monolith channel. These findings are consistent with our previous work on actively forced bubble columns.\(^ {114,123,131}\)

While the effects of catalyst preparation and pretreatment can often mask the advantages of novel reactors, we have shown that by using a correctly pretreated catalyst of larger Pd crystallite size, we can realize the benefits of the novel reactor design in the standard test reaction of AMS hydrogenation, while also achieving high selectivity to cumene and a stable catalyst. Volumetric mass transfer coefficients calculated based on literature correlations but adapted to the internal flows of the POMR were used to predict observed rates of reaction at our reaction conditions, and these values are in broad agreement with the experimental data. The large variation in catalyst preparation characteristic of some previous studies may explain some of the large discrepancies in observed rates.

So in conclusion the POMR provides for rapid mass transfer rates in gas-liquid transport limited reactions, superior to several other reactors of advanced design, and even superior to a
stirred tank when compared on a power-per-volume basis. The POMR comes with the added advantage of a fixed-bed catalyst, in a conventional package – a monolith. It is the type of oscillations (low frequency and amplitude), and how they are generated (by a piston-cam arrangement), that set the POMR apart from previous work in the area of novel gas-liquid contactors.

### 6.5 Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>interfacial area, ( \text{m}^2/\text{m}^3 )</td>
</tr>
<tr>
<td>( A )</td>
<td>piston amplitude, ( \text{m} )</td>
</tr>
<tr>
<td>( C )</td>
<td>concentration, ( \text{mol}/\text{m}^3 )</td>
</tr>
<tr>
<td>( C^* )</td>
<td>saturation concentration, ( \text{mol}/\text{m}^3 )</td>
</tr>
<tr>
<td>( d )</td>
<td>diameter, ( \text{m} )</td>
</tr>
<tr>
<td>( D )</td>
<td>molecular diffusivity, ( \text{m}^2/\text{s} )</td>
</tr>
<tr>
<td>( D_e )</td>
<td>effective diffusivity, ( \text{m}^2/\text{s} )</td>
</tr>
<tr>
<td>( E_a )</td>
<td>energy of activation, ( \text{J/mol} )</td>
</tr>
<tr>
<td>( f )</td>
<td>pulsing frequency, ( 1/\text{s} )</td>
</tr>
<tr>
<td>( g )</td>
<td>gravitational constant, ( \text{m}/\text{s}^2 )</td>
</tr>
<tr>
<td>( k )</td>
<td>mass transfer coefficient, ( \text{m}/\text{s} )</td>
</tr>
<tr>
<td>( k_0 )</td>
<td>rate constant, ( \text{m}^3/(\text{gPd.s}) )</td>
</tr>
<tr>
<td>( k_0' )</td>
<td>rate constant for Thiele modulus, ( \text{m}^3/\text{fluid/s.m}^3_{\text{catalyst}} )</td>
</tr>
<tr>
<td>( K )</td>
<td>equilibrium constant, ( \text{m}^3/\text{mol} )</td>
</tr>
<tr>
<td>( L )</td>
<td>characteristic length scale, ( \text{m} )</td>
</tr>
<tr>
<td>( N )</td>
<td>molar flux, ( \text{mol}/\text{m}^2\text{s} )</td>
</tr>
<tr>
<td>( N_I )</td>
<td>impeller speed, ( 1/\text{s} )</td>
</tr>
<tr>
<td>( N_o )</td>
<td>impeller constant (0.8 for marine propeller), dimensionless</td>
</tr>
</tbody>
</table>
\( P_v \)  Power per unit volume, kg/(m.s\(^3\))

\( r \)  rate, mol/(g\(\text{Pd}.s\))

\( R \)  gas constant, J/(K.mol)

\( S \)  selectivity, dimensionless

\( t \)  time, s

\( T \)  temperature, K

\( u \)  superficial velocity, m/s

\textit{greek letters:}

\( \delta \)  liquid film thickness, m

\( \varepsilon \)  hold-up, dimensionless

\( \eta \)  effectiveness factor, dimensionless

\( \Phi \)  Thiele modulus, dimensionless

\( \mu \)  viscosity, Pa.s

\( \rho \)  density, kg/m\(^3\)

\( \rho_c \)  reactor metal loading, kg\(\text{Pd}/m^3\)

\( \sigma \)  surface tension, N/m

\( \omega \)  pulsing frequency (2\(\pi f\), rad/s

\textit{dimensionless numbers}

\( \text{Ca} \)  Capillary number (=\(\mu u_T \rho_c /\sigma\))

\( \text{Re} \)  Reynolds number (=\(\rho u_L d_{ch}/\mu\))

\( \text{Sc} \)  Schmidt number (=\(\mu/\rho D\))

\( \text{Sh} \)  Sherwood number (=\(kL/D\))

\textit{subscripts:}
\begin{tabular}{ll}
\textit{b} & bubble \\
\textit{c} & catalyst \\
\textit{ch} & channel \\
\textit{film} & film \\
\textit{G} & gas \\
\textit{H} & hydrogen \\
\textit{I} & impeller \\
\textit{L} & Liquid \\
\textit{min} & minimum \\
\textit{GL} & gas-liquid \\
\textit{GS} & gas-solid \\
\textit{LS} & liquid-solid \\
\textit{obs} & observed \\
\textit{ov} & overall \\
\textit{S} & solid \\
\textit{TP} & two phase \\
\textit{slug} & slug \\
\textit{surf} & surface \\
\textit{UC} & unit cell \\
\end{tabular}
Chapter 7 Partial Hydrogenation of Soybean Oil in a Piston Oscillating Monolith Reactor

7.1 Introduction

The heterogeneous catalyzed hydrogenation of edible oils has long been an important process for the food industry, because it provides improved resistance to oxidation and better textural properties (e.g., a higher melting point). This reaction is traditionally carried out in a three-phase agitated tank at 0.1-0.7 MPa and 150-200°C using a Ni-based catalyst present as a slurry. While Ni-based catalysts are prevalent in industrial applications, supported Pd catalysts have also been investigated because of their higher activity, allowing for lower catalyst loadings and temperatures. Several continuous flow laboratory reactors have also been studied for this reaction, such as trickle beds, tubular reactors, and bubble columns. Winterbottom et al. showed a packed bubble column exhibited less trans product formation than a slurry bubble column, possibly due to a more plug-like flow pattern. Boger et al. noted a similar selectivity effect for soybean oil hydrogenation with a monolithic catalyst, compared to a slurry stirred tank, but they attributed this effect to differences in mass transfer.

While a high catalyst activity is desired, the selectivity to the intermediate mono- and diunsaturated triglycerides in the serial hydrogenation pathway is also important. The reaction has historically been operated in the external gas mass transfer-limited regime to avoid excessive hydrogenation. Furthermore, recent health concerns regarding the adverse effects of trans fatty acids (TFA) on LDL/HDL cholesterol ratios has spurred research into minimizing the formation of TFAs. Naturally occurring soybean oil has no trans-fat content and so the formation of TFAs is the result of stereoisomerization. Previous work has shown that a higher hydrogen concentration on the catalyst surface lowers the rate of TFA formation. The easiest way to increase the surface H$_2$ concentration is by increasing the H$_2$ pressure and the rate of agitation.
Unfortunately, this will in turn worsen the serial pathway selectivity, promoting the formation of saturates.

The effects of intraparticle mass transfer limitations have also been investigated. It has been shown that both the serial pathway selectivity and the stereoselectivity decrease when the reaction is pore diffusion-limited with respect to the triglycerides,\textsuperscript{173,174} under these conditions the partially hydrogenated triglycerides diffuse more slowly from the pores, giving them more opportunity to react further.\textsuperscript{163} Intraparticle diffusion limitations with respect to hydrogen have the opposite effect and improve selectivities by decreasing the pore average hydrogen pressure.\textsuperscript{175}

While agitated tank slurry reactors are now common for this process, it would be beneficial if a structured catalyst could be used instead, obviating an additional separation step. The presence of catalyst particles or dissolved transition metal is particularly troublesome for a food product. Previous work on three-phase structured reactors has shown they are a viable alternative for gas mass transfer-limited reactions such as hydrogenations.\textsuperscript{89,176} The two most common such systems are monoliths operated in the slug (Taylor) flow regime and trickle beds. Boger et al.\textsuperscript{68} did an economic evaluation of a process where a monolith reactor is used for the hydrogenation of edible oil, and showed cost reductions up to 40% can be achieved when compared to the conventional slurry reactor process. Monolith reactors in slug flow show improved surface wetting compared to trickle beds, which are known to suffer from rivulet formation and radial gradients in liquid concentrations at the catalyst external surface.

Improvements in trickle bed performance are possible when inducing pulsed flows, through the periodic modulation of the liquid feed flow.\textsuperscript{17,18,44,147,149,150,177} By alternating between gas- and liquid-rich conditions over the surface of the catalyst, the gradients in the gaseous reactant’s concentration can be reduced and the rate of mass transfer increased. Catalyst
monolith reactors exhibit alternating gas and liquid slugs passing over the catalyst surface, with the hydrodynamics approaching plug flow. However, the liquid phase reactants used in these systems have typically been characterized by low molecular weights and viscosities. Therefore, the logical extension of soyoil hydrogenation to a structured catalytic system is complicated by the higher viscosity and its effect on the mass transfer. One MRI study has shown that a sucrose solution with twice the viscosity of water increases the film thickness surrounding gas slugs in monoliths, presumably reducing mass transfer.

A piston oscillating monolith reactor (POMR) has previously been used to show activity enhancements of up to 84% and equal or better selectivity for the hydrogenation of alpha-methyl styrene (AMS) to cumene, compared to a stirred tank reactor at the same conditions. These improvements result from low frequency/amplitude oscillations that enhance external gas mass transfer to the surface, while also controlling the surface wetting phenomena. The liquid films are apparently reduced in thickness for at least part of the cycle. This work is an extension of the oscillating reactor system, exploring a more complex reacting system of higher viscosity and more possible products than present in the AMS hydrogenation work.

7.2 Experimental

7.2.1 Catalyst Preparation

The Pd/γ-Al₂O₃ catalyst was prepared by an ion-exchange technique. Pseudoboehmite (UOP V-250) was first calcined at 500°C in flowing air to de-hydroxylate it to the gamma phase. The Pd precursor used was PdCl₂. This was converted to Pd(NH₃)₄(NO₃)₂ by dissolving in excess NH₄OH and NH₄NO₃ at a pH of 11. Excess Cl⁻ was removed from this solution by contacting with an ion exchange resin (Amberlite IRA-400, Rohm and Haas). The solution was then contacted with γ-Al₂O₃ at a temperature of 60°C overnight. The sample was filtered, dried at 80°C and then calcined at 500°C in flowing air. The impregnation step was repeated two more
times with drying and calcination steps performed in between. Finally, the catalyst was reduced at 130°C in 10% H₂/N₂. This gave a final Pd loading of 0.5 wt% by ICP-AES analysis. The catalyst had a BET surface area of 290 m²/g, a pore volume of 0.46 cm³/g and an average pore diameter of 10 nm. Dispersion measured by H₂ chemisorption was 74%.

The catalyst was washcoated on 200 cpsi cordierite monolith supports (5 x 5 x 1.2 cm, 0.13 cm channel diameter) from an aqueous slurry of 25 wt% solids, maintained at pH 3.5-4 by the addition of 0.1 M HNO₃. The slurry was ball milled for 90 min before the washcoating in order to lower the average alumina particle size to <10 µm, as confirmed by SEM. The bare monoliths were dipped in the slurry, and compressed air was used to clear any blocked channels. The coated monolith was dried in air at 90°C and then calcined at 500°C in flowing air before being reduced again at 130°C in 10% H₂/N₂. The final coating thickness was ~100 µm.

7.2.2 Reactor Tests

An Autoclave Engineers Zipperclave (500 mL) agitated tank reactor was used for comparison purposes. The reactor was equipped with a 3-bladed marine propeller. The reactor was charged with 350 mL soybean oil (Soy Beginnings manufactured by Thumb Oilseed Producer's Cooperative, bleached, refined, de-odorized) and catalyst (either as a powder or a submerged monolith), and then it was purged to remove air. The reactor was brought to temperature under mild stirring and ~0.1 MPa H₂. Once the reactor attained the operating temperature the system was pressurized and the agitator set to the desired rate. This represented the start of a run. Samples were periodically obtained from a dip tube.

The POMR consists of three catalyst-coated monoliths separated by customized cross-flow heat exchangers arranged in a “sandwich” arrangement above a gas distributor (Figure 7.1). This assembly seats in a 1 L stainless steel square vessel. The H₂ is distributed in upflow through the monoliths and recycled using a gas booster. The gas booster is a positive displacement pump
with its own oscillatory frequency of 0.5 Hz. A superficial gas velocity of 17.5 cm/s was maintained using the recycle loop. Beneath the monolith/distributor stack is a piston/cam arrangement that allows for a maximum of 25.4 mm amplitude and 0-50 Hz frequency. Experiments were performed at frequencies of 0-17.5 Hz and amplitude 2.5 mm. A schematic of the entire system is shown in Figure 7.2.

![Figure 7.1 Schematic of the piston oscillating monolith reactor (POMR) reactor body.](image)

![Figure 7.2 Flowsheet for the POMR system.](image)
Previous work has shown this arrangement provides an oscillatory flow of both gas and liquid inside the monolith stack, as observed by high speed photography\textsuperscript{178} (Figure 7.3). It has also been shown that this arrangement allows for a more homogenous gas distribution and higher interfacial areas due to enhanced bubble breakage. The reactor is operated in semibatch mode as additional H\textsubscript{2} is allowed to enter the reactor to account for consumption. The POMR was charged with 1 L of soybean oil and brought to temperature under 0.1 MPa of H\textsubscript{2}. It was then pressurized and the oscillations started, marking the beginning of a run.

Figure 7.3 One complete cycle of oscillation, air-water in monolith mock-up assembly with oscillation: 121 channels (11x11) each 1.59mm diameter; Amplitude = 2.46 mm; Frequency = 2 Hz; Gas superficial velocity = 6.2 cm/s.
7.2.3 Analysis

Samples from the reactors were analyzed using gas chromatography (HP 5890) equipped with a FID and a SP-2560 (Supelco) capillary GC column (100 m x 0.25 mm). The GC was operated isothermally with an oven temperature of 200°C. Reactor samples were first converted to their corresponding fatty acid methyl esters (FAMEs) using IUPAC method II.D.19. Chromatograms were analyzed both for degree of saturation of the FAMEs (Cxx:y, where xx is the alkyl group chain length and y is the number of double bonds) and for trans/cis conformations. Positional isomers were lumped together.

The overall degree of oil unsaturation was measured in terms of iodine value (IV), calculated using IUPAC method II.D.7 and Equation 7.1.

\[
IV = \frac{12.69 \cdot N \cdot (V_0 - V_s)}{m}
\]  

(7.1)

where \( N \) is the normality of sodium thiosulphate titrating solution, \( V_0 \) is the titration volume of this solution for a blank, \( V_s \) is the titration volume for the sample, and \( m \) is the mass of the oil sample.

![Figure 7.4 Composition of oil as a function of reaction time in stirred tank. Conditions: T = 110 °C, P = 0.4 MPa, 2000 rpm, 1 g of 0.5% Pd/Al₂O₃ powdered catalyst.](image)
7.3 Results and Discussion

Figure 7.4 shows a graph of oil composition changing with respect to time during a typical run. Figure 7.5 shows a graph of $IV$ vs. time for a typical run. The overall reaction rate (rate of hydrogen consumption, $r_{H_2}$) was calculated from the $IV$ measurements. $IV$ represents the grams of Iodine required to saturate all double bonds in 100 g of oil. The number of moles of $H_2$ required to decrease the $IV$ of soy oil by an amount $\Delta IV$ is:

$$N_{H_2} = \frac{\Delta IV}{100} \times \frac{\rho_{oil}}{\text{Mol.Wt.} I_2} \left[ \frac{mol}{m^3} \right]$$  \hspace{1cm} (7.2)

Using Equation 7.2, the rate of hydrogen consumption can be calculated as:

$$r_{H_2} = N_{H_2} \times \frac{V}{W_{pd} \Delta t} \left[ \frac{mol}{g_{pd}.\text{min}} \right]$$  \hspace{1cm} (7.3)

where $V$ is the volume of reaction mixture, $W_{pd}$ is the weight of the active metal (Pd) in the catalyst, and $\Delta t$ is the time over which $\Delta IV$ was measured. The rate $r_{H_2}$ was calculated based on the first two data points of a run. As seen in Figure 7.4 the decrease in the slope is gradual. Therefore the rate of $H_2$ consumption we report is the maximum observed rate for the batch reaction.

Figure 7.5 Plot of iodine value ($IV$) vs. time in stirred tank. Conditions: $T = 110 \degree C$, $P = 0.4$ MPa, 2000 rpm, 1 g of 0.5% Pd/Al$_2$O$_3$ powdered catalyst.
Alternatively, the rate of hydrogen consumption can be obtained from the change in the concentration of the individual oil components as monitored by GC. The hydrogenation reactions can be represented as:

\[
\begin{align*}
\text{C18:3} & \xrightarrow{k_3} \text{C18:2} \\
\text{C18:2} & \xrightarrow{k_2} \text{C18:1} \\
\text{C18:1} & \xrightarrow{k_1} \text{C18:0}
\end{align*}
\]  

(7.4)

Let the concentration of individual component C18:X be represented as \( C_{Xi} \), where \( i \) is the sample number. Considering the serial reaction pathway and stoichiometry, the hydrogen consumption \( (N_{H_2}) \) can be calculated as:

\[
N_{H_2} = (C_{10} - C_{11}) + 2(C_{20} - C_{21}) + 3(C_{30} - C_{31})
\]

(7.5)

A detailed derivation of Equation 7.5 is presented in Appendix C. Once \( N_{H_2} \) is calculated, the overall rate of hydrogen consumption was obtained from Equation 7.3 as before.

Selectivities were computed based on the kinetic model of a serial hydrogenation pathway as shown in Equation 7.4. The selectivities are defined as:

\[
S_{32} = \frac{k_3}{k_2} \quad \text{and} \quad S_{21} = \frac{k_2}{k_1}
\]

(7.6)

The rate constants \( k_1, k_2, \) and \( k_3 \) were obtained by fitting the concentration vs. time data for all of the components. Let the concentration of C18:X be denoted \( C_x \). Then according to Equation 7.4, the differential equations for the concentrations become:

\[
\begin{align*}
\frac{dC_3}{dt} &= -k_3C_3 \\
\frac{dC_2}{dt} &= k_3C_3 - k_2C_2 \\
\frac{dC_1}{dt} &= k_2C_2 - k_1C_1 \\
\frac{dC_0}{dt} &= k_1C_1
\end{align*}
\]

(7.7) - (7.10)
Equation 7.10 is not used in the calculation of rate constants because it is not independent. The differential forms of Equations 7.7-7.9 are not desirable for the calculation of the selectivities; we smoothed the data through integration, in the process algebraically combining Equations 7.7-7.9 as shown below.

\[
[C_1 + C_2 + C_3]_t - [C_1 + C_2 + C_3]_0 = \frac{k_1}{k_2} \int_0^t \left( \frac{C_1}{C_2} \right) d(C_2 + C_3) \tag{7.11}
\]

\[
[C_2 + C_3]_t - [C_2 + C_3]_0 = \frac{k_2}{k_3} \int_0^t \left( \frac{C_2}{C_3} \right) dC_3 \tag{7.12}
\]

We are more interested in the selectivities than the actual rate constants, and these selectivities are obtained as the inverse slopes of Equations 7.11 and 7.12.

### 7.3.1 Observed Catalyst Activities

The soy oil hydrogenation rate was measured in the POMR at pulsing frequencies of 0, 8, and 17.5 Hz, keeping other operating parameters constant at \( T = 110 \, ^\circ\text{C} , P = 0.41 \, \text{MPa} \). While the rates shown in Figure 7.6 were calculated from \( IV \) measurements, we found that rates calculated from concentration data were in good agreement. Figure 7.6 shows that the reaction rate increases with the frequency of oscillation. Enhancements of >100% can be achieved with 17.5 Hz vibrations, as compared to no forced vibrations. It should be noted that when no piston oscillations are applied to the reactor, the system is still subjected to inherent low frequency (0.5Hz) and amplitude vibrations, due to the pulsation of the gas booster in the \( \text{H}_2 \) recycle loop. Previously it has been also reported that oscillations cause pressure fluctuations in the reactor.\(^{178}\)

The standard deviation of the changing pressure for various frequencies is listed in Table 7.1.

For comparison purposes, soy oil hydrogenation was also carried out in a stirred vessel using the same type of monolithic catalyst as in the POMR and under identical temperature (110°C) and pressure (0.41 MPa) conditions. From Figure 7.6 it can be seen that the reaction rate
in the stirred tank was substantially lower than in the POMR even without forced oscillations. These higher rates can be attributed to higher rates of mass transfer, as will be shown subsequently.

![Graph]

Figure 7.6 Effect of frequency on hydrogenation rate in the POMR, 0.5% Pd/Al₂O₃ on monolith catalyst. Stirred tank data shown for comparison. Conditions: T = 110 °C, P = 0.4 MPa, A = 2.5 mm.

Table 7.1 Summary of pressure data and power input for POMR.

<table>
<thead>
<tr>
<th>f</th>
<th>Pᵥ</th>
<th>Avg. pressure</th>
<th>Pressure std. deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hz</td>
<td>W/m³ x 10⁻³</td>
<td>MPa</td>
<td>MPa</td>
</tr>
<tr>
<td>0.5</td>
<td>1.47</td>
<td>0.41</td>
<td>0.04</td>
</tr>
<tr>
<td>8</td>
<td>1.81</td>
<td>0.40</td>
<td>0.07</td>
</tr>
<tr>
<td>17.5</td>
<td>5.05</td>
<td>0.43</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Equivalent power input per unit volume (Pᵥ) is a commonly used criterion for comparing two different reactor systems. For the POMR, Pᵥ was calculated (Equation 7.13) as shown in previous work.¹²³ This Pᵥ was then used to find the corresponding agitated tank rpm at identical Pᵥ using the correlation of Pandit et al.¹⁵⁵ for a stirred tank with a marine propeller and no gas sparger (Equation 7.14).
\[ P_v = \rho \omega \left( g u_d + \frac{A^2 \omega^3}{2} \right) \quad (7.13) \]

\[ P_v = N_o \rho L N_i^3 d_i^5 \quad (7.14) \]

At 8 Hz and 2.5 mm amplitude, \( P_v = 1.81 \times 10^3 \text{ W/m}^3 \) (Table 7.1), which is equivalent in power to the agitated tank operated at 520 rpm. When the corresponding reaction rates are compared, it is seen that the rate in the POMR is about three times higher than the rate in the agitated tank at an equivalent power input. To understand the effect of agitation speed on the reaction rate in the stirred tank, an additional experiment was carried out at 2000 rpm. No difference was observed in the reaction rate at 2000 rpm, compared to 520 rpm. This observation suggests that the reaction is not externally mass transfer-controlled in the stirred tank at typical operating conditions for the monolith catalyst.

### Table 7.2 Summary of results obtained in stirred tank reactor

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>RPM</th>
<th>Mean size, diameter or thickness</th>
<th>( r_{H_2} ) (conc) mol/gpd.min</th>
<th>( r_{H_2} ) (IV) mol/gpd.min</th>
<th>( \Phi_{WP/H_2} )</th>
<th>( \Phi_{WTAG} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolith</td>
<td>110</td>
<td>0.41</td>
<td>2000</td>
<td>100</td>
<td>0.21</td>
<td>0.21</td>
<td>10</td>
<td>3.06</td>
</tr>
<tr>
<td>Monolith</td>
<td>110</td>
<td>0.41</td>
<td>520</td>
<td>100</td>
<td>0.19</td>
<td>0.23</td>
<td>11</td>
<td>3.30</td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.41</td>
<td>2000</td>
<td>38</td>
<td>4.7</td>
<td>5.0</td>
<td>0.97</td>
<td>0.29</td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.41</td>
<td>2000</td>
<td>63</td>
<td>4.5</td>
<td>3.9</td>
<td>2.1</td>
<td>0.63</td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.41</td>
<td>2000</td>
<td>166</td>
<td>3.3</td>
<td>3.3</td>
<td>12</td>
<td>3.70</td>
</tr>
<tr>
<td>Powder</td>
<td>110</td>
<td>0.69</td>
<td>2000</td>
<td>63</td>
<td>8.8</td>
<td>8.8</td>
<td>4.7</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Additional experiments were performed using a powdered catalyst to discern the governing rate-limiting mechanism. The effect of catalyst particle size on the observed reaction rate was studied. The results of these experiments are summarized in Table 7.2. Hydrogen consumption rates obtained by both methods (IV and concentration data) are shown in the table and it is seen that the rates obtained by both methods are in reasonable agreement.
It was observed that the increasing particle diameter results in decreasing reaction rates. This suggests that the rate was limited by the intraparticle resistance to diffusion. For a reaction of arbitrary kinetics, the rate at constant temperature and bulk fluid concentrations should be inversely proportional to the characteristic pore diffusion length at high Thiele modulus. For spherical particles this characteristic pore diffusion length, L, can be taken as \( \frac{d_p}{6} \), while for the slab-like monolith-supported catalyst L corresponds to the washcoat thickness. A plot of \( r_{H_2} \) vs. \( L^{-1} \) (Figure 7.7) shows that the assumption of high Thiele modulus for the monolith looks correct, while for the smallest particle size we are approaching the true intrinsic kinetic rate of reaction.

![Figure 7.7 Effect of diffusion length on the rate of reaction.](image)

To verify this hypothesis, Weisz-Prater moduli\(^{180} \) for both the hydrogen and triglyceride reactants were calculated based on the observed reaction rates:

\[
\Phi_{_{WP_H2}} = \frac{(R_{H_2} \rho_c)_\text{obs} L^2}{D_{eH_2} C_{H_2}^s} \tag{7.15}
\]

\[
\Phi_{_{WP_{TAG}}} = \frac{(R_{H_2} \rho_c)_\text{obs} L^2}{D_{eTAG} C_{TAG}} \tag{7.16}
\]
where $R_{H_2}$ is the observed rate of hydrogen consumption in mol/g cat·s, $\rho_c$ is the catalyst density (833 g/L), $C_{H_2}^s$ is the concentration of hydrogen at the catalyst surface, which was assumed to be equal to the saturation concentration of hydrogen. It will be shown subsequently that this assumption is valid. The saturation concentration for H$_2$ was taken from solubility data for H$_2$ in cottonseed oil ($C_{H_2}^s = 1.25 \times 10^{-2} \text{mol/L}$).\textsuperscript{175} The concentration of triglycerides, $C_{TAG}$, was calculated from the density and average molecular weight of soy oil. $D_{ei}$ is the effective pore diffusivity of compound $i$:

$$D_{ei} = \frac{D_i \varepsilon_c}{\tau} \quad (7.17)$$

Due to lack of data, the molecular diffusivity of H$_2$ in soy oil ($D_{H_2}$) was assumed similar to its diffusivity in cottonseed oil ($= 12 \times 10^{-5}$ cm$^2$/s at 110 °C).\textsuperscript{181} Similarly, the molecular diffusivity of trioleate in cottonseed oil was used ($D_{TAG} = 1.2 \times 10^{-6}$ cm$^2$/s).\textsuperscript{181} The porosity $\varepsilon_c$ was determined from N$_2$ adsorption data, while the tortuosity $\tau$ was taken as 3, a typical value for this type of catalyst.\textsuperscript{182} Calculated values of the Weisz-Prater moduli are shown in Table 7.2. It can be seen that for the smallest size particle both Weisz-Prater moduli are $< 1$, suggesting effectiveness factors near 1. For the monolith catalyst, both moduli are $>>1$, suggesting strong intraparticle resistances to mass transfer. For the intermediate-sized particles, we are in the transition region between intrinsic kinetics control and large intraparticle resistances. This is qualitatively in agreement with the results in Figure 7.7.

These results are also in agreement with previous work showing that it is difficult to completely eliminate intraparticle diffusion limitations in the hydrogenation of triglycerides. Veldsink\textsuperscript{175} claimed that even at particle diameters as small as 12 μm, pore diffusion limitations occur in the hydrogenation of methyl linoleate over Pd/C catalysts. In the present work,
\( \Phi_{WPTAG} / \Phi_{WPH} \) (see Table 7.2) is around ~0.5, which is in agreement with observations made by Jonker et al.\(^{183} \) on the ratio of Weisz-Prater moduli in the hydrogenation of mono-saturated edible oils.

It is known that the hydrogenation of soybean oil reaction is first order with respect to concentration of double bonds and first order with respect to hydrogen concentration.\(^{175} \) When reaction pressure, which corresponds to the hydrogen concentration, was increased from 0.41 MPa to 0.69 MPa we observed that the reaction rate based on concentration data changed from 4.5 to 8.8 mol/g\(_{Pd}\)·min for a constant catalyst particle size. It can be seen that rate increased 1.9 times when pressure was increased 1.7 times. Thus the observed reaction rate shows a first order dependence on hydrogen concentration. This provides further support for the assumption that the small powder catalyst is almost intrinsic in its activity.

The reaction rates obtained in the stirred tank reactor are comparable to those reported in the literature for Pd catalysts. Thomson and Winterbottom\(^{184} \) reported that for a silica-supported Pd catalyst, observed rates of ~1.5 mol/g\(_{Pd}\)·min were obtained in a stirred tank at 2000 rpm, 110 °C, 0.1 MPa for a catalyst of particle size 150 µm. This rate can be corrected for pressure assuming a first-order reaction with respect to hydrogen as discussed previously, giving a predicted reaction rate of 6.3 mol/g\(_{Pd}\)·min at 0.41 MPa, near our value for the smallest size Pd/Al\(_2\)O\(_3\) catalyst. A list of reaction rates from the literature using Pd catalysts is provided in Table 7.3.

**Table 7.3 Reaction rates for hydrogenation of soy oil (unless noted) over a Pd catalyst in a stirred tank. Rates are corrected for \( P = 0.41 \) MPa assuming first order kinetics with respect to \( H_2 \).**

<table>
<thead>
<tr>
<th>Investigator</th>
<th>( T ) °C</th>
<th>rpm</th>
<th>( d_p ) µm</th>
<th>Catalyst loading wt% Pd</th>
<th>( r_{H2} ) mol/g(_{Pd})·min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thomson and Winterbottom(^{184} )</td>
<td>110</td>
<td>2000</td>
<td>150</td>
<td>2.5</td>
<td>6.27</td>
</tr>
<tr>
<td>Parry and Winterbottom(^{183} )</td>
<td>160</td>
<td>-</td>
<td>-</td>
<td>2.2</td>
<td>0.11</td>
</tr>
<tr>
<td>Savchenko and Makaryan(^{186} ) (Sunflower oil)</td>
<td>102</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>2.95</td>
</tr>
</tbody>
</table>
7.3.2 Selectivity

As discussed earlier the selectivity and catalytic activity are equally important. Two serial pathway selectivities, $S_{32}$ and $S_{21}$ (Equation 7.6) and also the selectivity toward trans isomer formation were determined. Of the two serial pathway selectivities, $S_{21}$ is more important because it dictates saturate formation. Formation of saturated triglycerides is undesirable and so a high value of $S_{21}$ is desired. The selectivity results for the POMR and for the stirred tank are listed in Table 7.4.

**Table 7.4 Selectivities for POMR and stirred tank runs. All runs done at 110° C.**

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Catalyst</th>
<th>$f$</th>
<th>rpm</th>
<th>$P$</th>
<th>$d_p$</th>
<th>$S_{21}$</th>
<th>$S_{32}$</th>
<th>Trans fat at IV = 75</th>
</tr>
</thead>
<tbody>
<tr>
<td>POMR</td>
<td>Monolith</td>
<td>0</td>
<td>N.A.</td>
<td>0.41</td>
<td>100</td>
<td>8.7</td>
<td>1.4</td>
<td>0.42</td>
</tr>
<tr>
<td>POMR</td>
<td>Monolith</td>
<td>8</td>
<td>N.A.</td>
<td>0.41</td>
<td>100</td>
<td>11.8</td>
<td>2.0</td>
<td>0.42</td>
</tr>
<tr>
<td>POMR</td>
<td>Monolith</td>
<td>17.5</td>
<td>N.A.</td>
<td>0.41</td>
<td>100</td>
<td>10.8</td>
<td>2.5</td>
<td>0.39</td>
</tr>
<tr>
<td>Stirred tank</td>
<td>Monolith</td>
<td>N.A.</td>
<td>2000</td>
<td>0.41</td>
<td>38</td>
<td>14.8</td>
<td>1.6</td>
<td>0.26</td>
</tr>
<tr>
<td>Stirred tank</td>
<td>Powder</td>
<td>N.A.</td>
<td>2000</td>
<td>0.69</td>
<td>63</td>
<td>9.9</td>
<td>1.4</td>
<td>0.25</td>
</tr>
</tbody>
</table>

For the POMR, we observed increases in selectivity with respect to frequency for $S_{21}$ and $S_{32}$, the latter being more marked. Figure 7.8 shows a plot of $S_{21}$ vs. the characteristic diffusion length scale. It can be seen that within the experimental error, $S_{21}$ does not change with diffusion length. For linoleate hydrogenation over 1wt% Pd/C (T = 121°C, P = 0.31 MPa), Cordova and Harriot\(^{173}\) has shown $S_{21}$ attains a constant value for length scales larger than 10 $\mu$m. Data from Cordova and Harriot\(^{173}\) is also plotted in Figure 7.8 for comparison purposes. They showed that $S_{21}$ decreases for diffusion lengths between 2-10 $\mu$m due to the intraparticle concentration gradients of the triglycerides, in agreement with theory for series reactions in pores\(^{180}\). Figure 7.8 also shows that the selectivity $S_{21}$ for a monolith catalyst in a stirred tank is similar to the
selectivities obtained with a POMR. This suggests that $S_{21}$ is more dependent on catalytic chemistry than pore structure. For the stirred tank runs, $S_{32}$ remained constant with increasing particle diameter, to within the precision of the data.

![Figure 7.8 Selectivity $S_{21}$ as a function of characteristic length scale of the catalyst.](image)

Trans fatty acid production was higher for the monolith catalyst irrespective of the reactor system. The monolith catalyst showed a trans fatty acid content ~40% as opposed to ~28% for a powder catalyst at similar operating conditions. This behavior can be attributed to both the higher internal diffusion resistance (with a larger catalyst) and differences in overall observed reaction rates. Veldsink\cite{175} claimed that the increase in observed reaction rate (either by increasing stirrer speed or by increasing hydrogen partial pressure) results in a decrease in trans fatty acid formation. However, that does not appear to be the case here as the rate more than doubled in the POMR with only a slight decrease in the trans product concentration observed. More data are necessary to come to a definite conclusion here.

### 7.3.3 Analysis of Mass Transfer

Hydrogenation of soy oil is kinetically “fast” at normal reaction conditions. It is to establish the effects of mass transfer on the observed rates of hydrogenation and on the selectivities. In the stirred tank, the catalyst surface is fully wetted and H$_2$ must dissolve in the
soy oil and then be transported through the liquid phase. The turbulence provided by the intense agitation results in a homogeneous bulk liquid with only a small boundary layer region near the catalyst. On the other hand, in monolith channels there are three external mass transfer steps for the transport of H₂ to the catalyst surface - gas to liquid, liquid to solid, and gas to solid\(^{89,176}\). Mass transfer coefficients for the individual steps were estimated through literature correlations that are listed in Table 7.5. A more detailed discussion of these mass transfer calculations can also be obtained from our previous work.\(^{178}\)

**Table 7.5 Correlations used to calculate mass transfer rates in catalyst monoliths, three-phase reactions.**

<table>
<thead>
<tr>
<th>Mass transfer step</th>
<th>Correlation</th>
<th>Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas to liquid through bubble cap</td>
<td>[ k_{GL}a_{GL} = \frac{0.111 \mu_{TP}^{1.2}}{e_{L}L_{UC}^{0.57}} ]</td>
<td>Bercic and Pintar (1997)(^ {14})</td>
</tr>
<tr>
<td>Liquid to solid</td>
<td>[ Sh = 20 \left( 1 + 0.003 \left( \frac{L_{UC}}{d_{ch}} \right)^{0.7} \right) ]</td>
<td>Kreutzer et al. (2001)(^ {13})</td>
</tr>
<tr>
<td>Gas to solid through liquid film</td>
<td>[ k_{GS} = \frac{D}{\delta} ]</td>
<td>Irandoust and Andersson (1989)(^ {12})</td>
</tr>
<tr>
<td></td>
<td>[ \delta = (d_{ch} - d_{b}) / 2 ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ \frac{d_{b}}{d_{ch}} = 0.64 + 0.36 \exp(-3.08Ca^{0.54}) ]</td>
<td></td>
</tr>
</tbody>
</table>

By combining these three steps the overall volumetric mass transfer coefficient \((k_{ov}a)\) can be determined as\(^ {13}\):

\[
k_{ov}a = k_{GS}a_{GS} + \left( \frac{1}{k_{GL}a_{GL}} + \frac{1}{k_{LS}a_{LS}} \right)^{-1}
\]  (7.21)
Using these equations, the values of the individual volumetric mass transfer coefficients were computed at the conditions of this study. The gas superficial velocity was fixed for all experiments based on the gas recycle rate. However, the liquid superficial velocity is a function of pulse frequency. The velocities are 45 and 97 cm/s at respective frequencies of 8 and 17.5 Hz. These values were calculated based on the volume of fluid displaced by each upward stroke per time and divided by the cross sectional area of the monolith channels. At pulsing conditions, the liquid hold up $\varepsilon_L$ is $\frac{u_L}{u_L + u_G}$, while at no pulsing conditions, the liquid superficial velocity was taken to be zero and the liquid hold up $\varepsilon_L$ as $1 - \frac{L_{slug}}{L_{ch}}$, with $L_{slug}$ taken as $3 \cdot d_{ch}$. The results are summarized in Table 7.6.

Increasing the frequency of the oscillations should result in increased mass transfer coefficients in the POMR, because the time-averaged superficial velocity of liquid in the monolith channels also increases, and because for at least part of the cycle (the upstroke of the piston) the liquid film thickness is small and gas flow dominates. This has been the typical explanation for the positive effects of pulsating flows on reaction rates. However, the results for soy oil hydrogenation in Table 7.2 and Figure 7.7 suggest that intraparticle transport is rate-limiting for the monolith catalyst. To further establish that external mass transfer is not the controlling resistance for the hydrogenation reaction, the external mass transfer rate of hydrogen was equated with the observed reaction rate as follows.

$$k_{m,\alpha}(C_{H_2}^* - C_{H_2}^s) = R_{H_2} \rho_{cc}$$ (7.22)

Here, $C_{H_2}^*$ is the solubility of hydrogen in soy oil, $C_{H_2}^s$ is the concentration of hydrogen at the catalyst surface and $\rho_{cc}$ is the catalyst loading expressed as kg of catalyst/ m$^3$ of reaction mixture volume. The hydrogen concentration at the catalyst surface was obtained from Equation
7.22 and the value of $C_{H_2}^* / C_{H_2}^*$ was calculated. From Table 7.6 it is seen that this ratio is close to unity and so again we conclude that the hydrogenation reaction in POMR is not external mass transfer controlled.

### Table 7.6 Results of mass transfer calculations for POMR.

<table>
<thead>
<tr>
<th>$f$ (Hz)</th>
<th>$u_L$ (cm/s)</th>
<th>$k_0a$ (1/s)</th>
<th>$C_{H_2}^* / C_{H_2}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.8</td>
<td>0.47</td>
<td>0.974</td>
</tr>
<tr>
<td>8</td>
<td>45</td>
<td>1.14</td>
<td>0.986</td>
</tr>
<tr>
<td>17.5</td>
<td>97</td>
<td>1.97</td>
<td>0.987</td>
</tr>
</tbody>
</table>

Similarly, it is possible to compute the ratio $C_{H_2}^* / C_{H_2}^*$ for the stirred autoclave. The overall volumetric mass transfer coefficient for the autoclave reactor was calculated using the correlation proposed by Albal et al.\textsuperscript{162}

\[
Sh = 1.41 \times 10^{-3} Sc^{0.5} Re_t^{0.67} We^{1.29}
\]  

(7.23)

where the Sherwood number is $Sh = \frac{k_La d_t^2}{D}$, and the other dimensionless quantities are defined as usual. Using Equation 7.23, $k_La$ was found to be $\sim 11$ s\textsuperscript{-1} at 2000 rpm. For the smallest catalyst size, this gives $C_{H_2}^* / C_{H_2}^* = 0.99$. This shows that the reaction is not external transport-limited in stirred tank either, as the intraparticle resistance scales more strongly with catalyst size. In summary, these calculations corroborate our earlier conclusion that the reaction is internally diffusion-limited for practical sizes of the catalyst, regardless of the reactor.

Although the reaction is not externally mass transfer-limited in the POMR, the frequency of pulsation does affect the observed rate of reaction. It has been shown that the reaction is internally diffusion-limited. Therefore it can be concluded that the forced pulsing either affects the intra-pore transport, or the wetting distribution of the reactants on the catalyst (i.e., some of
the catalyst is contacted by gas phase H₂). The relatively high viscosity and low surface tension of the soy oil argues against the latter. Recently Bakker et al. showed that alternating flow of gas bubbles and liquid slugs in a monolith can enhance internal convective diffusion in a macroporous structured catalyst. They used a honeycomb monolith structure made up of interlocked elongated mullite grains with interstitial voids of ~45 µm size. The silica used for the coating had an average pore size of 4.2 µm. They did not investigate the effect of frequency of the alternating gas-liquid slug flow.

In a previous study, Chandhok et al. achieved up to two orders of magnitude enhancement in \( k_{L,a} \) with pulsating flow through a liquid membrane, at frequencies in the 1 Hz range. Leighton and McCready explained that the enhancement of transport in membranes due to oscillating flows can result from enhanced Taylor dispersion in the pores, and that these effects can explain the enhancements observed in liquid membrane transport. They proposed that the transport enhancement in pores is a function of Womersley number \( \alpha = r(\omega / \nu)^{0.5} \) (\( r \) is pore radius) and Schmidt number \( Sc = \nu / D_e \) as shown in Equation 7.24.

\[
\frac{K}{D_e} = 1 + \left( \frac{\Delta x}{r} \right)^2 \left( 1 - \frac{4}{\beta} \frac{T_1(\beta)}{T_2(\beta)} \right)
\]  

(7.24)

where

\[
\beta = \alpha Sc^{0.5}
\]

\[
T_1(\beta) = \text{ber} \beta \text{ ber}' \beta + \text{bei} \beta \text{ bei}' \beta
\]

\[
T_2(\beta) = \text{ber} \beta \text{ bei}' \beta + \text{ber}' \beta \text{ bei} \beta
\]

\( K \) is the apparent diffusion coefficient due to pulsations, \( \Delta x \) is the amplitude of fluid pulsation penetrating inside the pores and the functions \( \text{ber} \beta \) and \( \text{bei} \beta \) are Kelvin functions, related to the Bessel function \( I_0 \) by \( I_0(\beta i^{-1/2}) = \text{ber} \beta + i \text{bei} \beta \). This equation is only valid for a limiting case of \( \alpha \to 0 \) and \( Sc \to \infty \), but \( \beta \) is of order one. For this study, \( \alpha \sim 10^{-5}, Sc \sim 10^4 \), and \( \beta \sim 0.1 \).
Using the above equation, enhancements in pore transport were calculated for our case. Values of macropore radius \(r\), macroporosity, and other parameters were obtained from SEM images of washcoated monoliths, which showed an average radius of interstitial pores (10 \(\mu\)m) and smaller interstitial pores (1 \(\mu\)m). To obtain the upper and lower bounds, two extremes were considered for \(\Delta x\). The largest possible value of \(\Delta x\) was taken as the product of washcoat thickness and tortuosity which gives a value of 300 \(\mu\)m. The conservative estimate was obtained by assuming that fluid is only able to penetrate to a distance of one tenth of the washcoat thickness (\(\Delta x = 30 \mu m\)).

Calculated values of the transport enhancement, \(K/D_e\), for the combination of two different pore radii and two different \(\Delta x\) values are reported in Table 6.7. Enhancements were calculated for 8 Hz, 17.5 Hz and also for 0.5 Hz which is the true frequency at no forced pulsing conditions due to the gas recycle booster. The values of \(K/D_e\) for \(r = 10 \mu m\) and \(\Delta x = 30 \mu m\) are of the order one, which is more likely to be the case in the POMR. The listed enhancements, \(K/D_e\), are relative to a true run at 0 Hz. Since in the present work the smallest frequency was 0.5 Hz and the observed improvement in the performance is relative to this frequency, the ratio \((K/D_e)_{fHz} / (K/D_e)_{0.5Hz}\) (keeping \(r\) and \(\Delta x\) values constant) represents the true performance enhancement in the POMR. For \(r = 10 \mu m\) and \(\Delta x = 30 \mu m\), this ratio is 1.8 and 1.9 for 8 and 17.5 Hz respectively. These values can be compared to the ratio of reaction rates obtained in the POMR, namely 1.3 and 2.1 mol/gPd·min for 8 and 17.5 Hz. The enhancement theory results scale qualitatively with the experimental observations. With better estimates of \(r\) and \(\Delta x\), it might be possible to theoretically better predict the enhancements observed in the POMR.

The present work suggests that significant enhancements to pore diffusion/convection can be achieved in the catalyst washcoat. The pulsations are propagated into the pore space, at least to some extent. It was also shown by Leighton and McCready\(^{25}\) that the smaller the pore
diffusivity and the larger the ratio of amplitude to pore size, the greater the enhancement. This result suggests that for the reactions of even heavier molecules the POMR would be an ideal reactor. But further investigation is required to systematically discern the effects of pulse frequency and amplitude on internal diffusion in the POMR.

<table>
<thead>
<tr>
<th>$f$</th>
<th>$r$</th>
<th>$\Delta x$</th>
<th>$K/D_e$</th>
<th>$(K/D_e)_{0.5 Hz}$</th>
<th>$(K/D_e)_{10 Hz}$</th>
</tr>
</thead>
<tbody>
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<td>µm</td>
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<td></td>
<td></td>
</tr>
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<td>3.6</td>
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</tr>
</tbody>
</table>

7.4 Conclusions

It was shown that by using low frequency and low amplitude mechanical oscillations, up to a 112% enhancement in the hydrogenation rate of soybean oil can be achieved in the POMR. On a power per unit volume basis, the POMR performs better than a stirred tank with an identical monolith catalyst. Experiments with a powdered catalyst having a shorter diffusion length showed higher reaction rates in the stirred tank. Experimental observations confirmed by Weisz-Prater moduli calculations showed that the reaction is intraparticle diffusion limited for larger catalyst sizes including the monolith. External mass transfer calculations showed that the reaction is not external mass transfer controlled. Due to higher intraparticle diffusion resistances, the monolith catalyst (in both the stirred tank and the POMR) exhibited smaller serial pathway selectivity ($S_{32}$ and $S_{21}$), towards the formation of monounsaturated and diunsaturated fatty acids.
Formation of trans fatty acids was also higher in a monolith catalyst as compared to the powdered catalyst. A theory proposed by Leighton and McCready\textsuperscript{25} was used to calculate the transport enhancement in the monolith catalyst washcoat. The theoretical predictions were in agreement with experimental observations. The current work suggests that it is possible to achieve internal transport enhancements in the washcoat using low amplitude and low frequency pulsation in the fluid.

### 7.5 Nomenclature

- \( a \) interfacial area, m\(^2\)/m\(^3\)
- \( A \) piston amplitude, m
- \( C \) concentration, mol/m\(^3\)
- \( C^* \) saturation concentration, mol/m\(^3\)
- \( d \) diameter, m
- \( D \) molecular diffusivity, m\(^2\)/s
- \( D_e \) effective diffusivity, m\(^2\)/s
- \( f \) pulsing frequency, 1/s
- \( g \) gravitational constant, m/s\(^2\)
- \( IV \) iodine value, dimensionless
- \( k \) rate constant, 1/min
- \( K \) apparent diffusivity, m\(^2\)/s
- \( L \) characteristic length scale, m
- \( m \) mass of sample, g
- \( N \) Normality, mol/L
- \( N_I \) impeller speed, 1/s
- \( N_o \) impeller constant (0.8 for marine propeller), dimensionless
- \( N_{H2} \) moles of H\(_2\) consumed per unit volume, mol/m\(^3\)
\begin{align*}
P & \quad \text{pressure, MPa} \\
P_v & \quad \text{Power per unit volume, kg/(m\cdot s^3)} \\
r & \quad \text{pore radius, m} \\
r_{\text{H}_2} & \quad \text{rate of hydrogen consumption, mol/(g_{\text{Pd}}\cdot \text{min})} \\
R_{\text{H}_2} & \quad \text{rate of hydrogen consumption, mol/(g_{\text{cat}}\cdot \text{s})} \\
R & \quad \text{gas constant, J/(K\cdot \text{mol})} \\
S & \quad \text{selectivity, dimensionless} \\
S_a & \quad \text{catalyst surface area, m}^2/\text{m}^3 \\
t & \quad \text{time, s} \\
T & \quad \text{temperature, K} \\
T_1, T_2 & \quad \text{function shown in equation 7.24, dimensionless} \\
u & \quad \text{superficial velocity, m/s} \\
V & \quad \text{reaction mixture volume, m}^3 \\
V_0 & \quad \text{titration volume for blank test, ml} \\
V_s & \quad \text{titration volume for sample, ml} \\
W & \quad \text{weight, g} \\
\Delta x & \quad \text{amplitude of fluid pulsation, m} \\
greek letters: \\
\alpha & \quad \text{Womersley number, dimensionless} \\
\beta & \quad = \alpha \cdot Sc^{0.5}, \text{ dimensionless} \\
\delta & \quad \text{liquid film thickness, m} \\
\varepsilon & \quad \text{hold-up, dimensionless} \\
\varepsilon_c & \quad \text{catalyst porosity, dimensionless} \\
\eta & \quad \text{effectiveness factor, dimensionless}
\end{align*}
$\Phi_{wp}$  Weisz-Prater modulus, dimensionless

$\mu$  viscosity, Pa·s

$\nu$  kinematic viscosity, m$^2$/s

$\rho$  density, kg/m$^3$

$\rho_{cc}$  catalyst loading, kg/m$^3$

$\sigma$  surface tension, N/m

$\tau$  tortuosity, dimensionless

$\omega$  pulsing frequency (2$\pi$f), rad/s

*dimensionless numbers:*

$\text{Ca}$  Capillary number ($= \frac{\mu u_{TP}}{\sigma}$)

$\text{Re}$  Reynolds number ($= \frac{\rho u_L d_{ch}}{\mu}$)

$\text{Re}_i$  impeller Reynolds number ($= \frac{\rho N_id_i^2}{\mu}$)

$\text{Sc}$  Schmidt number ($= \frac{\mu}{\rho D}$)

$\text{Sh}$  Sherwood number ($= \frac{kL}{D}$)

$\text{We}$  Weber number ($= \frac{\rho N_i^2 d_i^3}{\sigma}$)

*subscripts:*

$b$  bubble

c  catalyst

$ch$  channel

$\text{film}$  film

$G$  gas

$GL$  gas-liquid

$GS$  gas-solid
\(H_2\) hydrogen

\(I\) impeller

\(L\) Liquid

\(LS\) liquid-solid

\(obs\) observed

\(Oil\) oil

\(ov\) overall

\(p\) particle

\(Pd\) Palladium

\(S\) solid

\(TAG\) triglycerides

\(TP\) two phase

\(slug\) slug

\(surf\) surface

\(UC\) unit cell
Chapter 8  Summary and Future Work

Low frequency (0-30Hz) and low amplitude (0-2.5mm) mechanical vibrations were successfully used to improve the performance of two multi-phase contacting systems: 1) Bubble column for gas-liquid contacting (physical absorption) 2) Piston Oscillated Monolith Reactor (POMR) for gas-liquid-solid contacting (catalytic reaction).

The volumetric mass transfer coefficient ($k_{La}$) enhancements up to 500% and the gas hold-up ($\varepsilon$) improvements up to 200% were achieved under the application of vibrations in bubble column for air-water system. It was observed that both $k_{La}$ and $\varepsilon$ initially increase with increasing frequency ultimately reaching a plateau at higher frequencies. Experimentally it was found that $k_{La}$ increases with increasing amplitude, increasing gas superficial velocity and decreasing viscosity of the liquid.

Enhancements in $k_{La}$ and $\varepsilon$ were attributed to three effects associated with the oscillations in bubble column. The first observable effect of impressed oscillations is the retardation of bubble rise velocity due to the downward acting Bjerknes force. Retarded bubble rise velocity improves gas hold-up in the column. Second, forced oscillations caused breakage and the formation of smaller bubbles. Observed mean bubble diameter decreased with increasing power input according to Hinze model. The smaller bubble diameter results in the higher interfacial area available for mass transfer. Third, viscosity affects mass transfer coefficient owing to the dependence of diffusivity on viscosity, via the Stokes-Einstein effect.

A fundamental theory was developed from first principles to explain $k_{La}$ and $\varepsilon$ enhancements. The theory satisfactorily predicted the mass transfer coefficient and the gas hold-up as a function of operating parameters including the frequency and the amplitude of vibrations, the gas superficial velocity and the viscosity of the system. The theory also predicted “flooding”, which arises when bubbles are partially or fully retarded by Bjerknes forces at the point of
injection. Under flooding conditions, transport enhancement levels off as frequency or amplitude is increased.

Effects of frequency and amplitude and gas superficial velocity on the BSD in a bubble column were studied. Experimentally it was found that at low gas flow rates, breakage occurs at the injector and within the injector tube, whereas at high gas flow rates under jetting conditions, bubble breakage takes place within the column proper. As the frequency or the amplitude was increased, bubbles undergo breakage which resulted in a sharper (low variance) bell shaped distribution. Also the peak of the bell curve shifted towards the left indicating smaller mean bubble diameters. The BSD changed with increasing distance from the injector ultimately reaching equilibrium.

To help explain experimental results, population balance modeling simulations were performed using two fundamentally different breakage models, namely the Luo-Svendsen (LS) and the Martinez-Bazan (MB) model. The LS model favors unequal size bubble breakage whereas the MB model favors formation of two equal size bubbles. The predictions obtained from the MB model were in agreement with the experimental observations. We speculate that fluid vibrations enhance the production of nearly equal size bubble breakage, mainly owing to shear effects, which results in more uniform BSD and smaller bubbles.

Enhancements in the reaction rates were achieved using a novel three phase Piston Oscillated Monolith Reactor (POMR) for two reactions namely hydrogenation of alpha-methyl styrene to cumene and partial hydrogenation of soybean oil. Both these reactions are known to be kinetically fast and hence controlled by the rate of mass transfer. Activity enhancements (as compared to a no pulsing case) up to 84% and 112% at 17.5 Hz frequency and 2.5 mm amplitude were observed for alpha-methyl styrene hydrogenation and soybean oil hydrogenation respectively.
Mass transfer rates for POMR were calculated based on available correlations in the literature and when compared with the intrinsic kinetic rate of the alpha-methyl styrene hydrogenation reaction, it was found that under operating condition the reaction was external mass transferred controlled. It was concluded that vibrations improve external mass transfer rates in the monolithic reactor. It was shown that activity in the POMR was superior to other traditional reactors, and even superior to a stirred tank when compared on a power-per-volume basis. Catalyst pretreatment and its impact on Pd crystallite size played an important role in determining catalyst activity and long term stability in AMS hydrogenation.

Partial hydrogenation of soybean oil reaction was found to be internal diffusion controlled under the operating conditions. Increase in the activity of this reaction suggests that enhancements to pore diffusion/convection can be achieved in monolith washcoat with the application of vibrations. The POMR showed lower activity as compared to the powdered catalyst in the stirred tank due to higher internal diffusion resistance. The serial pathway selectivity was lower in the POMR and the trans fatty acid formation was higher which can be attributed to the diffusion resistance to triglyceride molecule. By changing the washcoat thickness and by tuning the vibrations it may be possible to achieve higher activity as well as higher selectivity in the POMR.

The theory developed to explain $k_La$ in a bubble column was based on few simplifying assumptions including the assumption to neglect the surface renewal rate. Under the effect of vibrations, bubble volume is continuously changing. As the bubble volume is changing the gas phase comes in contact with newer packets of liquid. In other words the surface renewal rate is enhanced by the application of vibrations. Current theoretical development ignores this effect. In future, the surface renewal rate may be included in the theory to obtain more accurate $k_La$ predictions.
Current bubble column experiments were carried out with batch liquid phase and continuous up-flow gas phase. Industrially, bubble columns are operated with both the phases in continuous mode. Various combinations of up-flow and down-flow configurations are possible. It would be important to understand the effects of vibrations when both the phases are operated in continuous mode. In Ideal case both the phases are assumed to behave as plug flow. In reality at higher gas flow rates a recirculating flow pattern is observed in the liquid phase which causes mixing to some extent. Deviations from the ideal plug flow behavior are generally quantified in terms of axial dispersion coefficient. It would be interesting to study the axial dispersion in the bubble column under the application of vibrations.

Measurements of velocity field inside the bubble column using either Laser Doppler Anemometer or Particle Image Velocimetry can be studied in the future. This will reveal the effects of vibrations on the velocity flow patterns inside the column. Information regarding the turbulence intensity, shear rates and energy dissipation rates can be obtained from such measurements. This information will be useful for further design improvements in the column or for the scale up purposes.

In present work, the POMR was used to study the effects of vibrations on the three phase gas-liquid-solid system. Alternatively, a vibrating slurry bubble column can be used to carry out three phase catalytic reactions. Since the hydrodynamics and the mass transfer characteristics of the two phase bubble column are well understood by this study, logical extension would be to investigate the effects of vibrations on a three phase slurry bubble column. Previous studies have shown that mass transfer rates from the suspended solids to the gas can be improved significantly with the help of pulsating motion of fluid. There were few studies reporting improvement of mass transfer from the solid to the liquid under vibrations. Studies on gas-solid fluidized bed have shown that fluidization of vibrating bed can be achieved at much lower gas
superficial velocity as compared to a static bed of solid particles. Previous studies suggest that it would be feasible to use vibrations for improvements in three phase slurry bubble columns or three phase fluidized bed reactors.
References


44. Urseanu, M. I.; Boelhouwer, J. G.; Bosman, H. J. M.; Schrijen, J. C. Induced pulse operation of high-pressure trickle bed reactors with organic liquids:


Appendix A  Supplementary Material for $k_La$ and $\varepsilon$ Measurements in a Bubble Column

A.1 Mass Transfer Measurements

For mass transfer experiments, a dissolved oxygen probe from Cole Palmer (Model 300mm) and signal conditioner (Model 01971-00) is placed in the bubble column, approximately 0.32 m above the injector. Gas bubbles do not directly impact the electrode. The column was initially purged of oxygen using nitrogen. After the dissolved oxygen content reached nearly 0 volume %, air flow was started.

The volumetric mass transfer coefficient was determined by measuring dissolved oxygen uptake in the bubble column as a function of time assuming the vessel to be well mixed. The rate of oxygen mass transfer in a differential cross section of the column of area $A_c$ and height $\Delta z$ can be given as,

$$R = k_L a'(C^* - C) A_c \Delta z$$  \hspace{1cm} (A.1)

Here, $C^*$ and $C$ represent the gas solubility and measured dissolved oxygen concentration, respectively. A solute balance on the liquid phase simply states the rate of accumulation equals the rate of transfer.

$$A_c \Delta z (1 - \varepsilon) \frac{dC}{dt} = k_L a'(C^* - C) A_c \Delta z$$ \hspace{1cm} (A.2)

where $\varepsilon$ is the gas holdup. Simplifying, yields the first order equation:

$$\left(1 - \varepsilon\right) \frac{dC}{dt} = k_L a' \left(C^* - C \right) \hspace{1cm} (A.3)$$

Integration of equation (A.3) with respect to time yields,

$$C(t) = C^* - \left(C^* - C_0\right) \exp\left(-\frac{k_L a'}{\left(1 - \varepsilon\right)} t\right)$$ \hspace{1cm} (A.4)
where \( C_0 \) (\( C \) at \( t = 0 \)) is the initial oxygen concentration. For all the experimental runs \( C_0 \) was always zero. Let the volumetric mass transfer coefficient based on the dispersion volume be 
\[ k_L a = k_L a'/(1 - \varepsilon) \]. Rearranging yields 
\[
\ln \left( \frac{C(t) - C^*}{C_0 - C^*} \right) = -k_L a \cdot t
\]  
(A.5)

Figure A.1 shows the voltage signal obtained from the oxygen probe as a function of time. Since LHS of the equation A.5 is non-dimensional, hence the concentration terms in A.5 can be easily replaced with the voltage signal \( S \).
\[
\ln \left( \frac{S(t) - S^*}{S_0 - S^*} \right) = -k_L a \cdot t
\]  
(A.6)
The slope of the plot of the LHS of equation A.6 against time gives the \( k_L a \) value as shown in Figure A.2.

![Graph showing signal from oxygen probe as a function of time](image)

**Figure A.1** Signal from oxygen probe as a function of time; \( f = 0 \text{ Hz} \), \( A = 2.46 \text{ mm} \), \( U_{og} = 0.25 \text{ cm/s} \)
Figure A.2 Plot of $\ln\left(\frac{(S(t) - S^*)}{(S_0 - S^*)}\right)$ vs. time showing $k_La$ as the slope of the line. $f = 0$ Hz, $A = 2.46$ mm, $U_{og} = 0.25$ cm/s

A.2 Voidage Measurements

The gas hold up was determined by the manometric method. Two taps are used, one 11 cm from the rubber sheet and the other 77 cm above the rubber sheet. The manometer fluid is Meriam Red 295 with a specific gravity of 2.95. A pressure balance on each leg of the manometer allows voidage ($\varepsilon$) to be determined using,

$$\varepsilon = \left(\frac{\rho_m - \rho_L}{\rho_L}\right) \frac{\Delta h}{H} \tag{A.7}$$

The height differential in Meriam Red 295, $\Delta h$, was determined using a cathetometer which provided an accuracy of plus or minus 0.01 mm. Here $H$ is the distance between the two taps.

A.3 Summary of $k_La$ Data

$A = 1.66$ mm; Viscosity = 1 cP

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<th>$U_{og}$ (cm/s) =</th>
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\(A = 2.46 \text{ mm}; \text{Viscosity} = 1 \text{ cP}\)

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\(A = 1.66 \text{ mm}; \text{Viscosity} = 62 \text{ cP}\)

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### A.4 Summary of Voidage Data

#### $A = 2.46$ mm; Viscosity = 62 cP

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#### $A = 1.66$ mm; Viscosity = 1 cP

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#### $A = 2.46$ mm; Viscosity = 1 cP

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Appendix B  Supplementary Material for BSD and PBM

B.1 Procedure for Image Analysis Using ImageJ Software for BSD Measurements:

Open the raw image file (Figure B.1) obtained from the high-speed camera (Photron Fastcam PCI-R2) in ImageJ. Perform the following sequence of operations using ImageJ toolbar. The change in image after each step of operation is shown in Figure B.2

1) Process → Subtract background → Rolling ball radius 50. This will subtract the background. (Figure B.2a)

2) Process → Binary → Threshold. This will convert the image in only two tones, black and white. (Figure B.2b)

3) Fill in the white holes in the middle of bubble if any. (Figure B.2c)

4) Process → Binary → watershed. This will separate joined bubbles. (Figure B.2d)

5) Analysis → Analyze particles. This will calculate the area of each bubble in the image. Results obtained after this step are shown in Table B.1 for the original image.

Figure B.1 Raw image obtained from high-speed camera.
Figure B.2 Figure illustrating image after each step of processing.

Table B.1 Results obtained from particle analysis of image shown in Figure B.1

<table>
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<th>Area cm²</th>
<th>Bubble #</th>
<th>Area cm²</th>
<th>Bubble #</th>
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B.2 Procedure for Obtaining Bubble Size Distribution (BSD) Data

Data for area of bubbles was collected at least from five images. Total bubble volume range was divided into number of classes such that the volume of class $i$ is twice the volume of previous class $v_{i} = 2v_{i-1}$. Volume of smallest class was $2.21 \times 10^{-4}$ cm$^2$. The number of bubbles in each size class was calculated based on bubble area data and using the following MATLAB code. (Note: Comments are written after % sing)

B.3 Program for Calculating Number Density Based on Bubble Area Data

```matlab
% Name     : BSD_Vol
% Purpose  : To calculate the number density of bubbles in each volume class by using data of area of bubbles.
% Input    : File named "area.txt" which contains the data of area of each bubble
% Output   : number density and sauter mean bubble diameter

clc
clear output
n=zeros(1);nd=zeros(1);ndd=zeros(1);vmean=zeros(1);volfraction=zeros(1);dia=zeros(1);deltav=zeros(1);
% clears old values in the array

nframe=5; % total number of frames used to get the data
Aframe=7.1*6.7; % area of observation window
samplevol = nframe*(pi*(0.071^2)/4)*0.067; % volume of dispersion in observation window
A = load('area.txt'); % reads input file
B = sort(A);
dia = ((4*B)/pi).^0.5; % calculates diameter of each bubble based on area information
vol = pi.*dia.^3/6;% calculates volume of each bubble
vol1=2.2089*10^-4; % volume of smallest volume class
for i=1:100 % defines volume of all the bubble classes
    vmean(i) = vol1*2^(i-1);
end
d=0.01*((6/pi).*(vmean)).^(1/3); % defines corresponding diameter of each bubble class

count=0;
for j=1:100 % counts total number of bubbles in each volume class
    if j=1
        for i=1:length(B)
            if ((0<vol(i))&(vol(i)<vmean(j)+(vmean(j+1)-vmean(j))/2));
                count=count+1;
                n(j)=count;
            else
                end
        end
    else
        for i=1:length(B)
            if ((vmean(j)-(vmean(j)-vmean(j-1))/2<vol(i))&(vol(i)<vmean(j)+(vmean(j+1)-vmean(j))/2));
```
count = count + 1;
    n(j) = count; % Total number of bubble in each bubble class
else
    end
end
count = 0;
end

for i = 2:length(n)
    deltax(i) = ((vmean(i+1) - vmean(i-1))/2); % delta V between two volume classes
end
deltax(1) = (vmean(2) + vmean(1))/2;

nd(1) = n(1)/(samplevol*d(1));
nd(length(n)) = n(length(n))/(samplevol*d(length(n)-1));
nd(1) = n(1)/(samplevol);
nd(length(n)) = n(length(n))/(samplevol);
for i = 2:length(n)-1
    nd(i) = n(i)/(samplevol); % nd = number density = number of bubbles/(vol of dispersion)
    ndd(i) = n(i)/(samplevol*(d(i) - d(i-1))); % ndd = number of bubbles/(vol of dispersion. delta d)
end
vmean = vmean(1,1:length(nd));
d = d(1,1:length(nd));
volfraction = ndd.*vmean/sum(n./samplevol.*vmean); % volfraction/(vol. of dispersion.delta d)
plot(d, volfraction)

output(:,1) = d;
output(:,2) = nd;
output(:,3) = volfraction;
num2str(output) % Prints the output

d32 = sum(nd.*d.^3)/sum(nd.*d.^2) % the sauter mean diameter

% Population Balance Modeling Program

% Name: PBM
% Purpose: To solve population balance equation
% Input: File named "numd.txt" which contains number density data at H = 10.6 cm. This is used as the boundary condition
% Output: number density and sauter mean bubble diameter as a function % of height

function PBM2

global v n void epsilon d surften rhoc rhod visco i j h u A fr cm bm % defines global variables
n = zeros(1,1); d = zeros(1); v = zeros(1); % clears old values in the array
clc

% switch for selecting different breakage and coalescence models
% bm = 1; % LS breakage
% bm = 2; % MB breakage
% cm = 1; % coalescence efficiency by Luo(1993)
\( fHz = 20; \) % input frequency here

%Experimental data of d32 vs height for comparison purposes

\begin{verbatim}
switch fHz
  case 15
    HExp=[0.106,0.25,0.538,0.677]; % for 10, 15,20 Hz
    expd32= [0.0066; 0.0059; 0.0047; 0.0048]; %for 15Hz
    epsilon = 1.16;
  case 17.5
    HExp=[0.106,0.25,0.377,0.538,0.677]; % for 17.5 Hz
    expd32= [0.0068; 0.0045; 0.0044; 0.0043;0.0041]; %for 17.5Hz
    epsilon = 1.85;
  case 20
    HExp=[0.106,0.25,0.538,0.677]; % for 10, 15,20 Hz
    expd32= [0.0057; 0.0042; 0.0039; 0.0041]; %for 20Hz
    epsilon = 2.75;
end
\end{verbatim}

% Physical properties

\( void = 0.025; \) % voidage
\( surfen = 0.0726; \) % surface tension N/m
\( visco=0.9*10^{-3}; \) % viscosity in Pa.s
\( rhoc = 998; \) % contineous phase density in kg/m^3
\( rhod = 1.2; \) % dispersed phase density in kg/m^3
\( Nu = \frac{visco}{rhoc}; \) % kinematic viscosity in m^2/s
\( fr=fHz*2*pi; \) % radial frequency in rad/s
\( A=1.66*10^{-3}; \) % amplitude in m
\( deltax=0.005; \) % differential element of height in m

% Data input and grid generation

\( ini = load('numd.txt'); \) % reading the input data for boundary condition
for \( i=1:length(ini) \)
  \( n(i,1)=ini(i); \)
end
\( N = length(ini); \) % total number of classes
\( v_1=2.2089*10^{4}; \) % volume of smallest bubble class
for \( i=1:N \) % defining volume and diameter for all the bubble classes
  \( v(i)=v_1*2^{(i-1)}; \)
  \( d(i)=(6*v(i)/pi)^{(1/3)}; \)
end

% Solving PBE

for \( h=1:120 \) %iteration at each node
  \( height(h)=0.106+deltah*(h-1); \) %defining nodes along the height of the column
  \( M = 0.5.*(0.78-height(h)).*rhoc.*A^2.*fr.^4/(9.81*101325); \) % Bjerknes number
for i=1:N  % Calculation of bubble rise velocity for each bubble size
    AA = 0.85*(d(i)/Nu)^0.5;
    B = 10;
    C = (4/3)*d(i)^(3/2) * 9.81 * (1-M)/Nu^0.5;
    P = [AA B 0 0 -C];
    r = roots(P);
    uu = r(find(r>0));
    u(i)=uu^2;
end

% calculation of source term and Bb,Db,Bc,Dc
for i=1:N
    if i==N
        Bb1=0;
    else
        sum=0;
        for k=i+1:N
            sum=sum+breakage(k,i);
        end
        Bb1=sum;
    end
    if i==N
        Bb2=0;
    else
        sum=0;
        for k=1:i
            sum=sum+2^(k-i)*breakage(i+1,k);
        end
        Bb2=sum;
    end
    if i==1
        Bb3=0;
    else
        sum=0;
        for k=1:i-1
            sum=sum+(1-2^(1+k-i))*breakage(i,k);
        end
        Bb3=sum;
    end
    Bb(i)=Bb1+Bb2+Bb3;
end

if i==1
    Db(i)=0;
else
    sum=0;
    for k=1:i-1
        sum=sum+breakage(i,k);
    end
    Db(i)=sum;
end

if i==1
    Bc(i)=0;
else
    if i==N
        Bc1=0;
    else
        if i==N
            Bc1=0;
sum = 0;
for j = 1:i-1
    sum = sum + (1 - 2^(j-i)) * coalescence(i,j);
end
Bc1 = sum;
end
sum = 0;
for j = 1:i-1
    sum = sum + (2^(j-i+1)) * coalescence(i-1,j);
end
Bc2 = sum;
Bc(i) = Bc1 + Bc2;
end
if i == N
    Dc(i) = 0;
else
    sum = 0;
    for j = 1:N-1
        sum = sum + coalescence(i,j);
    end
    Dc(i) = sum + coalescence(i,i);
end
rate(:,h) = Bb(:,h) - Db(:,h) + Bc(:,h) - Dc(:,h);
for i = 1:length(nini)
    if h == 1
        ddeltah = deltalh;
    else
        ddeltah = height(h) - height(h-1);
    end
    n(i,h+1) = n(i,h) + (ddeltah/u(i)) * (Bb(i)-Db(i)+Bc(i)-Dc(i));% descretized PBE differential equation
end
sum3 = 0;
for i = 1:length(Bb)
    sum3 = sum3 + n(i,h) * v(i);
end
volfraction(1,h) = n(1,h) * v(1) / (sum3 * d(1));
for i = 2:N
    volfraction(i,h) = n(i,h) * v(i) / (sum3 * (d(i) - d(i-1))); % volume fraction occupied by each bubble class
end
sum1 = 0;
for i = 1:length(Bb)
    sum1 = sum1 + n(i,h) * d(i)^3; % Third moment
end
sum2 = 0;
for i = 1:length(Bb)
    sum2 = sum2 + n(i,h) * d(i)^2; % Second moment
end
d32(h) = sum1 / sum2; % Sauter mean diameter
end
% Post processing of results
% defining legends

```
type=['ro:'; 'b>:'; 'md:'; 'gp:'; 'c<:'; 'k>:'];
post=[['H = 10.6 cm']; %for 17.5 Hz
     ['H = 25.0 cm'];
     ['H = 37.7 cm'];
     ['H = 53.8 cm'];
     ['H = 67.7 cm'];
]
```

```
post=[['H=' num2str(HExp(1)*100,'%1.1f') ' cm'];    %for 15, 20 Hz
     ['H=' num2str(HExp(2)*100,'%1.1f') ' cm'];
     ['H=' num2str(HExp(3)*100,'%1.1f') ' cm'];
     ['H=' num2str(HExp(4)*100,'%1.1f') ' cm']];
```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Fig d32 vs H

```
handleFig1=figure(1)
clf
handlePlot=plot(height.*100, d32.*100, 'ro:', HExp.*100,expd32.*100,'b>);
xlabel('Height, H [cm]','FontSize',16)
ylabel('Sauter mean diameter, d32 [cm]','FontSize',16)
hLeg=legend('Simulation','Experiment');
set (hLeg,'FontSize',16,'LineWidth',1.5)
axis([10 80 0.2 0.8])
```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Fig BSD

```
handleFig2=figure(2)
clf
volfraction1=volfraction(:,1); %H=10.6 cm
volfraction2=volfraction(:,30); %H=25 cm
volfraction3=volfraction(:,56); %H=37.7 cm
volfraction4=volfraction(:,88); %H=53.8 cm
volfraction5=volfraction(:,116); %H=67.7 cm
handlePlot=plot(d.*100,volfraction1,type(1,:),d.*100,volfraction2,type(2,:),d.*100,volfraction3,type(3,:),d.*100,volfraction4,type(4,:),d.*100,volfraction5,type(5,:));
xlabel('Bubble diameter, d [cm]','FontSize',16)
ylabel('Volume fraction/delta d [1/(m)]','FontSize',16)
hLeg=legend(post);
set (hLeg,'FontSize',16,'LineWidth',1.5)
axis([0 1.2 0 400])
save output
```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% Breakage kernel
function r=breakage(i,k)
global v n void epsilon d surften rhoc visco cf h ii xi ds bm

switch bm
    case 1      %LS breakage
        ii=i;
        fBV = v(k)/v(i);
        cf = fBV^(2/3)+(1-fBV)^(2/3)-1;
        lamdamin=((visco/rhoc)^3/epsilon)^0.25;
        zmin=lamdamin/d(i);
        Q = quad(@F1,zmin,1);
        r = 0.05*0.923*(1-void)*n(i,h)*(epsilon/d(i)^2)^(1/3)*Q;
    case 2      %MB breakage
        Kg = 1.0;
        bbeta = 8.2;
        omega = Kg*(max(0,n(i)))*(bbeta*(epsilon*d(i))^2/3+12*surften/(rhoc*d(i)));
        zi = d(k)/d(i);
        diac = (12*surften/(bbeta*rhoc))^(3/5)*epsilon^(-2/5);
        dmin = (12*surften/(bbeta*rhoc*d(i)))^(3/2)*epsilon^(-1);
        dmax = d(i)*(1-(dmin/d(i))^3)^(1/3);
        xi = diac/d(i);
        zimin = dmin/d(i);
        zimax = dmax/d(i);
        if zi<zimin
            P = 0;
        else
            if zi>zimax
                P = 0;
            else
                numer = (zi^2/3-xi^5/3)*((1-zi^3)^2/9-xi^5/3);
                denom = quad(@F2,zimin,zimax);
                P = numer/denom;
            end
            end
        end
    r = 2*omega*P;
end

% integrand in LS breakage
function y=F1(z)
global cf surften rhoc epsilon d ii
y = ((1+z).^2./z.^(11/3)).*exp(-12.*cf.*surften./(2.0457.*rhoc.*epsilon^(2/3).*d(ii).^(5/3).*z.^(11/3)));

% integrand in MB breakage
function y=F2(zi)
global xi
y = (zi^(2/3)-xi^(5/3)).*((1-zi^3)^2/9-xi^5/3);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%Coalescence calculations
function r = coalescence(i,j)
global v n void epsilon d surften rhoc rhod h u A fr cm

Wct = 0.089*(pi).*n(i,h).*n(j,h).*d(i)+d(j)).^2*epsilon^2/(2.3).*d(i).^(2/3)+d(j).^(2/3)).^0.5; %collision frequency due to turbulence
\( W_c = W_{ct}; \)

switch cm
    case 1 % coalescence efficiency by Luo(1993)
        \( z = d(i) / d(j); \)
        \( u_i = 2.0457^{0.5}(\epsilon d(i))^{0.5}; \)
        \( u_j = 2.0457^{0.5}(\epsilon d(j))^{0.5}; \)
        \( u_{ij} = (u_i^2 + u_j^2)^{0.5}; \)
        \( We = \rho c d(i) u_{ij}^2 / surften; \)
        \( Pc = \exp(-0.75(1+z^2)(1+z^3))^{0.5} We^{0.5} / ((\rho_d/\rho_c + 0.5)^{0.5}(1+z^3)); \)
end
\( r = Pc \times W_c; \)

"
Appendix C  Supplementary Material for POMR

C.1 POMR Operating Procedure

1. Charge the POMR with 1L of reactant the top.

2. POMR was kept under ~1 atm H$_2$ purge when not in use.

3. Set heater bath temperature around 20-30°C higher than the desired temperature in the reactor. All heat exchanger lines were insulated. A centrifugal pump supplied the heat transfer fluid to the exchangers, with the flow started in bypass mode (ball valve to heat exchangers closed, needle valve on return line to bath wide open). The flow through the exchangers was slowly increased by opening the ball valve and slowly closing the needle valve until the pressure gauge on the heat transfer fluid inlet was ~35 psig. This set the flow rate to ~100 mL/min. Other flow rates were set by adjusting the needle valve.

4. Pulse at ~1 Hz to make the system temperature uniform.

5. Allow the reactant mixture to go ~5 °C above desired set-point because the gas flow (once started) will have a cooling effect.


7. Set POMR piston to desired frequency.

8. The system is pressurized. Care was taken to pressurize the top and bottom of the diaphragm at near identical rates (no more than 10 psi differential).

9. Record pressure transducer voltage with LabView® software.

10. Keep both H$_2$ and N$_2$ valves to the POMR open to account for any minor leaks and for H$_2$ consumed by reaction.

11. Sample (~1 mL) during a run using the needle valve connected to the POMR body (similar to a dip-tube) attached to sample into vial at periodic intervals. Care must be taken to first purge dead volume in the valve before taking the sample.
12. Shutdown
   a. Stop oscillations and heating.
   b. Decrease instrument air to booster until it stops pumping.
   c. System is depressurized by bleeding gas to the fume hood vent. Care was taken to
      depressurize the top and bottom of the diaphragm at similar rates.
   d. Drain ~800 mL of fluid through the bottom port on the process side.
   e. POMR must be disassembled to access the diaphragm for complete cleaning.

13. In-situ catalyst treatment
   a. The maximum temperature in the POMR was 120°C with silicone heat transfer
      fluid.
   b. Pressurize with desired gas (H₂ for reduction) and connect bubbler to gas outlet.
   c. Set gas flow using the needle valve at the gas outlet.
   d. Start heating, bring to temperature.

C.2 Agitated Tank Operating Procedure

1. The agitated tank was an Autoclave Engineers Zipperclave with a marine propeller. Heat
   was supplied by wrapping the vessel in heating tape controlled by a Variac.

2. Place catalyst-coated monolith at bottom of vessel. Reduce in situ (if desired) by heating
   until thermocouple reads ~120 °C under hydrogen purge, exiting through a bubbler.

3. After cooling, fill the system through the dip-tube using a 100 mL glass syringe and
   maintaining 1 atm H₂ purge by venting through the bubbler.

4. After filling to 350 mL to completely submerge the impeller blade, begin heating the
   system while applying ~50 rpm stirring.

5. Once the reactor is at the desired temperature, increase the stirring rate and pressurize the
   system.
6. Sample at regular intervals using the dip-tube connected to a needle valve. Purge ~2 mL of dead volume from the system before sampling. The valve was also wrapped with heating tape to avoid hardening of the oil.

7. For reactor shutdown, stop the stirring and heating. Depressurize the system using the purge valve, through the bubbler.

8. For repeated runs, the system can be drained using the dip-tube, and fresh reactant re-introduced via the syringe. However, ~100 mL of liquid will remain in the vessel because the dip-tube does not go all the way to the bottom.

9. If complete liquid removal is required, the vessel must be removed.

C.3 Calculations of Alpha-methyl Styrene Hydrogenation Reaction Rates from Literature


For the slurry reactor, the rates were computed from the regressed kinetics equation (Eq. (1) of paper) at 46°C and 0.44 MPa, for 0.5 wt% Pd/Al₂O₃. These were determined in cumene solvent (50–100 mol% AMS, zero order) at 2000 rpm stirring speed. Germain et al. demonstrated by the usual particle size and variable speed tests that the mass transfer resistances were negligible under these conditions.

\[
\text{Rate} = 55 \text{ mmol/(s* gPd)}
\]


For the slurry reactor, the rates were computed from the regressed kinetics equation (Eq. (4) of paper) at 46°C and 0.44 MPa, for 1 wt% Pd/Al₂O₃. These were determined in methylcyclohexane solvent (0.5–100 wt% AMS, zero order) at 1500 rpm stirring speed. Meille
et al. demonstrated by the usual particle size and variable speed tests that the mass transfer resistances were negligible under these conditions.

\[
\text{Rate} = 460 \ \text{mmol/(s* gPd)}
\]


For the \textit{trickle bed reactor}, data were obtained at variable temperature due to heat effects (but 50°C max.) and 0.3 MPa, with hexane solvent at 1582 mol/m\(^3\) AMS, using a small diameter 0.5\% Pd/Al\(_2\)O\(_3\). The slope of the initial rate plot (conversion vs. residence time) was taken from Fig. 2 of the paper and multiplied by the initial concentration of AMS, and divided by the catalyst density and fraction of Pd to give the result.

The calculated liquid and gas superficial velocities are 0.03 and 6.6 cm/s, respectively.

\[
\text{Rate} = 0.112 \ \text{mmol/(s* gPd)}
\]

For the \textit{pulsed trickle bed reactor}, data were obtained at similar conditions except 1484 mol/m\(^3\) AMS, with a pulse frequency of 1.7 x 10\(^{-2}\) Hz and a split (on flow/total flow for the liquid pulse) of 0.25. The slope of the initial rate plot was taken from Fig. 3a of the paper and multiplied by the initial concentration of AMS, and divided by the catalyst density and fraction of Pd to give the result.

\[
\text{Rate} = 0.162 \ \text{mmol/(s* gPd)}
\]


For the \textit{trickle bed reactor}, data were obtained at 41°C and 0.1 MPa, with pure AMS using a 2 mm eggshell 0.5\% Pd/Al\(_2\)O\(_3\). The rate in mmol/(gcat*s), from Fig. 2 of the paper, was divided by the fraction of Pd to give the result.

The calculated liquid and gas superficial velocities are 0.45 and 3.0 cm/s, respectively
Rate = 0.2 mmol/(s * gPd)

For the **pulsed trickle bed reactor**, data were obtained at similar conditions with a pulse frequency of 1.7 x 10^{-3} Hz and a split (on flow/total flow for the liquid pulse) of 0.3. The rate in mmol/(gcat*s), from Fig. 6 of the paper, was divided by the fraction of Pd to give the result.

Rate = 0.86 mmol/(s * gPd)


For the **rotating trickle bed reactor**, the rates were measured at 40°C and 1 bar, with pure AMS. The rate for the 1% Pd/Al_{2}O_{3} catalyst (1.5 mm spheres) was used, at rotation speed 2200 rpm, the maximum rate at the maximum rotational speed. The rate per bed volume from Fig. 5 of the paper, 40 x 10^{-7} mol/(cm^{3} bed*s), was divided by the catalyst density (1.17 g/cm^{3}, Table 6.1) and by the Pd loading to give the rate in mmol/(s*g Pd).

The liquid superficial velocity for this calculation was 0.12 cm/s, approximately the highest used here. The gas flow rate was not given.

Rate = 0.34 mmol/(s * gPd)


For the **tubular membrane reactor**, the rate was interpolated from Fig. 7 of the paper, at 46°C and 0.1 MPa, with pure AMS,. This rate is in mmol/(s*g cat), which is multiplied by (100/2) to put in mmol/(s*g Pd), since there was 2% Pd on the membrane catalyst.

The computed velocities at reaction conditions are: 0.15 cm/s for liquid, 27 cm/s for gas.

Rate = 1.0 mmol/(s * gPd)

For the slurry reactor, rate data were taken from Fig. 3, for a 0.5% Pd/Al₂O₃ catalyst at 1 MPa, 53°C, >1600 rpm, 50 vol% AMS in cumene. At these conditions, Purnama et al. estimated no intraparticle or external limitations to mass transfer, and found first-order behavior with respect to H₂ pressure. At 4 MPa H₂, the rate was 4 mmol/(s*g Pd) with 80% conversion in 52 min, for the most active catalyst. For the same catalyst at 1 MPa, the conversion was 80% in 25 min, so the rate ~ (4)(52/25).

\[
\text{Rate} = 8.3 \text{ mmol/(s*g Pd)}
\]

For the flow-through membrane reactor, the reaction conditions are: 0.1 MPa, 40°C, 0.35 mol/L AMS in heptane, at maximum liquid flow rate. The rate was taken from Fig. 5, using the maximum rate.

The computed liquid superficial velocity is 0.37 cm/s. The H₂ was dissolved in the liquid (1600 rpm) prior to contact with the membrane.

\[
\text{Rate} = 9.0 \text{ mmol/(s*g Pd)}
\]


For the metal mesh microreactor, the rate was measured at 0.28 MPa, 40°C, pure AMS, with a 1% Pd/Al₂O₃ catalyst. The observed rate in mol/(m³ liquid*s) was taken from Table 6.1 of the paper, multiplied by the ratio of liquid to catalyst volume (155/15), then divided by the catalyst density and the Pd loading to give the rate in mmol/(s*g Pd).

The calculated liquid and gas superficial velocities are 0.036 and 0.11 cm/s, respectively

\[
\text{Rate} = 8.6 \text{ mmol/(s*g Pd)}
\]

For the monolith reactor, the rates were determined at 46°C and 1 MPa from Fig. 6 of the paper. The first-order rate constant is given, which is then multiplied by the equilibrium concentration of H₂ in the liquid to obtain an overall rate on a reactor volume basis. A hydrogen solubility in toluene of 36.5 mol/m³ was used, extrapolating from the data of Yin and Tan.

The liquid superficial velocity was 15 cm/s, the gas velocity 20 cm/s.

**Rate = 2.1 mmol/(s*g Pd)**


Data were obtained at 40°C, 0.1 MPa, with no solvent – pure AMS feed.

The liquid superficial velocity is the highest used. The gas superficial velocity is 1.1 cm/s.

**Rate = 0.8 mmol/(s*g Pd).**

### C.4 Pictures of Monolith Acrylic Mockup Operated with Glycerol

Figure C.1 Flow of N₂/glycerol (1260 mPa•s, 0.09 m/s) in monolith; (a) with oscillations; A = 2.5 mm, f = 1 Hz (b) without oscillation.
C.5 Calculation of Hydrogen Consumption Rate for Soy Oil Hydrogenation Based on Concentration Data (Derivation of Eq. 7.5)

The hydrogenation reaction for the individual compounds can be represented as:

\[
\begin{align*}
C_{18:3} & \xrightarrow{H_2, k_3} C_{18:2} \\
C_{18:2} & \xrightarrow{H_2, k_2} C_{18:1} \\
C_{18:1} & \xrightarrow{H_2, k_1} C_{18:0}
\end{align*}
\]  
(C.1)

Let the concentration of individual components \(C_{18:X}\) be represented as \(C_{Xi}\), where \(i\) is the sample number. We desire to calculate the hydrogen consumption at each step of the reaction.

1. Consumption of \(H_2\) due to step 1 = \(x\) mol/L

\[
C_{18:3} \xrightarrow{H_2, k_3} C_{18:2}
\]

\[x = C_{30} - C_{31}\]

2. Consumption of \(H_2\) due to step 2 = \(y\) mol/L

\[
C_{18:2} \xrightarrow{H_2, k_2} C_{18:1}
\]

Note that \(C_2\) increases by amount \(x\) due to step 1, and decreases by amount \(y\) due to step 2. Hence the total change in \(C_2\) concentration is:

\[C_{20} - C_{21} = y - x\]

\[y = (C_{20} - C_{21}) + x = (C_{20} - C_{21}) + (C_{30} - C_{31})\]

3. Consumption of \(H_2\) due to step 3 = \(z\) mol/L

\[
C_{18:1} \xrightarrow{H_2, k_1} C_{18:0}
\]

Note that \(C_1\) increases by amount \(y\) due to step 2, and decreases by amount \(z\) due to step 3. Hence the total change in \(C_1\) concentration is

\[C_{10} - C_{11} = z - y\]
\[ z = (C_{10} - C_{11}) + y = (C_{10} - C_{11}) + (C_{20} - C_{21}) + (C_{30} - C_{31}) \]

Combining steps 1, 2 and 3, we get for total H\textsubscript{2} consumption, \( N_{H_2} = x + y + z \)

\[ N_{H_2} = (C_{10} - C_{11}) + 2(C_{20} - C_{21}) + 3(C_{30} - C_{31}) \quad (C.2) \]

Once the hydrogen consumption \( N_{H_2} \) is calculated, the overall rate of hydrogen consumption can be obtained from equation (C.2) as before.
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Vita

Yogesh Waghmare was born in Pune, India, in September, 1981. After completing high school he joined the University Institute of Chemical Engineering at the University of Mumbai, India, and graduated with a Bachelor of Chemical Engineering in 2003. Then he made the biggest decision of his life to move to Baton Rouge, very far from his hometown of Mumbai, India, but not too different in terms of hot and humid weather. He enrolled in the graduate school at the Department of Chemical Engineering at Louisiana State University in 2003. He is looking forward to starting his career in industry and may come back to academia in the distant future.