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Yanxiang Shi
Iowa State University

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Experimental and computational investigation of turbulent mixing in microscale reactors

by

Yanxiang Shi

A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Program of Study Committee:
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Iowa State University
Ames, Iowa
2012

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DEDICATION

I would like to dedicate this thesis to my wife Yanjie Zhang without whose support I would not have been able to complete this work. I would also like to thank my family for their loving guidance and support during the writing of this work.
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ACKNOWLEDGEMENTS

I would like to take this opportunity to express my thanks to those who helped me with various aspects of conducting research and the writing of this dissertation during the four and half years of my PhD career at Iowa State University.

First and foremost, I would like to thank Dr. Michael G. Olsen and Dr. Rodney O. Fox for their guidance, patience and support throughout this research and the writing of this dissertation. They have helped me in a variety of ways, not just limited to research.

I am also thankful to other committee members: Dr. Aaron R. Clapp for the valuable discussions on the confocal laser scanning microscopy, Dr. James C. Hill for the interesting conversations and insights on different aspects of research and life, and Dr. Shankar Subramaniam for teaching me the multiphase flow knowledge as well as kind suggestions on the POD analysis.

In addition, I also appreciate the support, encouragement and assistance that come from my colleagues and friends, Dr. Kong, Dr. Somashekar, Dr. Cheng, Dr. Passalacqua, Dr. Bai, Dr. Xue, Ram, Cansheng, Maulik, Katrine and Michael, and undergraduate helpers, Hongyu, Yu, Setche, Neila and Wong.

My special thanks go to Margie Carter, who helped me a lot with the confocal microscope and Dan Jones, who built the microscale reactor and other components for us.

Last but not least, I would like to thank National Science Foundation for the financial support.
ABSTRACT

Flash Nanoprecipitation (FNP) is a promising technique for mass production of nanoparticles for use in various areas. Mixing time is such a crucial factor that it affects the particle size distribution as well as the particle morphology. Turbulent mixing in microscale nanoprecipitation reactors, i.e., the planar confined impinging-jet reactor (CIJR) and the multi-inlet vortex reactor (MIVR), is therefore investigated by means of numerical simulations as well as experimental flow visualization methods. In the process of studying, the computational fluid dynamics (CFD) models are validated by comparing simulation results with experimental data. One of the experimental visualization techniques developed in this work uses the phenolphthalein as the tracer that characterizes the acid-base neutralization reaction. Mixing is qualitatively and, by applying a special image processing technique, also quantitatively evaluated. Coherent flow structures are also analyzed through spatial correlation and POD. For the MIVR, the microscale particle velocimetry (µ-PIV or microPIV) is first employed to measure the velocity field. Results from Reynolds-averaged Navier-Stokes (RANS) simulations and large eddy simulations (LES) are compared to the µ-PIV results. Comparisons show LES is more suitable for simulating flow field in these reactors. In addition, another experimental method developed in this work is also applied to the MIVR, which couples the confocal laser scanning microscopy (CLSM) and the microscale laser induced fluorescence (µ-LIF). More detailed and quantitatively accurate data are obtained for the CFD model validation. Passive scalar mixing and reactive mixing experiments are both accomplished to quantify the mixing at the macroscale and microscale respectively.
CHAPTER 1 GENERAL INTRODUCTION AND BACKGROUND

This research project is motivated by the production of uniform-sized functional nanoparticles that have found numerous applications. Flash NanoPrecipitation (FNP) is developed for such use and has shown great promise. As in traditional precipitation processes, it requires supersaturation created by mixing active solution with anti-solvent in chemical reactors. Mixing, as such, plays a crucial role in FNP and a comprehensive and fundamental understanding of mixing is important. The major objective is thus to study the mixing in microscale nanoprecipitation reactors developed along with FNP by means of experiments and simulations. In order to accomplish this task, novel flow visualization techniques have been developed and applied to the nanoprecipitation reactors. In addition, computational fluid dynamics (CFD) models are validated against the experimental data in the hope of achieving “experimental-free” design of this type of microscale reactors. As they provide more information than experiments can ever do, numerical results are also analyzed to obtain a deeper insight on the mixing effects.

1.1 Nanoparticles and FNP

Nanoparticles, formerly known as ultra-fine particles, was traditionally defined as particles of sizes less than 100 nm [1]. However, as nanotechnology, one of the major subjects in modern science and engineering, developed rapidly during the past a few decades, the definition has been implicitly broadened to include all tiny particles within
the nanometer range (< 1 μm) [2, 3]. As compared to bulk materials, they exhibit significantly different yet useful optical, electrooptical and some other physical properties [4], which explains the fact that they are used in various areas, such as cosmetics, dyes, pesticides and drug delivery. [1, 3–6] Manufacturing techniques of such particles fall into one of the two categories, either top-down or bottom-up [7]. For the former category, sizes of larger particles are reduced mechanically by means of milling of all sorts, while in the latter, however, chemical processes are usually involved, such as crystallization, precipitation and chemical vapor deposition (CVD) etc [1, 7]. However, in this work, we will limit ourselves to nanoparticles used in pharmaceuticals and drug delivery.

Some of the advantages of nanoscale drug particles are apparent. For one thing, they are more soluble in water than their raw counterparts [8], because not only of the smaller size [7], but also of the fact that raw drug particles are usually organic and hydrophobic [7, 9–12]. However, uniform particle-size distribution (PSD) is an important factor in the production of drug nanoparticles as it largely affects the recirculation and bioavailability of the actives [11]. It is proven FNP is able to produce nanoparticles with reasonably good PSD [13], making it a competent technique for such purposes. The basic idea is briefly discussed below.

As shown in Figure 1.1, a typical FNP process involves a solvent containing the organic active as well as the diblock copolymer and an anti-solvent, which are mixed rapidly in a microscale nanoprecipitation reactor. In the case of water being the anti-solvent, a diblock copolymer has a hydrophilic head and hydrophobic tail. As the supersaturation is created in the chemical reactor, the precipitation is initiated. More precisely, three subprocesses can be identified, i.e., the aggregation of copolymers, the nucleation and growth of the actives and the stabilization of the active particles due to the attachment of hydrophobic tails. A suitable ‘combination’ of the latter two produces the desirable nanoparticles within small size range. Only with a precipitation Damköhler number less than unity, defined as the ratio of mixing time $\tau_{\text{mix}}$ to precipitation time $\tau_{\text{flash}}$, can this
‘combination’ be obtained and thus the products [9, 10, 13].

Two types of nanoprecipitation reactors are designed as shown in Figure 1.2, the confined impinging-jets reactor (CIJR) and the multi-inlet vortex reactor (MIVR). As will be seen in the later chapters, mixing chambers and inlet channels of both are on the order of millimeters. The CIJR and its derivatives are still under a lot of research because it can create a zone of high energy dissipation where the two inlet jets collide, which is ideal for fast mixing [6]. However, its use is limited for FNP because of the requirement of equal inlet momenta [14]. MIVR, on the other hand, is developed to overcome this limitation. With four inlet channels attached tangentially to the mixing chamber, its inlet momenta can be varied independently. This way, MIVR offers not only the flexibility in operations but also higher stability of the final products [15]. Nevertheless, the mixing effectiveness of MIVR is yet to be fully proven. Therefore, in this work, both these two types of reactors will be studied.
1.2 Turbulent mixing and chemical reactions

1.2.1 General Review on Turbulence

In most chemical engineering processes, mixing is associated with turbulence and indeed, only with turbulent flow can fast mixing be achieved. As a consequence, a brief introduction to turbulence is presented here. Readers can refer to classical materials for more details, such as, Bradshaw [16], Tennekes and Lumley [17], Hinze [18] and Pope [19] and so on.

The Nature of Turbulence

Although turbulence can be encountered almost everywhere in daily life, from water flow running out of a faucet to the air flow around a car or an airplane, scientists and engineers are far from certain about some of its most fundamental aspects. Worse even, the very precise definition is still up in the air. Nevertheless, following Tennekes and Lumely [17], a few characteristic features can be written out to describe the nature of turbulence:

- *irregularity*, or randomness, which makes a deterministic approach to turbulence
problems impossible, but instead, statistical models are more desirable;

- *diffusivity*, which causes rapid mixing and increased rates of momentum and heat transfer and is of extreme importance in this context;

- *large Reynolds number*, meaning that the inertial stresses far outweigh the viscous stresses, to which the instabilities can be mainly attributed;

- *three-dimensional vorticity fluctuations*, indicating that turbulence must be rotational and three-dimensional;

- *dissipation*, caused by viscous deformation, responsible for the loss of kinetic energy and decay of turbulence;

- *continuum*, suggesting that turbulence is also governed by the equations of fluid mechanics;

- *turbulent flows are flows*, i.e., turbulence is not a feature of fluids, but rather of fluid flows.

**Conservation Equations**

The continuum property of turbulent flows deserves some special attention. First, the Knudsen number is defined to characterize the separation of length scales \( \text{Kn} \equiv \frac{\lambda}{l} \), where \( \lambda \) is the mean free path between fluid molecules and \( l \) is the smallest characteristic flow length scale. As in the example given by Pope [19], \( \lambda \) is \( 6 \times 10^{-8} \) m for air under atmospheric conditions while \( l \) for this case would typically be larger than \( 10^{-4} \) m. This leads to \( \text{Kn} \ll 1 \) and therefore the continuum assumption is valid. The same can also be proved to be true in similar manner for liquids. In other words, so long as the smallest length scale can be observed in a turbulent flow is much greater than the characteristic
molecular scale, the continuum assumption is satisfied. Consequently, turbulent flows are governed by the well-known Navier-Stokes equations.

Given the continuum feature, the continuity equation and momentum equation can be obtained by applying the mass conservation law and Newton’s second law (conservation of momentum) to an infinitesimal control volume

\[
\frac{\partial U_i}{\partial x_i} = 0, \quad (1.1)
\]

\[
\frac{\partial U_i}{\partial t} + U_j \frac{\partial U_i}{\partial x_i} = \nu \frac{\partial^2 U_i}{\partial x_j \partial x_j} - \frac{1}{\rho} \frac{\partial p}{\partial x_i}, \quad (1.2)
\]

where \( U_i \) is the component of the velocity vector \( \mathbf{U} \), \( \rho \) the density, \( p \) the modified pressure and \( \nu \) the kinematic viscosity, defined as the ratio of the viscosity \( \mu \) and the density, \( \nu = \mu / \rho \). Repeated indices indicate Einstein summation rule. Here, the conditions of constant physical properties and Newtonian fluid are implicitly applied, which are usually the case in chemical engineering processes. These conditions will be used throughout this work unless specified otherwise.

**Statistical Description of Turbulence**

As mentioned previously, one essential feature of turbulent flows is its irregularity, or randomness. That states at high Reynolds number, the velocity field \( \mathbf{U} \) is random. In the theory of turbulence, the probability density function (PDF) is employed to completely characterize the random velocity field \([19, 20]\).

Following the notations used by Pope \([19]\), the probability of the event \( \{ U_1 < V_1 \} \) is expressed as \( P\{U_1 < V_1\} \), where \( V_1 \) is the sample space variable corresponding to \( U_1 \). The one-point PDF of \( U_1(\mathbf{x}, t) \) at fixed spatial location \( \mathbf{x} \) and time \( t \), \( f_{U_1}(V_1; \mathbf{x}, t) \), is then defined such that on a small interval \( dV_1 \), the probability of \( U_1 \) falls in between \( V_1 \) and \( V_1 + dV_1 \) is just \( f_{U_1}(V_1; \mathbf{x}, t)dV_1 \), or mathematically

\[
f_{U_1}(V_1; \mathbf{x}, t) \equiv P\{V_1 \leq U_1(\mathbf{x}, t) < V_1 + dV_1\}. \quad (1.3)
\]
In order to include all three components of the velocity field, the one-point joint velocity PDF is written

\[ f_U(V; x, t) dV = f(V_1, V_2, V_3; x, t) dV_1 dV_2 dV_3 \]

\[ \equiv P\{V_1 \leq U_1(x, t) < V_1 + dV_1\} \]
\[ \cap \{V_2 \leq U_2(x, t) < V_2 + dV_2\} \]
\[ \cap \{V_3 \leq U_3(x, t) < V_3 + dV_3\} \]. \quad (1.4) \]

For a given point in a flow, the one-point PDF contains all the information about the random variable of interest. The mean can be constructed from the PDF

\[ \langle U_1 \rangle \equiv \int_{-\infty}^{+\infty} V_1 f_{U_1}(V_1; x, t) dV_1 \]

\[ = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} V_1 f_U(V; x, t) dV \] \quad (1.5)

where

\[ f_{U_1}(V_1; x, t) = \int_{-\infty}^{+\infty} f_U(V; x, t) dV_2 dV_3 \] \quad (1.6)

is termed as the marginal PDF of \( U_1 \). More generally, for any function \( h(U) \) of \( U \), the mean (or expected value) can be defined

\[ \langle h(U) \rangle \equiv \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} h(V) f_U(V; x, t) dV. \] \quad (1.7)

Thus, by defining the velocity fluctuations

\[ u(x, t) \equiv U(x, t) - \langle U(x, t) \rangle, \] \quad (1.8)

\( n \)th central moment can also be written in terms of PDF

\[ \mu_{n,1} \equiv \langle u_1^n \rangle = \int_{-\infty}^{+\infty} (V_1 - \langle U_1 \rangle)^n f_{U_1}(V_1; x, t) dV_1. \] \quad (1.9)
When $n = 2$, $\mu_{2,1}$ is the variance $\sigma_{u_1}^2$. In addition to these basic definitions, more statistical quantities can be defined. For example, the velocity covariance

$$\langle u_i(x, t) u_j(x, t) \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (V_i - \langle U_i \rangle)(V_j - \langle U_j \rangle) f(U; x, t) dV$$

recognized as the Reynolds stresses, is the mixed second moments [19, 21].

It needs to be stressed one more time that the one-point PDF $f(V; x, t)$ fully describe the random variable $U(x, t)$. From the statistical point of view, random variables with the same PDF are considered to be identical, which is called “statistically identical” [19]. In general, more sophisticated high-order (namely, more spatial and/or temporal points and more variables) PDF’s contain more statistical information. Nevertheless, extra complexity will be inevitably brought in as well. For spatial structural information, a two-point joint PDF would normally suffice.

The process of taking the mean of Equations 1.1 and 1.2 is called Reynolds averaging, which then results in the equations for the mean velocity

$$\frac{\partial \langle U_i \rangle}{\partial x_i} = 0 \quad (1.11)$$

$$\frac{\partial \langle U_i \rangle}{\partial t} + \langle U_j \rangle \frac{\partial \langle U_i \rangle}{\partial x_j} = \nu \frac{\partial^2 \langle U_i \rangle}{\partial x_j \partial x_j} - \frac{1}{\rho} \frac{\partial \langle p \rangle}{\partial x_i} - \frac{\partial \langle u_j u_i \rangle}{\partial x_j}. \quad (1.12)$$

The unclosed Reynolds stresses appear in the last term of Equation 1.12 and require closure. Modeling approaches are to be presented in later sections.

1.2.2 Mixing of Substances

Turbulent flows are more attractive to a chemical engineer than laminar flows because of the diffusive nature of turbulence. Due to turbulent diffusion, the transport of mass is greatly enhanced. Therefore, chemical species are more quickly distributed uniformly in reactors than merely molecular diffusion, which can be crucial for mixing-sensitive processes [22].
Transport of Scalars

The governing equation for the transport of a scalar $\phi_\alpha$ reads

$$\frac{\partial \phi_\alpha}{\partial t} + U_j \frac{\partial \phi_\alpha}{\partial x_j} = \Gamma_\alpha \frac{\partial^2 \phi_\alpha}{\partial x_j \partial x_j} + S_\alpha(\phi).$$  \hspace{1cm} (1.13)

Note that the first three terms in Equation 1.13 resemble those in Equation 1.2, each representing the accumulation of mass, convection of mass and molecular diffusion respectively. Depending on the physical meaning of $\phi_\alpha$, i.e., concentration of chemical species $\alpha$ or enthalpy, the coefficient $\Gamma_\alpha$ can be molecular diffusivity or thermal conductivity [21]. The last term appearing in Equation 1.13 is the chemical source term, which in general is a non-linear function and requires closure. For chemical species $\alpha$ involved in $N_r$ elementary reactions with a total number of $N$ species, it takes the general form [23]

$$S_\alpha(\phi) = \sum_{i=1}^{N_r} \left[ (v_{\alpha i}^r - v_{\alpha i}^f) \left( k_i^f(T) \prod_{\beta=1}^{N} \phi_\beta^{v_{\beta i}^f} - k_i^r(T) \prod_{\beta=1}^{N} \phi_\beta^{v_{\beta i}^r} \right) \right]$$  \hspace{1cm} (1.14)

where $v_{\alpha i}^r$ and $v_{\alpha i}^f$ are stoichiometric coefficients for species $\alpha$ acting as reactant and product in $i$th reaction, and $k_i(T)$’s are the rate constants with the “forward” and “reverse” reaction directions denoted by the superscripts “f” and “r” on them respectively [24]. Note that, however, on the left hand side of Equation 1.14, $\phi$ is the composition vector containing the $N$ components $\phi_\alpha$, $\alpha = 1, 2, \cdots, N$. If $S_\alpha(\phi) = 0$, indicating the no reaction occurs when mass is transported, it is called passive scalar mixing, or reactive mixing otherwise. In this work, both passive scalar mixing and reactive mixing will be investigated.

The one-point joint velocity-composition PDF can be defined the way we define the velocity PDF

$$f_{U,\phi}(V, \psi; x, t)dVd\psi \equiv P[\{V \leq U(x, t) < v + dV\} \cap \{\psi \leq \phi(x, t) < \psi + d\psi\}],$$  \hspace{1cm} (1.15)
or, simpler, the one-point composition PDF

\[
f_\phi(\psi; \mathbf{x}, t) \, d\psi \equiv P[\psi \leq \phi(\mathbf{x}, t) < \psi + d\psi]. \tag{1.16}
\]

where \( \psi \) is the sample-space variable of \( \phi \). Again, using these definitions, statistical quantities can be defined. For example, the scalar flux is written

\[
\langle \mathbf{U}(\mathbf{x}, t) \phi(\mathbf{x}, t) \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int V \psi f_{U,\phi}(\mathbf{V}, \psi; \mathbf{x}, t) \, d\mathbf{V} \, d\psi. \tag{1.17}
\]

These quantities will be used in the Reynolds-averaged Navier-Stokes (RANS) framework, but can also be extended to the large eddy simulations (LES).

Similarly, the Reynolds averaging process is also performed on Equation 1.13 to obtain

\[
\frac{\partial \langle \phi_\alpha \rangle}{\partial t} + \langle U_j \rangle \frac{\partial \langle \phi_\alpha \rangle}{\partial x_j} = \Gamma_\alpha \frac{\partial^2 \langle \phi_\alpha \rangle}{\partial x_j \partial x_j} + \langle S_\alpha(\phi) \rangle - \frac{\partial \langle u_j \phi_\alpha \rangle}{\partial x_j}. \tag{1.18}
\]

Here, the last two terms, the chemical source term and the scalar flux term, are unclosed and need to be modeled.

**Levels of Mixing**

Because of the complexity of the turbulent mixing process, Baldyga and Bourne [25] proposed the concepts of macromixing, mesomixing and micromixing based on different lengths scales. Each of these is a prerequisite of the next. Marcomixing takes place on the scale of the entire vessel, mesomixing on the scale of large eddies and micromixing on the scale viscous deformation and molecular diffusion. Physically, macromixing represents the global blending. Large blobs of fresh fluid are relocated and redistributed. Mesomixing then breaks down these large blobs of fluid and reduces their scales, preparing them for the next stage. Micromixing then stretches the fluid through viscous stresses to form thin lamellar structures so that molecular diffusion can happen. [6, 26]

Similar to the smallest velocity scale, the famous Kolmogorov scale \( \lambda_K \equiv (\nu^3/\varepsilon)^{1/4} \), introduced by Kolmogorov in 1941 [27], a length scale that is of extreme importance in
the context of turbulent mixing is the Batchelor scale $\lambda_B$ and is related to $\lambda_K$ by \cite{28}

$$\lambda_B \simeq \lambda_K \text{Sc}^{-1/2}. \quad (1.19)$$

where $\text{Sc}$ is the Schmidt number, defined as the ratio of the kinematic viscosity and the molecular diffusivity $\text{Sc} \equiv \frac{\nu}{\Gamma}$. The Batchelor scale describes the smallest length scale on which scalar fluctuations can still exist. The Schmidt number is a measure of how close the two microscales are to each other. For gases, $\text{Sc} \approx 1$, indicating the two microscales are comparable, while for liquids, where $\text{Sc} \approx 600–3000 \gg 1$, much finer diffusion scales can be observed than the viscous scales \cite{29}. Spectral analysis shows that when the scalar length scale ($l_\phi$) falls between $\lambda_B$ and $\lambda_K$, viscous deformation of the micromixing process occurs and molecular diffusion becomes dominant after $l_\phi$ gets smaller than $\lambda_B$ \cite{21, 26}.

**Mixing Time versus Reaction Time**

Another key aspect in turbulent flows with reactions is the mixing time. Briefly brought up in Section 1.1, the Damkohler number $\text{Da}$ is defined as $\text{Da} \equiv \frac{\tau_{\text{mix}}}{\tau_{\text{react}}}$, where $\tau_{\text{mix}}$ and $\tau_{\text{react}}$ are the characteristic mixing time and reaction time. The mixing time can be interpreted as the time needed to reduce the scalar length scale $l_\phi$ from the integral scale $L_\phi$ to the Batchelor scale $\lambda_B$. For flows with non-premixed reactants, it is dependent upon the turbulent flow as well as the Schmidt number \cite{21}. On the other hand, given the reaction rate constants and initial chemical species concentrations, the reaction time is fixed. Based on the magnitude of $\text{Da}$, reactions can be classified as follows: \cite{6, 26, 30}

- slow chemistry, if $\text{Da} \ll 1$;
- finite-rate chemistry, if $\text{Da} \approx 1$;
- instantaneous chemistry, if $\text{Da} \gg 1$;
In the first case, the mixing process has completed before the reactions start. Therefore, mixing has no effect on the final products and micromixing can be ignored. In the last two cases, however, the distribution of scalars has a great influence on the reactions and micromixing comes in as an important factor. More specifically, for instantaneous reactions, as local equilibrium state is reached, it is sufficient just to predict the distribution of scalar, whereas, in the case of finite-rate chemistry, it appears in the chemical source term, which further complicates the problem [30]. As the mixing time plays such a significant role in the prediction of the final product distribution, great care must be taken in its modeling, and indeed, it is not a trivial task to accomplish.

1.3 Research approaches

As seen previously, the mixing process in turbulent flows involves a great deal of physics. Theoretically, given an appropriate mesh, the physical quantities, such as the velocity and the concentration, can be solved straight from the governing equations for any space-time point, which is called the direct numerical simulation (DNS). However, in practice, it is currently not feasible for high-Reynolds-number flows, especially in industrial complex geometries. The grid points $N_{xyz}$ required to resolve the smallest scales of velocity can be estimated from $N_{xyz} \approx Re^{9/4}$. The computation time is thus normally large [22, 31]. To make matter worse, the mesh size is even several orders of magnitude smaller for DNS of a scalar field in liquid-phase flows where $\lambda_B \ll \lambda_K$. More computationally economical are the RANS and LES simulations with models, whose essentials are described below.

Nevertheless, models of turbulence are largely built on certain physically meaningful assumptions and empirical coefficients. Accuracy of these models must be verified. In most cases, they are validated against experimental data. On the other hand, experiments themselves also give us insights on turbulent flows. Since most techniques are
developed for reactors of large scale, they are ported to our microscale systems in this work. Fundamental aspects of the methods employed in this work are outlined in this section.

1.3.1 Mathematical models

Starting from the conservation equations introduced in Section 1.2, the RANS models and LES framework are briefly discussed here. Reactions encountered in this work are instantaneous and thus the source terms are exclusively determined by turbulent mixing. As a consequence, closures for chemical source terms are omitted here.

**RANS Models**

As pointed out in their corresponding sections, unclosed terms are present in the RANS equations, namely, the Reynolds stresses in the momentum equation 1.12 and the scalar flux in the scalar transport equation 1.18.

By introducing the concept of turbulent viscosity \( \nu_T \), the Boussinesq assumption states

\[
\langle u_i u_j \rangle = \frac{2}{3} k \delta_{ij} - 2 \nu_T S_{ij},
\]

where \( k = \frac{1}{2} \langle u_i u_i \rangle \) is the turbulent kinetic energy, \( S_{ij} \) is the mean rate-of-strain tensor

\[
S_{ij} = \frac{1}{2} \left( \frac{\partial \langle U_i \rangle}{\partial x_j} + \frac{\partial \langle U_j \rangle}{\partial x_i} \right),
\]

and \( \delta_{ij} \) is the Kronecker delta function. The job left now is to find an appropriate formulations for \( \nu_T \). It can be expressed as the product of a length \( l^* \) and a velocity \( u^* \), \( \nu_T = u^* \cdot l^* \). Various models are developed based on the concept, the zero-equation (or algebraic) mixing length model, the one-equation turbulent-kinetic-energy model and the two-equation \( k-\omega \) model, to name a few. More details of RANS models in this category and some others can be found elsewhere [19, 31]. However, for the sake of
conciseness, only the $k$-$\varepsilon$ model, which perhaps is the most widely RANS model, is discussed herein.

In this particular model, $\nu_T$ is written in terms of the turbulent kinetic energy $k$ and the turbulent dissipation rate $\varepsilon \equiv \nu_T \left\langle \frac{\partial u_i}{\partial x_i} \frac{\partial u_i}{\partial x_j} \right\rangle$ as follows

$$\nu_T = C_{\mu} \frac{k^2}{\varepsilon}, \quad (1.22)$$

The transport equations for $k$ and $\varepsilon$ take the form

$$\frac{\partial k}{\partial t} + \langle U_j \rangle \frac{\partial k}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \nu_T \frac{\partial k}{\partial x_j} \right) + P - \varepsilon \quad (1.23)$$

$$\frac{\partial \varepsilon}{\partial t} + \langle U_j \rangle \frac{\partial \varepsilon}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \nu_T \frac{\partial \varepsilon}{\partial x_j} \right) + C_{\varepsilon 1} \frac{P \varepsilon}{k} - C_{\varepsilon 2} \frac{\varepsilon^2}{k} \quad (1.24)$$

where the five model constants are $C_{\mu} = 0.09, C_{\varepsilon 1} = 1.44, C_{\varepsilon 2} = 1.92, \sigma_k = 1.0, \sigma_\varepsilon = 1.3$, and $P \equiv -\langle u_i u_j \rangle \frac{\partial \langle U_i \rangle}{\partial x_j}$ is the production term.

By analogy to the Fickian diffusion law, the scalar flux model proposed by Taylor [32] reads

$$\langle u_j \phi_\alpha \rangle = -\Gamma_T \frac{\partial \langle \phi \rangle}{\partial x_j} \quad (1.25)$$

where $\Gamma_T$ is the turbulent diffusivity defined as $\Gamma_T \equiv \frac{\nu_T}{Sc_T}$ with $Sc_T$ being the turbulent Schmidt number.

**LES Framework**

The RANS models are developed upon a set of Reynolds-averaged equations, whose major idea is the ensemble averaging. LES, however, stems directly from DNS. From the kinetic energy spectrum, it can been seen that most of the energy are contained in the larger-scale motions, whereas, the majority of computational effort in DNS is spent on resolving the smallest-scale counterpart, which are more universal [19]. This very fact leads to the filtering operation that results in the LES on the exact solution in the
hope of significantly reducing the computational cost but retaining reasonable accuracy. The filtered part will be solved from transport equations while the residual is modeled. This process is expressed mathematically below. First, the general definition of the filtering operation following Leonard’s proposal [33] is given

\[ \mathbf{U}(x, t) \equiv \int \int \int_{-\infty}^{+\infty} G(r, x)\mathbf{U}(x - r, t)dr \] (1.26)

where \( G(r, x) \) is the filtering kernel satisfying the normalization condition [19],

\[ \int G(r, x)dr = 1. \] (1.27)

The velocity is thus decomposed into two parts, i.e., the filtered velocity \( \mathbf{U}(x, t) \) and the residual \( u'(x, t) \)

\[ \mathbf{U}(x, t) = \mathbf{U}(x, t) + u'(x, t) \] (1.28)

The filtered continuity and momentum equation then follow

\[ \frac{\partial \mathbf{U}_i}{\partial x_i} = 0, \] (1.29)

\[ \frac{\partial \mathbf{U}_i}{\partial t} + \mathbf{U}_j \frac{\partial \mathbf{U}_i}{\partial x_j} = \nu \frac{\partial^2 \mathbf{U}_i}{\partial x_j \partial x_j} - \frac{1}{\rho} \frac{\partial p}{\partial x_i} - \frac{\partial \tau_{ij}}{\partial x_j}. \] (1.30)

Here, we define the residual-stress tensor \( \tau_{ij} \)

\[ \tau_{ij} \equiv \mathbf{U}_i \mathbf{U}_j - \mathbf{U}_i \mathbf{U}_j. \] (1.31)

Then the anisotropic residual-stress tensor is defined by

\[ \tau_{ij}^r \equiv \tau_{ij} - \frac{1}{3} \tau_{kk} \delta_{ij} \] (1.32)

and modified filtered pressure with the isotropic residual stress included is

\[ p \equiv \int p(x - r, t)G(r, x)dr + \frac{1}{3} \rho \tau_{kk} \] (1.33)

Again, closure of Equation 1.30 can be obtained by modeling the anisotropic residual stress term \( \tau_{ij}^r \). The Smagorinsky model employed in this work is discussed here.
As mentioned earlier, motions on the smallest scale are considered to be isotropic and universal. A simple model might just suffice for the description of these motions. The Smagorinsky, being the simplest of its class, is given by

$$\tau_{ij} = -2(C_S \Delta)^2 |S| S_{ij}$$  \hspace{1cm} (1.34)

where $\Delta$ is the filter width, usually taken to be the grid size, and the constant $C_S$ ranges from 0.1 to 0.24 [31]. The filtered rate of strain is defined by $S_{ij} \equiv \frac{1}{2} \left( \frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right)$ and the characteristic filtered rate of strain is $|S| \equiv (2S_{ij}S_{ij})^{1/2}$.

Filtered transport equation for a scalar takes the form

$$\frac{\partial \bar{\phi}}{\partial t} + U_j \frac{\partial \bar{\phi}}{\partial x_j} + \frac{\partial \tau^r_{\phi i}}{\partial x_i} = \Gamma \frac{\partial^2 \bar{\phi}}{\partial x_j \partial x_j}$$  \hspace{1cm} (1.35)

with the residual scalar flux being

$$\tau^r_{\phi i} \equiv U_j \bar{\phi} - U_j \bar{\phi}$$  \hspace{1cm} (1.36)

which is modeled by analogy with the Smagorinsky model

$$\tau^r_{\phi i} = -\Gamma_{sgs} \frac{\partial \bar{\phi}}{\partial x_i}$$  \hspace{1cm} (1.37)

where $\Gamma_{sgs} \equiv \frac{2(C_S \Delta)^2}{S_{csgs}} |S|$ is the subgrid-scale (SGS) turbulent diffusivity. The SGS turbulent Schmidt number $S_{csgs}$ normally takes the value of 0.4 in turbulent flows.

**Mixing Models**

Turbulent mixing can be accounted for in CFD with the scalar variance $\langle \phi'^2 \rangle$ whose Reynolds-averaged transport equation reads

$$\frac{\partial \langle \phi'^2 \rangle}{\partial t} + \langle U_j \rangle \frac{\partial \langle \phi'^2 \rangle}{\partial x_j} = \Gamma \frac{\partial^2 \langle \phi'^2 \rangle}{\partial x_j \partial x_j} - \frac{\partial \langle u_j \phi'^2 \rangle}{\partial x_j} + P - \varepsilon_{\phi}$$  \hspace{1cm} (1.38)

where $\phi' \equiv \phi - \langle \phi \rangle$ is the scalar fluctuation, $P \equiv -2(u_j \phi) \frac{\partial \langle \phi \rangle}{\partial x_j}$ the production of scalar variance whose closure can be achieved by using Equation 1.25, and $\varepsilon_{\phi} \equiv 2\Gamma \left\langle \frac{\partial \phi'}{\partial x_i} \frac{\partial \phi'}{\partial x_i} \right\rangle$
the scalar dissipation rate. Similar to Equation 1.25, the scalar-variance flux \( \langle u_j \phi'^2 \rangle \) can be closed with

\[
\langle u_j \phi'^2 \rangle = -\Gamma_T \frac{\partial \langle \phi'^2 \rangle}{\partial x_j}.
\]

In finding a closure for the scalar dissipation rate, the proportionality is assumed between the mechanical time scale \( \tau_u \) and the scalar time scale \( \tau_\phi \)

\[
C_\phi = \frac{\tau_u}{\tau_\phi} = \frac{k/\varepsilon}{\langle \phi'^2 \rangle/\varepsilon_\phi}.
\]

Simple manipulation then yields

\[
\varepsilon_\phi = C_\phi \varepsilon \langle \phi'^2 \rangle
\]

where the model constant \( C_\phi \approx 2 \) provides reasonably good approximation for high-Reynolds-number flows.

Likewise, in terms of the filtered density function (FDF) [34]

\[
h_\phi(\psi; \mathbf{x}, t) = \int_{-\infty}^{+\infty} \delta[\phi(\mathbf{r}, t) - \psi] G(\mathbf{r} - \mathbf{x}) d\mathbf{r},
\]

we can also define the subgrid-scale scalar variance \( V_\phi \) in the LES framework

\[
V_\phi = \int \left[ \psi - \int \psi h_\phi d\psi \right]^2 h_\phi d\psi
= \int \left[ \psi - \langle \phi \rangle \right]^2 h_\phi d\psi
= \bar{\phi}^2 - \bar{\phi}^2
\]

The transport equation of \( V_\phi \) is given by

\[
\frac{\partial V_\phi}{\partial t} + \frac{\partial \bar{u}_i V_\phi}{\partial x_i} = \frac{\partial}{\partial x_i} \left[ (\Gamma + \Gamma_T) \frac{\partial V_\phi}{\partial x_i} \right] + 2(\Gamma + \Gamma_T) \frac{\partial \overline{\phi \partial \phi}}{\partial x_i \partial x_i} - 2\Gamma \frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_i}
\]

The only remaining open term in this equation is the filtered scalar dissipation,

\[
\chi = 2\Gamma \frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_i}.
\]
One particular closure proposed by Jiménez et al. [35] again by assuming proportionality between the mechanical time scale and the scalar time scale reads

$$\chi = \frac{\nu + C_S \Delta^2 |S|}{ScC_I \Delta^2} (\bar{\phi}^2 - \bar{\phi})$$  (1.46)

where \(\Delta\) is a box filter of characteristic size 10 times the grid size, \(\Delta = 10\Delta\) and the value of the constant \(C_I\) can be between 0.06 and 0.09.

The CFD-based mixing models introduced above could be used to predict concentration fields for slow and instantaneous reactions where the chemical source term can be safely ignored or be expressed in algebraic functions of concentrations. For finite-rate chemistry, however, the source term that appears in Equation 1.18 requires closure. Because the chemical source term is a non-linear function of the Eulerian concentration fields, its closure is difficult. Instead, Lagrangian formulation can solve this problem, as pointed by Fox [30], wherein the chemical source term \(S(\phi)\) is closed. Various micromixing models in this category can be found in the literature [21, 30, 36, 37]. Though in this work, chemical source term is not an important issue, for completeness and for future use, the direct-quadrature-method-of-moments interaction-by-exchange-with-the-mean (DQMOM-IEM) model without the source term [38, 39] is described here.

For a two-feed non-premixed system, a conserved scalar (usually the mixture fraction \(\xi\)) is used to describe the mixing [21, 24]. By using a presumed form of the composition PDF (fine grained PDF) coupled with a multi-environment formulation [19, 21], the mixture fraction in \(n\)th environment can be denoted by \(\xi_n\) with its probability by \(p_n\). For the case of total environment number of 2, \(p_1 + p_2 = 1\), and the mixture-fraction mean \(\langle \xi \rangle\) and mixture-fraction variance \(\langle \xi^2 \rangle\) can be expressed

$$\langle \xi \rangle = p_1 \xi_1 + p_2 \xi_2$$  (1.47)

$$\langle \xi^2 \rangle = p_1 \xi_1^2 + p_2 \xi_2^2 - \langle \xi \rangle^2$$  (1.48)
Here, the variables to be solved in a CFD code are $p_1$, $p_1\xi_1$ and $p_2\xi_2$, whose RANS transport equations are respectively give by

$$\frac{\partial p_1}{\partial t} + \nabla \cdot (\langle U \rangle p_1) = \nabla \cdot (\Gamma_T \nabla p_1)$$

(1.49)

$$\frac{\partial (p_1\xi_1)}{\partial t} + \nabla \cdot (\langle U \rangle p_1 \xi_1) = \nabla \cdot (\Gamma_T \nabla (p_1\xi_1)) + \gamma p_1p_2(\xi_2 - \xi_1) + \frac{\Gamma_T}{\xi_1 - \xi_2} (p_1|\nabla \xi_1|^2 + p_2|\nabla \xi_2|^2)$$

(1.50)

$$\frac{\partial (p_2\xi_2)}{\partial t} + \nabla \cdot (\langle U \rangle p_2 \xi_2) = \nabla \cdot (\Gamma_T \nabla (p_2\xi_2)) + \gamma p_1p_2(\xi_1 - \xi_2) + \frac{\Gamma_T}{\xi_2 - \xi_1} (p_1|\nabla \xi_1|^2 + p_2|\nabla \xi_2|^2)$$

(1.51)

The last two terms in Equations 1.50 and 1.50 are due to micromixing, and the micromixing parameter $\gamma$ is modeled by $\gamma = \frac{C_\phi \varepsilon}{2k}$.

When the chemical source term is too significant to be left out, this micromixing model can be extended by simply adding additional reaction-related variables and their corresponding transport equations. More details can be found elsewhere [21, 39]. Although the model described here is developed using the RANS approach, extension to LES has been proved to be straightforward [40].

1.3.2 Experimental techniques

The validation of the models introduced in the previous section is threefold: a) fluid dynamics; b) macromixing and 3) micromixing. Therefore, each of the experimental techniques used must suit for one of the three purposes. In other words, microscale particle image velocimetry ($\mu$-PIV) is employed to study the velocity field and corresponding statistics, confocal-based microscale laser induced fluorescence (Confocal $\mu$-LIF) of passive scalar mixing is for the investigation of the macromixing and the micromixing is examined via the phenolphthalein visualization technique and the confocal $\mu$-LIF of reactive mixing. Short introductions to these methods are given here. Presentation of details follows in later chapters.
Microscale PIV

Initially developed for obtaining velocity data in large scale flows, PIV is a laser-based technique. Its non-intrusive nature and the ability of acquiring full-field information make it attractive to engineers and scientists in the field, and are responsible for its rapid development ever since its first appearance in literature.

The main idea behind this method is simple. Provided the time interval $\Delta t$ between laser pulses, one is to find the displacement of the embedded particles within small boxes, called “interrogation windows”. Fluorescent particles are illuminated by the thin laser sheet. More explicitly, frames at these two different times are taken. Cross-correlation is then carried out from which the displacement (average in certain interrogation window) is computed. A velocity vector can thus be represented in this area.

In recent years, PIV has also been applied to microscale flow systems. In addition to the microscope required to view the image the flow field, one key difference between $\mu$-PIV and the conventional PIV is the depth of the illuminated volume; it is equal to the thickness of the laser sheet in the latter while in the former, the height of the reactor is on the same order of magnitude of the laser sheet and therefore the concept of “depth of correlation” has to be introduced to correct calculate the correct particle concentration. A number of authors have successfully measured the turbulent velocity field in microscale systems, proving its practicability.

Confocal-Based Microscale LIF

Just like the PIV method, the LIF technique has been extended to microscale flow systems, and is called microscale LIF or in short $\mu$-LIF. Fluids are stained with fluorescent dye. At very low dye concentration, linear relation exists between the concentration and the fluorescence intensity. That is, from the gray-scale values in the data images, the normalized concentration can be computed, which corresponds to the extent of mixing.
However, the use of ordinary epi-fluorescence microscope poses the difficulty that light from out-of-focus plane blurs the image. To crack this problem, the confocal microscope will be used. By introducing two pinholes—one in front of the laser, the other in front of the detector—confocal is able to reject out-of-focus light. This effect, termed “optical sectioning”, produces a thin focus slice and enhances the resolution and accuracy of the data.

Both passive scalar mixing experiments and reactive mixing experiments are conducted using this setup. The only difference between the two is the fluorescent dye; for the former, Rhodamine 6G is used, whereas, for the latter, a pH-sensitive dye, sodium fluorescein is chosen. Despite that, the physics involved is significantly different, which is explained more later.

Phenolphthalein Visualization Method

In flow visualizations and mixing characterization, pH indicators have long been utilized because of its simplicity in implementation. They are typically used with acid-case neutralization reactions. Normally, pH indicators change color according to pH values. In turbulent flows where local pH changes due to the acid-base reaction, regions with different pH values are marked with distinguishable colors. Flow and mixing patterns can therefore be easily observed with this method.

One major flow visualization technique developed in this work is based on a very common pH indicator, phenolphthalein, after which the name of the method is name. In order to capture the turbulent motion and thus increase the temporal resolution, a pulsed flash lamp is used as the light source. Even with that, the data obtained are normally qualitative. By employing a unique image processing technique, mixing performance and coherent structures can be quantified and analyzed, as will be seen.
1.4 Report outline

The rest of the material is organized as follows:

1. Detailed description of the phenolphthalein visualization technique and its application to the CIJR are provided in Chapter 2.

2. Fluid dynamics in the MIVR is investigated using $\mu$-PIV in Chapter 3 and RANS and LES models are validated against the experimental data in Chapter 4.

3. The confocal $\mu$-LIF method is presented in Chapters 5 with its application in visualizing passive scalar mixing in the MIVR.

4. Micromixing effects are studied in Chapter 6 using confocal-based $\mu$-LIF system with an acid-base neutralization reaction.

5. Chapter 7 concludes the thesis and points out directions for future work.
CHAPTER 2 VISUALIZATION OF TURBULENT REACTIVE MIXING IN A PLANAR MICROSCALE CONFINED IMPINGING-JET REACTOR

This chapter is modified from a paper published in

*Journal of Micromechanics and Microengineering*\(^1\)

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2.1 Introduction

In many chemical process applications, microscale reactors can have superior performance characteristics compared to their conventional large scale counterparts. For example, microscale reactors possess enhanced heat and mass transfer performance due to high surface area to volume ratio \([41]\). Moreover, characteristic mixing times due to the small volumes of microreactors can be greatly reduced, enabling the control of fast reactions \([42, 43]\). Common applications of microreactors range from sample preparation for chemical/biological analysis \([44, 45]\) to industrial production of nanoparticles \([13, 46]\).


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Nanoparticle production has become a popular area of research over the past decade. Nanoparticles with uniform size distribution have applications in various areas, such as pesticides, cosmetics and drug delivery [1, 3, 4]. Yet despite their growing popularity, nanoparticles can prove difficult to manufacture with existing technologies. One recently developed nanoparticle manufacturing technique, first proposed by Johnson and Prud’homme [6], *Flash Nano-Precipitation*, is a very promising technique for the synthesis of functional nanoparticles. Two types of microreactors, the *Confined Impinging-Jet Reactor* (CIJR) and *Multi-Inlet Vortex Reactor* (MIVR), have been developed with a particular emphasis on their usefulness in *Flash Nano-Precipitation*.

Rapid mixing and the resulting ‘homogeneity’ of the flow field are essential for the optimum realization of *Flash Nano-Precipitation*. These conditions imply shorter fluid mixing times than particle formation times. Both the CIJR and MIVR have demonstrated the capability to produce such short mixing times and good mixing [6, 13]. Past studies have attempted to characterize the mixing performance and/or hydrodynamics of the flow using various experimental and numerical techniques. Johnson and Prud’homme [13] quantified the mixing performance of their custom designed CIJR by measuring the dimethoxypropane (DMP) produced in the slow reaction in a carefully chosen second order Bourne pair. Note that this technique only provides information on the output of the reactor and provides no data on the flow field or mixing performance within the reactor. For the same reactor geometry, Liu and Fox [39] performed *computational fluid dynamics* (CFD) simulations and obtained satisfactory agreement with Johnson and Prud’homme’s experimental results. The same techniques were also applied to investigating the MIVR [47]. Once again the simulation results displayed satisfactory agreement with the experimental data. More recently, Cheng et al. [14] and Liu et al. [48] employed *microscopic particle image velocimetry* (microPIV) to directly measure the turbulent velocity field in the MIVR and the planar CIJR, respectively, for comparisons with CFD simulations. The comparisons turned out quite well.
To complement the previous studies, in the present research we utilize a non-intrusive technique for visualizing and quantifying turbulent reactive mixing in a confined impinging jet microreactor. This flow visualization technique is simple and inexpensive, but as we shall demonstrate, quite effective. By utilizing the pH indicating dye phenolphthalein, this technique provides striking visualization of turbulent reactive mixing in the CIJR and can also provide a quantitative measure of fluid mixing and turbulent structure characteristics. In the following sections, the fabrication of the reactor, the experimental setup and procedures, and an image processing technique for quantifying reactive mixing will be described, followed by results and discussions from which some conclusions will be drawn.

2.2 Reactor geometry and Flow-delivery system

![Figure 2.1 Geometry of the planar confined impinging jet reactor](attachment:image.png)

Unlike the axisymmetric cylindrical CIJR design used in some previous studies [13, 39], the reactor geometry in the present work is rectangular in cross-section so as to
avoid the optical distortion effects resulting from imaging through curved surfaces. A drawing of the reactor used in this study is shown in Fig. 2.1. The resulting three-plate reactor is similar to the one described by Liu et al. [48], where the fabrication technique is discussed in detail. For brevity, only a brief description of the fabrication is presented here. In Liu et al. [48], the reactor shape was carved out by electrical discharge machining (EDM) on a stainless steel plate.

In the present work, the same stainless steel plate has been used as in Liu et al. [48], but the top and bottom walls have been replaced by Plexiglas™ plates due to the high pressure provided by specially designed clamps, which may easily break glass slides. The purpose of these clamps is to strengthen the seal between the Plexiglas™ plates and the stainless steel and prevent leaks. In addition to the clamps, thin pieces of Parafilm (Pechiney Plastic Packaging Inc.) with the shape of the channel cut out are also inserted between the Plexiglas™ plates and the stainless steel plate to improve sealing. Any leakage issues at high Reynolds numbers have been eliminated this way while still leaving the flexibility of disassembling the reactor for cleaning whenever needed. However, since the thickness of Parafilm (0.127 mm) is slightly different from that of the adhesive film used by Liu et al. [48], the depth of the reactor (denoted by $D$ in Fig. 2.1) is 1.12 mm compared to 0.92 mm in the work of Liu et al. [48]. The width of the impinging jets, $w$, is 0.5 mm. The chamber width $W$, height $H$, length $Z$ and the outlet width $\delta$ have scaled values $W/w = 4.76$, $H = 0.8W$, $Z = 1.2W$, and $\delta = 2w$ respectively. The length-to-width ratio of the inlets is $L_1/w = 20$ and the length-to-width ratio of the outlet is also $L_2/\delta = 20$.

A schematic of the flow-delivery system is shown in the upper portion of Fig. 2.2. Fluid is delivered to the two inlets of the reactor by a dual-syringe pump (model KDS210P, KD Scientific Inc.). Two 60 ml syringes, one containing a sodium hydroxide solution and one containing a hydrochloric acid solution, are placed on the rack of the syringe pump and attached with flexible tubings (C-flex tubing, Cole-Parmer Instrument
Co.) to the inlets of the reactor. The mixed fluid exits the reactor through another flexible tube and is collected in a waste bottle.

2.3 Experimental Technique and Apparatus

2.3.1 Technique Overview

Numerous experimental methods have been developed to visualize turbulent flow features and to either quantitatively or qualitatively characterize mixing performance. Methods for characterizing mixing performance typically fall into one of two categories. The first category involves mixing-sensitive processes [13], such as second-order competitive/consecutive chemical reactions [49], and the second category includes dye-based visualization techniques [50]. The first category has the advantage of easy implementation and is typically used as “chemical ruler” for the micromixing time due to well
defined reaction kinetics. However, these techniques have the disadvantage of only measuring the output from reactor and provide no information on mixing and turbulence details within the reactor. In the second category, laser induced fluorescence (LIF) with its capability of providing both instantaneous flow visualization snapshots as well as quantitative statistical data on mixing and reaction processes is perhaps the most widely used [51, 52]. However, LIF inevitably requires rather expensive equipment, such as lasers, sensitive cameras, triggering and timing units, etc. [53] From this point of view, a simpler technique using non-fluorescent dyes is an attractive alternative that could potentially reduce experimental cost significantly and provide more researchers with access to the technique, while still providing valuable insights on the mixing performance and allowing turbulent structures to be visualized. For this reason, a number of researchers have found phenolphthalein, a common pH indicator, particularly useful in turbulent mixing studies for numerous reasons [50, 54–57]. First, phenolphthalein is widely available and inexpensive. Second, phenolphthalein reacts to changes in pH so rapidly that the process is usually considered diffusion-limited [58]. Third, the pink or purple product created within a certain pH range can be easily distinguished from the colorless reactants [59].

Although the mixing extent can be quantified by the amount of phenolphthalein reacted in pure base-dye reaction [50, 54], the protocol established by Abarca and Clement [53] is employed here. Non-premixed binary mixing can be mathematically described by mixture fraction (or in this case equal to mass fraction), $\xi$. With the boundary conditions, $\xi = 1$ for basic solution in one inlet and $\xi = 0$ for acidic solution in the other, the pH at any location in the reactor can be related to this quantity

$$
\xi = \begin{cases} 
\frac{C_{a0} - 10^{-\text{pH}}}{C_{a0} + C_{b0}} & \text{pH} < 7 \\
\frac{10^{-(14-\text{pH})} + C_{a0}}{C_{a0} + C_{b0}} & \text{pH} \geq 7
\end{cases}
$$

(2.1)
Figure 2.3  pH–ξ relation for given pH\(_a\) and pH\(_b\) in non-premixed binary mixing system

where \(C_a\) and \(C_b\) are concentrations of H\(^+\) and OH\(^-\) at the inlets respectively, which are fixed given initial acid and base pH values, pH\(_a\) and pH\(_b\). For pH\(_a\) = 3 and pH\(_b\) = 11.02 in our system, this relation can be illustrated as in Figure 2.3. Complete mixing corresponds to a mixture fraction \(ξ = 0.5\) and a pH of 9.3. In Figure 2.3, a sudden increase in pH is observed in a tiny range of ξ. This fact provides a basis for the numerical color separation between the reacted and the unreacted because phenolphthalein changes color at a typical pH of 9.3. Therefore, any point in the field that shows purple color can be considered to have a \(ξ\) (or equivalently base volume fraction) greater than 0.5. With that in mind, the mixing performance can be quantitatively evaluated, by thresholding the local values by using an image processing technique, which is to be described in Section 2.3.3.
2.3.2 Experimental Setup and Procedure

The reaction solutions are prepared such that the solutes are dissolved in a solvent mixture consisting of 30% ethyl alcohol and 70% deionized water by volume. The alcohol is added to increase the solubility of phenolphthalein and thus allow for a greater concentration of phenolphthalein to be dissolved than would be possible in pure deionized water. The higher concentration of phenolphthalein is necessary to increase the contrast of the images so the phenolphthalein can be clearly imaged. After the solution is prepared, 30ml of phenolphthalein stock solution (abbreviated Hln in schematic) is then added to 1L of the solutions for both inlet streams. The phenolphthalein stock solution consists of 3.1832 g of phenolphthalein dissolved in 100 ml of ethyl alcohol. Dissolving phenolphthalein in both inlet streams was done to minimize density differences between the two streams, and more importantly, to reduce the two factors (pH and concentration of phenolphthalein) to one (only local pH) that influence the visibility of phenolphthalein [53] since the concentration of phenolphthalein will be constant throughout the reaction chamber. In the prepared solutions, phenolphthalein is saturated and the precipitated powders are filtered out to obtain precipitate free solutions after the solutions settle for two hours. The resulting base solution has a pH of 11 and the pH of the acid solution is 3. The solutions are then degassed to minimize the possibility of bubbles forming in the reactor chamber and in the inlet.

The flow visualization system is shown in Fig. 2.2. While the flow-delivery system has been described previously, the imaging components, highlighted by the dashed box, are described here. The light path in this system is denoted by the solid arrows. The main body of an inverted biological microscope (model Eclipse T300 Inverted Microscope, Nikon Inc.) is omitted here for simplicity. In order to freeze the turbulent fluid motion and provide an instantaneous snapshot of the flow field, a pulsed light source (model PAX-1001-4 10Watt Precision Aligned Pulsed Xenon light source, Perkin Elmer Inc.),
labeled flash lamp in the figure, with extremely short pulse duration (5 μs) is used to provide the illumination. For such a short pulse duration, a fluid element moving at 4.5 m/s, which is the maximum velocity in these experiments, travels only 22.5 μm, demonstrating the effectiveness of the flash lamp in freezing the fluid motion. The flash lamp is powered by a power supply (model EFB Filtered DC power supply, Epsco Inc.) and the light intensity can be varied by adjusting the voltage. The non-uniformity of the light from the flash lamp is reduced by using a diffuser (10°, model 10DKIT-C2 Light Shaping Diffuser®, Newport Corp.) to generate a visually uniform field of view. The instantaneous flow field images are recorded by a color CCD camera (model Stingray F-080C, Allied Vision Technologies GmbH), digitized and stored on a computer. Both the flash lamp and CCD camera are triggered by a pulse generator (model DG535 4-channel Digital Delay/Pulse Generator, Stanford Research Systems Inc.), operating at a frequency of 15 Hz providing synchronization so that each captured image is illuminated by a single pulse of the flash lamp. A 2X objective coupled with a 0.45X video coupler gives a broad field of view such that the entire reactor chamber can be imaged. The experiments are carried out for three different jet Reynolds numbers, 25, 1000 and 1500, as defined in $Re_j = \frac{u_{jet} D_h}{\nu}$, where $u_{jet}$ is the mean velocity of the inlet channels, $D_h$ the hydraulic diameter of the inlet channels and $\nu$ is the kinematic viscosity. Over 5000 images are collected for each of these Reynolds numbers.

### 2.3.3 Image Processing Technique

As will be seen in the results section, this technique can provide striking qualitative visualization of the turbulent reactive mixing in the reactor chamber. However, extracting quantitative data is more challenging. Phenolphthalein is clear at acidic and neutral pH, but turns a bright pink at basic pH. This color change in phenolphthalein is a sharp transition. This makes it difficult to simply attempt to calibrate the observed image intensity with pH, since the dynamic range of the signal is small. Instead, a more
promising technique for extracting quantitative mixing data from the phenolphthalein images is to recognize that transition from clear to pink in the solutions used in these experiments occurs at a pH of 9.3, identify which regions of the flow field are clear and pink, and consequently, in each instantaneous image identify regions pH less than 9.3 and regions with pH greater than or equal to 9.3. This pH is also the pH at the outlet of reactor where the two solutions are completely mixed. The ensemble of images thresholded in this manner can be used to determine the probability of local pH being equal to or greater than 9.3 at various locations throughout the flow field. The seemingly easiest way of doing this is to convert the color images to gray scale and carry out the thresholding on the gray scale images. However, this technique was rejected after a few attempts since it failed to identify the interface between colored and uncolored region even when applied to the laminar case where there exits a sharp interface between the colorless and colored regions because of the low contrast in the gray scale images. One might argue this problem can be readily resolved by normalizing the images using images containing only uncolored phenolphthalein solutions, but this was found to be not of much help. However, a completely digital image processing method has been adopted in this work that is not only easy to perform but also successfully identifies colored and uncolored regions. Similar to the “gray-scale” idea, in this image processing technique, the images are first converted into CIELAB color space, where the three coordinates $L^*$, $a^*$ and $b^*$ represent the luminosity (or simply brightness), the positive component (consisting mainly of red hues) and the negative component (consisting mainly of green hues), respectively [60]. By only computing the $a^*$ and $b^*$ values, the purple (colored phenolphthalein) and green (uncolored phenolphthalein) regions, which are the principle colors in the collected images, can be successfully separated. In other words, dark and light colors are treated identically if this $L$ value is ignored. The steps involved in this process are described below:
1. find characteristic $a^*$, $b^*$ values from the average calibration image, where the reactor is filled with completely mixed solution with a pH of 9.3, for green and purple, denoted by $a_{cg}^*$, $a_{cp}^*$, $b_{cg}^*$ and $b_{cp}^*$ respectively;

2. evaluate for each point in each image the distances from the two characteristic values,

$$d_{i,\text{green}} = \sqrt{(a_i^* - a_{cg}^*)^2 + (b_i^* - b_{cg}^*)^2}, \quad (2.2)$$

$$d_{i,\text{purple}} = \sqrt{(a_i^* - a_{cp}^*)^2 + (b_i^* - b_{cp}^*)^2}; \quad (2.3)$$

3. assign the point a tag purple if $d_{i,\text{green}} > d_{i,\text{purple}}$, but a tag green otherwise;

4. let the intensity of a point $I_i = 1$ if the tag is purple and $I_i = 0$ if it is green.

This process is performed by utilizing the Image Processing Toolbox in Matlab®, which results in a set of binary images. Example thresholded images created using this technique are presented in the next section.

### 2.4 Results and Discussion

#### 2.4.1 Instantaneous Images

Three example instantaneous images for $Re_j = 25$ are shown in Fig. 2.4. In these images (and all images presented), the left inlet stream is acidic (and hence colorless), and the right inlet stream is basic (and hence pink). The two inlet streams impinge in the center of the reactor, and the flow is turned downwards towards the outlet. At this Reynolds number, the flow is laminar and steady and so the interface between the fluid of the two inlet streams remains sharp as they convect towards the outlet. The only mixing between the two streams is due to diffusion. The pink fluid observed above the inlets in the reactor is due to two counter-rotating recirculation eddies that appear in this region (these recirculation eddies were observed in both CFD simulations and microPIV
Figure 2.4  Sample original instantaneous images for $\text{Re}_j = 25$.

Figure 2.5  Sample original instantaneous images for $\text{Re}_j = 1000$. 
measurements as reported by Liu et al. [48]). Three instantaneous images for Re\textsubscript{j} = 1000 are shown in Fig. 2.5. Several features of the flow and mixing performance are suggested by these images. First, the inlet streams are not fully mixed or reacted when they exit the reactor. The fully reacted inlet fluids have a pH of 9.3, as pointed out previously, and thus produce a pink color in the phenolphthalein. Next, the highly convoluted interfaces between the colored and uncolored regions are indicative of the flow in the reactor being turbulent. Swirling patterns suggest the presence of large-scale turbulent vortices. Finally, the varying orientation of the impingement plane between the two inlet streams indicates an unsteady flapping motion of this impingement plane (a finding consistent with the large eddy simulation (LES) and direct numerical simulation (DNS) results of Icardi et al. [61, 62] for an axisymmetric impinging jets reactor). Fig. 2.6 shows three instantaneous images for Re\textsubscript{j} = 1500. The flow at this Reynolds number is also turbulent and unsteady, with the turbulent features and oblique flapping of the impingement plane even more pronounced than at Re\textsubscript{j} = 1000. The images also suggest improved mixing performance compared to Re\textsubscript{j} = 1000. For example, in the first two panels of Fig. 2.6, broad swatches of clear fluid from the left inlet jet are observed to penetrate nearly to
the outlet of the reactor, but this penetration is reduced at $Re_j = 1500$.

2.4.2 Image Thresholding and Statistical Analysis

Example thresholded images created using the image processing technique described in Section 2.3.3 are shown in Fig. 2.7 for $Re_j = 25$, 1000 and 1500. In these images, the colored and uncolored phenolphthalein regions have been identified, with the colored regions tagged with a value of 1 and the uncolored regions with a value of 0. The resulting images identify regions where the local pH is less than 9.3 (value of zero) or
greater than or equal to 9.3 (value of one).

This thresholding was performed for each of the over 5000 realizations collected for each Reynolds number. Ensemble averages using these thresholded instantaneous realizations for all three Reynolds numbers investigated are shown in Fig. 2.8, and presented in the form of contour plots. The value at each location in the ensemble average contour plots falls between zero and one, and this value represents the probability at each point in the flow field that the local pH is greater than or equal to 9.3 in one instantaneous realization. Recall that for fully mixed and reacted inlet fluid, the pH is 9.3, and would thus result in a thresholded image value of 1. Thus, a flow in the reactor resulting in complete mixing and reaction within the reactor chamber would have fluid leaving the reactor with an ensemble-averaged value of one all across the exit of the reactor. Thus, the ensemble-average shown in Fig. 2.8 can provide a means of comparing mixing performance at the different Reynolds numbers investigated.

The first panel in Fig. 2.8 shows the ensemble-average of the thresholded images for $\text{Re}_j = 25$. The results are nearly binary, with the left side of the flow field having a value of zero and the right side having a value of one. Only a thin region in the center
of the reactor has intermediate values, indicating the steady state laminar nature of the flow at this Reynolds number. As expected, mixing performance is poor. The middle panel of Fig. 2.8 shows the ensemble-average of the thresholded images for $Re_j = 1000$. Here, the improved mixing performance due to the presence of turbulence is readily observed. At the outlet of the reactor (below $y = -3$ mm), the exiting fluid does not have a nearly uniform binary value of 0 or 1, as it did in the $Re_j = 25$ case. Instead, the exiting fluid has ensemble-averaged values ranging from 0.6 to 1.0. Also, on the left side of the reactor, pure inlet fluid does not penetrate to the outlet of the reactor, as in the $Re_j = 25$ case, but instead penetrates to only $y = -1.5$ mm before it begins reacting with fluid from the other inlet stream. Finally, the last panel in Fig. 2.8 shows the ensemble-average of the thresholded images for $Re_j = 1500$. Here, the contours suggest better mixing performance than for $Re_j = 1000$ (as would be expected). There are several indications of this. First, the pure inlet fluid on the left side of the reactor is less able to penetrate far into the reactor before reacting with basic fluid, penetrating to only $y = -0.75$ mm. Moreover, at the exit of the reactor the ensemble-average value is nearly uniform at 0.8. The fluid is still not fully mixed and reacted, but this uniform value indicates that fluid from each of the inlet jets is nearly equally distributed at the reactor exit. Also, unlike the $Re_j = 25$ and $Re_j = 1000$ cases, none of the pure inlet fluid from the right inlet seemingly passes through the reactor before encountering acidic fluid, as below $y = -2.0$ mm, none of the contours have a value greater than 0.9. Even the regions of 0.6 and 0.7 ensemble-averaged value in the lower right side of the reactor are indicative of the superior mixing at this Reynolds number, as they indicate some of the fluid from the left inlet must be advected to this far corner of the reactor.

2.4.3 Spatial Correlations and Large-Scale Structures

The ensembles of instantaneous images can also be used to investigate the properties and behavior of large-scale turbulent structures by calculating spatial auto-correlations
Figure 2.9  Contours of two-point spatial auto-correlation coefficient for $Re_j = 1000$ (top), $Re_j = 1500$ (bottom) at three different locations (marked with the ‘+’ sign)
of the thresholded images. Let $I(x, y)$ represent the ensemble-average of the thresholded images, as shown in Fig. 2.8. If $i(x, y)$ represents an instantaneous realization of the thresholded image ensemble, then for each instantaneous image, an instantaneous fluctuation, $i'(x, y)$, can be defined as $i'(x, y) = i(x, y) - I(x, y)$. Then the two-point spatial auto-correlation coefficient of $i'$ can be computed as,

$$ R(x, y; X, Y) = \frac{\langle i'(x, y)i'(X, Y) \rangle}{\sqrt{\langle i'^2(x, y) \rangle \langle i'^2(X, Y) \rangle}}, $$

(2.4)

where $R$ is the correlation coefficient, $(X, Y)$ is the basis point about which the spatial correlation is measured and $(x, y)$ is a displacement from the point $(X, Y)$. The spatial auto-correlation of $i'$ for three different measurement locations in the flow field for $Re_J = 1000$ and 1500 are presented in Fig. 2.9. The three measurement locations are all along vertical centerline of the reactor. The first point is at the same vertical location as the centerlines of the two inlet channels and roughly corresponds to the stagnation point in the flow. This location is denoted as $y = 0.0$ mm. The other two measurement locations are 0.7 mm and 1.5 mm below this location. The top three panels in Fig. 2.9 are the auto-correlation fields around the three measurement locations for $Re_J = 1000$. In each panel, the location of the basis point is shown by the ‘+’ symbol. One interesting feature of these correlations is that the area of the correlation peaks becomes larger as downstream distance increases. Since the size of the correlation peaks is expected to be related to the size of large-scale turbulent structures in the flow, this suggests that the turbulent structures become larger as the flow convects downstream, a finding consistent with large-scale structure behavior in turbulent shear flows [51]. Also, at each measurement location, the positive auto-correlation peak is accompanied by a weakly negatively correlated region either upstream or downstream of the measurement location. This behavior is due to the unsteady oblique flapping of the interface between the two incoming streams. Because of this oblique flapping, if one location along the reactor has
colored phenolphthalein, then locations above or below this location are likely to have uncolored dye, resulting in the observed anti-correlation.

The bottom three panels in Fig. 2.9 are the auto-correlation fields around the three measurement locations for Re$_j$ = 1500. The features of the correlations are similar to those observed for Re$_j$ = 1000 indicating similar flow behavior.

2.4.4 POD Analysis

These energy-containing coherent structures can also be well identified by the proper orthogonal decomposition (POD). First introduced to low-dimensional descriptions of turbulent flows by Lumley [63], POD is also known as principle component analysis, the Karhunen–Loeve decomposition and the single value decomposition (SVD) [64, 65]. Its formulation is briefly described here.

For a scalar field $z(x, t)$ in a turbulent flow (applicable to velocity field too), an approximation by using a set of uncorrelated spatial functions $\phi_n(x)$ weighted by their corresponding temporal coefficients $a_n(t)$ can be written as follows

$$z(x, t) \approx \sum_{n=1}^{M} a_n(t) \phi_n(x). \quad (2.5)$$

As $M$ goes to infinity, this approximation tends to the exact reconstruction. The decomposition, however, is not unique. POD provides a mathematical device for finding a particular set such that it is optimal in terms of energy by maximizing [65–67]

$$\frac{\langle (z, \phi)^2 \rangle}{\langle \phi, \phi \rangle} = \lambda, \quad (2.6)$$

where the angle brackets denote the ensemble average and $(a, b)$ is defined by

$$(a, b) = \int_D a(x, t)b(x, t)dx. \quad (2.7)$$

This results in the following eigenvalue problem
Figure 2.10  Distributions of modal energy (cross) and cumulative energy (circle) for (a) $Re_j = 25$, (b) $Re_j = 1000$ and (c) $Re_j = 1500$. 
Figure 2.11  Fluctuating eigenfunctions for modes $n = 1–3$ at $\text{Re}_j = 25$

Figure 2.12  Fluctuating eigenfunctions for modes $n = 1–3$ at $\text{Re}_j = 1000$

\[
\int_D R_{ij}(x, x') \phi_n(x')dx' = \lambda_n \phi_n(x) \quad (2.8)
\]

with the kernel

\[
R_{ij}(x, x') = \frac{1}{T} \int_T z(x, t)z'(x', t)dt. \quad (2.9)
\]

However, as very often used by other researchers [68, 69], the ‘method of snapshot’ is applied in this work. First proposed by Sirovich [70], the ‘method of snapshot’ defines
he ensemble average as the spatial average instead of temporal average. Thus, the eigenvalue problem becomes

\[ \int_T C(t, t') a_n(t') dt' = \lambda_n a_n(t) \]  \hspace{1cm} (2.10)

where the kernel \( C(t, t') \) is a temporal auto-correlation function and it reads

\[ C(t, t') = \frac{1}{T} \int_D z(x, t) z(x, t') dx. \]  \hspace{1cm} (2.11)

Once \( a(t) \) is determined, the spatial eigenfunctions can be calculated using the following formula

\[ \phi_n(x) = \frac{1}{\lambda_n T} \int_T a_n(t) z(x, t) dt \]  \hspace{1cm} (2.12)

In this work, the POD analysis is performed on fluctuations of the grayscale ‘snapshots’ converted from the original RGB images (not the ones with the threshold). The analysis is also bounded only in the impingement zone same as in the spatial-correlation contours. 1,000 realizations are used, which would definitely suffice to obtain the most energetic structures as will be seen. Again, the Matlab package is utilized to simplify
the coding process. In Figure 2.10, the content of energy represented by the eigenvalue $\lambda$ is shown on the left axes while the cumulative energy defined as the ratio of the sum of the first $n$ modes to the total energy of the 1000 ‘snapshots’ is given on the right. Since most of the energy is contained in the first a few modes, data for the first 100 modes are plotted. Contours of the fluctuating eigenfunctions are given for the modes 1 to 3 (from left to right) in Figures 2.11–2.13.

At $Re_j = 25$, the flow is laminar. The content of energy drops rapidly as the mode number increases from a few hundreds to a few tens (Figure 2.10(a)). The cumulative energy shows that the first 10 modes account for nearly 40% of the total energy, after which it gradually goes up to 1. The three major fluctuating modes are displayed in Figure 2.11. However, it is nothing more than a straight line in all three modes, indicating the interface of the two streams only moves back and forth in between this small region.

The energy is distributed more evenly over the modes at high Reynolds numbers (Figures 2.10(b) and 2.10(c)), where the flow is turbulent with many more small scale fluctuating structures; the higher the more evenly. In other words, the content of energy decreases at a slower pace at the first a few modes. With that been stated, nevertheless, the first 10 out of the 1000 modes still represent approximately 20% of the total energy at $Re_j = 1000$ and 15% at $Re_j = 1500$ respectively. From the POD analysis, the main fluctuating structures are clear. Comparison between the eigenfunctions at these two Reynolds numbers leads to conclusions consistent with those from the spatial correlation. First, notice the dark and bright regions in the contours of eigenfunctions each with positive and negative values, so depending on the sign of the temporal coefficient $a_n(t)$, each of the eigenfunctions can be added to the mean flow to reconstruct the flapping motion. Taking the first mode in Figure 2.12 for example, $a_n(t)$’s with opposite signs give exactly opposite flow motions. The third mode, on the other hand, represents the horizontal flapping. Second, the increase in Reynolds number stretches the structures
in the $x$-direction but suppresses them in the $y$-direction, indicating better mixing. The overall fluctuating structures remain similar.

### 2.5 Conclusions

In the presented work, turbulent reactive mixing in a rectangular *confined impinging-jet microreactor* was investigated using the pH indicator phenolphthalein. The experiments were performed for three different inlet jets Reynolds numbers $Re_j = 25$, 1000 and 1500. The visualizations show the flow is laminar at $Re_j = 25$ and turbulent at $Re_j = 1000$ and 1500. The visualizations suggest an unsteady motion of the impingement plane consisting of an interface that obliquely rocks back and forth. A technique was then described for extracting quantitative mixing data from the instantaneous images by using image processing to identify regions in the flow field with pH greater than or equal to 9.3 and regions with pH less than 9.3. The thresholded images were then ensemble averaged to yield pH probability fields. The ensemble-averaged images indicate poor mixing performance for $Re_j = 25$, and better mixing performance for $Re_j = 1000$, and further improved mixing performance for $Re_j = 1500$. However, even at $Re_j = 1500$ complete mixing and reaction was not observed at the outlets.

Finally, spatial auto-correlations of the thresholded images fluctuations were calculated. The correlations suggested that large-scale turbulent structures grew as they convected towards the reactor outlet and provided further evidence of oblique flapping of the impingement zone. POD analysis gives a better illustration on the major fluctuating structures.
CHAPTER 3 MEASUREMENTS OF TURBULENCE IN A MICRO-SCALE MULTI-INLET VORTEX REACTOR

This chapter is modified from a paper to be submitted to

*Lab on a Chip*

Yanxiang Shi\(^1\)\(^2\), Janine Chungyin Cheng\(^1\)\(^3\), Rodney O Fox\(^1\)\(^4\) and Michael G Olsen\(^5\)\(^6\)

3.1 Introduction

Nanoparticles have become an important subject in modern science and technology. Due to their specially useful physical properties compared to bulk materials [4], they are widely used in various areas, such as dyes, cosmetics, and pharmaceuticals [1, 4–6]. However, precisely controlling the particle size distribution (PSD) is a challenging task. Flash NanoPrecipitation (FNP), a technique proposed by Prud’homme and his colleagues [6], has shown great promise in the mass production of functional nanoparticles with precise control of PSD. In Fig. 3.1, the concept of the technique is demonstrated in a microscale reactor. A solvent containing a saturated solution of actives along with block copolymers is pumped into one or more of streams while a non-solvent into the

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others. Mixing between the streams within the reactor chamber leads to supersaturation of both the actives and the polymers, which in turn stimulates precipitation and aggregation. The aggregates of the actives are then protected by the copolymers to form stable nanoparticles. In the FNP process, particle size and morphology thus are largely dependent upon the mixing.

The multi-inlet vortex reactor (MIVR) is one of the microscale nanoprecipitation reactors that have been used in the FNP process. Due to its special arrangements of the inlets and the mixing chamber, it not only is able to provide good mixing at high Reynolds numbers, but also has the flexibility of allowing different flow rates (and thus momenta) from different streams [14, 15, 71]. Because of its importance in the FNP process, the MIVR mixing and flow in the reactor have been studied by previous researchers. The first effort on this particular subject came from Liu et al. [15], who used computational fluid dynamics (CFD) models to simulate mixing and reaction. Later, Cheng et al. [14] used large eddy simulations (LES) to model turbulent flow in the MIVR and compared the results with preliminary $\mu$-PIV experiments and found satisfactory agreement. This work is extended here with the first detailed velocity and Reynolds shear stress results presented for turbulent flow in the MIVR. Recently, Shi et al. [71] used confocal microscopy to study turbulent mixing of a passive scalar in the MIVR.

The $\mu$-PIV technique has gained popularity in the measurements of full field velocity information in microscale devices since its first introduction by Santiago et al. [72] In general, $\mu$-PIV shares the common principles with the standard PIV but differs in the method of illumination. [73] Initially, $\mu$-PIV was developed to study laminar microscale flow, but several researchers have since demonstrated its effectiveness in investigating turbulent microscale flows. [14, 48, 61, 74, 75] Compared to its macroscopic counterpart, measurement of turbulent microscopic flows requires special consideration. As pointed out by Liu et al. [48], numerous parameters have to be taken into consideration in applying $\mu$-PIV to turbulent microscale flows. The greatest challenge in collecting $\mu$-
PIV data for a turbulent flow is obtaining the proper seed particle concentration. In studying laminar flows, seed density is not as crucial as a large ensemble of $\mu$-PIV image pairs can be used in the sum of correlation technique [76] to analyze the data. However, in studying a turbulent flow, each individual $\mu$-PIV image pair must be sufficiently seeded to provide an accurate instantaneous velocity field.

In the present work, the first detailed experimental measurements of velocity and turbulent Reynolds stress for flow in an MIVR are presented and discussed. These data are crucial for the development of accurate, validated computational models of turbulent flow and mixing in the MIVR that can be used to aid in the design and optimization of FNP in microscale chemical reactors.
Figure 3.2 Schematic (top left) and photograph (top right) of the MIVM and schematic of the μ-PIV setup (bottom)
3.2 Experimental section

3.2.1 Microreactor design and fabrication

A sketch of the microscale MIVR studied in this work is given in Fig. 3.2. The reactor has four inlets attached tangentially to the circular mixing chamber. The reactor outlet protrudes perpendicularly from the reactor. Dimensions of the reactor as denoted in Fig. 3.2 are the inlet channel width \( w = 1.19 \text{ mm} \), the channel height \( H = 1.78 \text{ mm} \), the diameter of the mixing chamber \( 2R = 6.26 \text{ mm} \) and the outlet diameter \( 2r = 1.40 \text{ mm} \).

The fabrication of the microscale nanoprecipitation reactor is customized such that it has the following features [48]:

- an imaging window that is transparent for the illuminating laser light as well as the emitted fluorescence light to pass through;
- chemical resistance such that it is inert to the materials used in FNP;
- tight seals to prevent fluid leakage;
- precision manufacturing to ensure the correct geometry;
- ease of disassembly for cleaning.

The final design takes the form of a three-piece assembly, the main body made of stainless steel, a quartz window and a threaded plastic lid with the center drilled through (allowing for optical access through the quartz window). The main body is also threaded and can be screwed into the lid with the quartz sandwiched in between. To prevent leakage, an O-ring is placed between the main body and the quartz. Fittings are fixed to the top of the reactor for connections with tubing to allow fluid to flow in and out of the reactor.
3.2.2 Experimental setup

As shown at the bottom of Fig. 3.2, the experiment setup consists of the flow delivery system (upper portion with a solid box) and the imaging system (lower portion bounded by the dashed line).

A syringe pump with a multi-syringe holder is used to generate the flow. Four syringes are filled with seeded working fluid (water in this study) and are connected via soft tubing with the four inlets of the MIVR, which is placed on the stage of the inverted microscope. A small container collects the exiting fluid, which is used to refill the syringes when they are emptied.

The source of illumination in the system is a dual cavity Nd:YAG laser coupled with a frequency doubler. The resulting wavelength (532 nm) is nearly identical to the optimal excitation wavelength of the seeding particles (535 nm). The laser beam is expanded to cover the field of view of the microscope. A dichroic mirror (or beam splitter in the schematic) is in place to separate the emitted light from the fluorescent seed particles from the scattered and reflected illuminating laser light. A 4×/0.2NA objective is used with a 0.45× coupler to give an overall magnification of 1.8×. The µ-PIV images are recorded using a CCD camera.

3.2.3 Experimental methodology

The µ-PIV analysis method used here is the cross-correlation technique used in its conventional macroscopic counterpart. Two dimensional (2D) images of the seeded flow field are divided into small square areas, called the “interrogation window”. The primary objective of µ-PIV is therefore to find the average displacement of seeding particles in each interrogation windows between lasers pulses with time interval $\Delta t$ [77]. By means of cross-correlation of two frames taken at these two distinct time instants, this purpose can be efficiently fulfilled. Laser pulse lasts so short that the turbulent motion is “frozen”
onto the grayscale images. The time interval $\Delta t$ must be set to ensure the displacement is noticeable but the majority of the particles remain in a certain interrogation window.

Particle concentration is another key aspect which needs great care. By introducing the concept of “depth of correlation” for $\mu$-PIV [73, 78, 79]:

$$2Z_{corr} = 2 \left[ \frac{1 - \sqrt{\varepsilon}}{u \sqrt{\varepsilon}} \left( f^# d_p^2 + \frac{5.95(M + 1)^2 \lambda^2 f^#^4}{M^2} \right) \right]^{\frac{1}{2}}$$

(3.1)

where $\varepsilon = 0.01$; $d_p$ is the particle diameter; $\lambda$ is the emission wavelength of the particle; $M$ is the magnification of the lens and $f^#$ the focal number, which is related to its numerical aperture (NA) by:

$$f^# = \frac{1}{2NA},$$

(3.2)

the minimum particle concentration is then computed by using

$$C = \frac{N}{2Z_{corr} \times A}$$

(3.3)

where $N$ is the minimum number of particles in each interrogation volume, which is typically taken to be 5–10 [80], and $A$ is the area of each interrogation window.

Particle size is chosen to meet certain requirement of Stokes number (St) defined as the ratio of particle response time and the flow time scale [81]

$$St \equiv \frac{\gamma \rho_p d_p^2}{12 \mu_t}$$

(3.4)

where $\gamma$ is approximated by $u/R$ with $u$ being the inlet bulk velocity, $\rho_p$ is the particle density and $\mu_t$ is the fluid viscosity. In other words, it should be small so the time lag between the fluid motion and the particle motion can be ignored.

### 3.2.4 Experimental parameters

For the particular setup used in this study, the depth of correlation is 72.27 $\mu$m and therefore, with fixed $N = 5$, the minimum concentration $C$ of particle ($2 \mu$m, 1.05 g/cm$^3$ nile red FluoSpheres, Invitrogen Corporation) is found to be $2.09 \times 10^7$ #/ml and St
Figure 3.3 Instantaneous velocity field at the midplane (top), and mean tangential (middle) and radial (bottom) velocity profiles of center lines at three data acquisition planes at $Re_j = 53$. In the legend, $m$ (□) represents the midplane, $q2b$ (♦) the quarter-of-reactor-height-to-bottom plane and $q2t$ (△) the quarter-of-reactor-height-to-top plane.
Flow rates (ml/min) | $U_j$ (m/s) | Re$_j$ | Re
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<tbody>
<tr>
<td>4.93</td>
<td>0.0369</td>
<td>53</td>
<td>911.40</td>
</tr>
<tr>
<td>8.64</td>
<td>0.0647</td>
<td>93</td>
<td>1,597.27</td>
</tr>
<tr>
<td>22.30</td>
<td>0.1670</td>
<td>240</td>
<td>4,122.58</td>
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Table 3.1  Re$_j$ and Re at different flow rates

$\sim 10^{-7} \ll 1$. Interrogation windows are chosen to be $32 \times 32$ squares with 50% overlap between adjacent windows. Each pixel is also a square of size $3.6 \, \mu m$ and this leads to a vector spatial resolution of $57.6 \, \mu m$.

Flow rates are equal in all four inlets in this study and we define the Reynolds number Re$_j$ in terms of the characteristic inlet velocity (or jet velocity) $U_j$ by

$$Re_j \equiv \frac{d_h U_j}{\nu}$$

(3.5)

where $d_h$ is the hydraulic diameter of the inlet channel and $\nu$ is the kinematic viscosity of the fluid. Note that MIVR can be operated in such a way that each of the inlets can have its own flow rate (or even fluid), a more general definition of Reynolds number based on the mixing chamber is given by

$$Re \equiv \sum_{i=1}^{4} 2R \frac{U_i}{\nu_i}$$

(3.6)

where $U_i$ and $\nu_i$ are the mean inlet velocity and the kinematic viscosity in $i$th inlet, respectively. As can be seen, contributions from each inlet are appreciated in this definition. In order to distinguish the two, the first definition is termed as “jet Reynolds number”. Table 4.1 lists the three different jet Reynolds numbers investigated as well as their corresponding Re’s. They each represent a flow regime, i.e., laminar at Re$_j$ = 53, transitional at Re$_j$ = 93 and turbulent at Re$_j$ = 240. For each Re$_j$, over 1000 realizations are acquired on three planes (shown in the middle left of Fig. 3.2, i.e., the quarter-of-reactor-height-to-bottom plane, the mid-plane and the quarter-of-reactor-height-to-top plane), from which the mean velocity field is computed.
3.3 Results and discussion

3.3.1 Instantaneous and mean velocity fields

Results for mean velocity the case of Re$_j = 53$ are given in Fig. 3.3. As the flow is steady in this case, only an instantaneous velocity field from the middle plane is shown instead of the mean velocity field since the flow patterns at different time instants are identical to the mean velocity field. As can be seen from the top panel of this figure, the flow is axisymmetric with lower velocities distributed in the outer region and higher velocities near the center. However, note that the $\mu$-PIV technique used in this study is two dimensional (2D) providing only velocity measurements in the imaging plane, and does not provide velocities in the out-of-plane direction. The significance of the third velocity component (in the $z$ direction) grows relative to the in-plane components as the flow approaches to the center, and near the center of the reactor, the resolved velocity components drop to zero.

In order to compare the velocity behavior at the different measurement planes, mean profiles along the center lines ($y = 0$ mm) at each plane are also plotted in the two lower panels of Fig. 3.3. Because of the swirling nature of the flow, the velocity components are transformed from Cartesian coordinates to polar coordinates to obtain tangential and radial components. These are then normalized by the mean inlet velocity. Similar tangential velocity profiles at the different planes are observed. The profiles are all symmetric about the reactor center ($x = 0$ mm) and consist of a low-slope velocity increase section (approximately $|x| > 1$ mm), a high-slope velocity increase section (approximately $0.2 \text{mm} < |x| < 1$ mm) and a section (approximately $|x| < 0.2$ mm) where velocity drops rapidly. The increase in tangential velocity as the fluid spirals towards the center of the reactor is a consequence of conservation of angular momentum (similar to a spinning figure skater spinning more rapidly as she brings her arms tightly into her body). However, this increase in tangential velocity is partly counteracted by
Figure 3.4  Instantaneous velocity field at the midplane (top), and mean tangential (middle) and radial (bottom) velocity profiles of center lines at three data acquisition planes at $Re_j = 93$. 
viscosity acting to decrease the tangential velocity by dissipating the kinetic energy of the flow. This effect of viscosity was clearly seen in flow visualization experiments in this reactor [71] where at Re$_j$ = 10, the inlet streams head nearly directly towards the reactor exit, because the strong viscous effects at Re$_j$ = 10 rapidly dissipate the tangential motions of the fluid.

The Re$_j$ = 93 case is just below the transition to turbulence and the flow is still in a steady state. As such, only a single instantaneous velocity field is shown in Fig. 3.4. Overall, this case is very similar to the Re$_j$ = 53 case, but a couple of distinguishable changes should be noted. First, the velocity magnitude nearly doubles due to the increased flow rate at the inlet. Moreover, the maximum normalized tangential velocity, as shown in the middle panel of Fig. 3.4, now peaks at around 7, compared to 4 in the previous case. This is a consequence of the decreasing effects of viscosity at this higher Reynolds number. At Re$_j$ = 53, the effect of viscosity are more significant and so the tangential velocity is retarded as the flow spirals towards the center. Viscosity is less significant at Re$_j$ = 93, so this tangential slowing is less significant. On the hand, the maximum normalized radial velocity (the bottom panel in Fig. 3.4) remains similar in magnitude. This results in a greater tangential-to-radial velocity ratio, indicating a stronger vortex at this Reynolds number. Moreover, as the velocity increases, the inertial forces start to dominate and wall effects become less significant and thus the slowing effects of friction with walls take longer to take effect. This can be seen from the tangential velocity profiles at different planes that almost fall on each other, unlike at Re$_j$ = 53, where the bottom velocity profile is lower than the others due to the interaction with the lower wall. More apparently even, the normalized radial velocity profile at the lower-most plane differs greatly from the other two in the shape. The smaller differences between planes indicate a more homogeneous flow.

For the Re$_j$ = 240 case, mean velocity fields at the three measurement planes are shown in Fig. 3.5 in addition to the instantaneous velocity field from the midplane.
Numerous seemingly randomly perturbed velocity vectors appear in the instantaneous image, indicating the turbulent nature of the flow field. However, the ensemble-averaged mean velocity fields show similar flow patterns to the previous cases. That is, the mean velocity fields at all planes are axisymmetric with tangential velocities increasing as the flow spirals towards the center. The mean normalized tangential velocity profiles from different planes are all similar, indicating less significant wall effects. What is worth noting at this Reynolds number is that, in the region close to the center, as it goes from the bottom of the reactor to the top, the mean velocity actually decreases. This phenomenon can be attributed to the vortex stretch in the z direction as the fluid exits the reactor which causes the angular momentum to be transferred into axial momentum. Consistent conclusions can be made from the radial profiles where more points with positive velocities are present (note that negative radial velocity means fluid flows towards the center of the reactor while positive radial velocity indicates otherwise).

For all three Reynolds numbers, while the maximum normalized tangential velocity increases with the mean inlet velocity, the normalized radial velocities are always of the same magnitude. This is a consequence of conservation of mass and the incompressible nature of the fluid. Fluid must exit the reactor at the same rate that it enters.

### 3.3.2 Turbulent statistics

#### 3.3.2.1 Velocity fluctuations

From an ensemble of over 1000 realizations, the turbulent statistics are computed for the case of Re\textsubscript{j} = 240. Herein, the root-mean-square (RMS) fields of both tangential and radial velocity as well as the Reynolds shear stress fields will be discussed.

Contours of the normalized tangential velocity fluctuation $u'_{\theta}/U_j$ at all three planes and the corresponding profiles along the reactor centerline are shown in Fig. 3.6. The
Figure 3.5  Instantaneous velocity field at the midplane (top left), mean velocity fields at the lower plane (top right), the midplane (middle left) and the upper plane (middle right), and mean tangential (bottom left) and radial (bottom right) velocity profiles of center lines at three data acquisition planes at $Re_j = 240$. 
Figure 3.6 RMS fields of the tangential velocity $u'_\theta$ at the lower plane (top left), the midplane (top right) and the upper plane (bottom left), and the corresponding profiles (bottom right) across the centers of all three planes at $Re_j = 240$
Figure 3.7  RMS fields of the radial velocity $u'_r/U_j$ at the lower plane (top left), the midplane (top right) and the upper plane (bottom left), and the corresponding profiles (bottom right) across the centers of all three planes at Re$_j = 240$
Figure 3.8  Reynolds stress fields $\langle u_\theta u_r \rangle / U_j^2$ at the lower plane (top left), the midplane (top right) and the upper plane (middle), and a table of the corresponding minimum and maximum values (bottom) all three planes at $\text{Re}_j = 240$

<table>
<thead>
<tr>
<th></th>
<th>lower plane</th>
<th>midplane</th>
<th>upper plane</th>
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<tbody>
<tr>
<td>Minimum value</td>
<td>-4.32</td>
<td>-3.68</td>
<td>-2.82</td>
</tr>
<tr>
<td>Maximum value</td>
<td>4.78</td>
<td>3.58</td>
<td>2.70</td>
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shapes and distributions of the contour plots display similar characteristics, with the values continuously increasing from the outer regions of the reactor and moving towards the center. That is consistent with the increase seen in the mean tangential velocity except in the region close to the center. This behavior is more apparent in the RMS profiles plots. Instead of suddenly dropping from the maximum to zero like the mean tangential velocity, the RMS values of tangential velocity fluctuation continue increasing until reaching a maximum at the reactor center. Moreover, the rate of increase in the inner region, where the mean velocity quickly approaches zero, is higher than that in the outer region. This is because in addition to small scale turbulent motions the center of the vortex moves about the center of the reactor instead of staying at one single location as in the lower Reynolds number cases. The fluctuation intensity at the center is strong since its magnitude is about 5 times that of the mean inlet velocity. Due to the suppression of turbulence by wall effects, higher fluctuations of the tangential component occur at the midplane than the other two measurement planes across the region investigated, and at the lower-most plane, a sharp jump in $u'_\theta/U_j$ is observed when it enters the inner region at $|x| \approx 0.2$ mm. Still, the profiles from different planes are still very close to each other, which is a strong indication of the homogeneity of the flow.

Despite the significant difference in the mean velocity magnitude between the tangential and radial components, very similar patterns are observed in the contours of the normalized radial velocity fluctuations $u'_r/U_j$ in Fig. 3.7, namely, circular shapes centered around from the center of the reactor, with the intensity decreasing moving away from the center. Similarly, a more clear representation of the behaviors displayed is shown in the profile along the center line. From $|x| > 1$ mm, the values slowly increase from around 0.1 m/s to about 0.3 m/s at $|x| \approx 0.5$ mm and jump from there to the maximum, which is approximately 1 m/s at the center. The region where the values increase faster has broadened compared to the tangential RMS profiles. This is consistent with the mean velocity profiles and is reasonable considering the high ratio of tangential to ra-
dial mean velocity at this Reynolds number. Nevertheless, the magnitudes of \( u_\theta'/U_j \) and \( u_r'/U_j \) are comparable at all points across the entire profile, which suggest the turbulence is locally isotropic in the measurement planes.

### 3.3.2.2 Reynolds shear stresses

The normalized Reynolds shear stress fields \( \langle u_\theta u_r \rangle/U_j^2 \) are plotted in Fig. 3.8. As can be seen from the contours, for all three planes, the Reynolds shear stress has a value of zero at the center of the reactor and positive and negative regions to each side, and these two regions are only confined close to center, where the motions of the major vortex core take place. At the lower plane, the positive and negative zones are anti-symmetric about the line \( y = 0 \text{ mm} \), whereas, for the upper two planes, the line of symmetry is tilted to about 45°. This inclination of the line of symmetry is caused by the vortex feature of the flow. In other words, the fluid exits the reactor rotating along the axis of the reactor chamber. The table at the bottom of Fig. 3.8 lists all minimum and maximum values in the contour plots. For all three cases, the respective absolute values of the negative and positive peaks are comparable. From the lower plane to the upper plane, the values decrease from greater than 4 to less than 3, which, along with the growth in area of the contours, indicates a axial stretch of the vortex and less in-plane turbulence.

### 3.4 Conclusions

The \( \mu \)-PIV technique is applied to the microscale nanoprecipitation MIVR in this work to study the velocity fields as well as the turbulent statistics. Three Reynolds numbers are investigated, i.e., \( \text{Re}_j = 53, 93, 240 \), each representing a different flow regime. At \( \text{Re}_j = 53 \), the flow is laminar and steady over time. Wall effects are so strong in this case that flow patterns are distinct from plane to plane. As the Reynolds number
is increased to 93, the wall effects are less significant and the tangential velocity profiles along the centerline are close to each other. However, the flow is still not yet fully turbulent. The unsteadiness of the flow is apparent at the highest Reynolds number. Mean velocity fields at different planes are similar. A higher ratio of tangential to radial velocity indicates a more developed vortex flow. For this case, the tangential velocity RMS and radial velocity RMS are also discussed. Due to motions of the vortex core about the center of the reactor, more fluctuations are observed close to the center. Two zones with opposite signs are present in the Reynolds shear stress fields.

Acknowledgements

The authors would like to acknowledge the financial support from National Science Foundation through the Grant No. CBET-0730250.
CHAPTER 4 VALIDATION OF CFD MODELS FOR PREDICTION OF FLUID DYNAMICS IN MIVR USING MICRO-PIV

A paper in preparation

Yanxiang Shi $^{1,2}$, Rodney O Fox $^{1,3}$ and Michael G Olsen $^{4,5}$

4.1 Introduction

Computational fluid dynamics (CFD), due to its ability of providing comprehensive field information and relatively cost-effective setup, has experienced a dramatic increase in importance, especially in chemical engineering, during the past a few decades. The Reynolds-averaged Navier-Stokes (RANS) approach, which requires the least computational resources, has been applied to various areas. In recent years, thanks to the rapid advancement in computing power, much attention has been paid in the community to large eddy simulation (LES). In spite of its moderately higher computational cost, it delivers better time-dependent solutions compared to only statistics from RANS.

Validation of models involved is indispensable for them to be used with confidence in practice. The usual starting point of this process is to verify their accuracy in predicting the velocity field and it is accomplished by comparing the simulations with certain

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velocimetry methods. The microscale PIV (abbreviated micro-PIV or μ-PIV) technique is ideal for this purpose for a couple of reasons. First, the theory is well-established and data analysis routines are optimized. Second, unlike some other probe-based methods, μ-PIV is non-intrusive, allowing high-quality measurements. Third, it provides full-field information, from which physically meaningful statistical quantities can be computed, such as turbulent kinetic energy and Reynolds stresses etc.

Tailored specially for velocity measurements in microscale flow systems from conventional PIV, μ-PIV also uses a laser to illuminate the fluorescent particles in fluid flows in microscale systems. Instead of a thin laser sheet as in conventional PIV, however, the entire volume of the microscale reactor is illuminated. Hence, the effective thickness of the illuminated portion is quantified by the “depth of correlation”, which will be discussed in detail in the next section.

The μ-PIV was first applied by Santiago et al. [72] to a Hele-Shaw flow around an elliptical cylinder. Although the flow was laminar and a mere Hg-arg lamp was used, the velocities were measured reasonably accurately, demonstrating the realizability of the technique. Following that, a few other successful attempts have also been reported in the literature. Meinhart et al. [82], for example, upgraded their μ-PIV system with Nd:YAG laser, and verified its accuracy by comparing it with a known velocity field. Zeighami et al. [83] took this method one step further. They studied the turbulent transition in microchannels with μ-PIV and fluctuations of the velocity fields were observed, from which they concluded transition occurred when the Reynolds number was between 1200 and 1600. Also, Islam et al. [84] investigated the turbulent water-flow structure over one-side micro-repeated ribs in a narrow two-dimensional rectangular channel using this technique and found that rotating and counter-rotating eddies were formed close to the rib height.

In this project, the μ-PIV is applied to the MIVR and the results are used to validate the CFD models.
4.2 Experimental Apparatus and Methodology

4.2.1 The Microreactor

A sketch of the microreactor, MIVR, studied in this work is given in Figure 4.1. It has four inlets attached tangentially to the circular mixing chamber. The outlet is in the third direction. Dimensions of the reactor as denoted in the sketch are the inlet channel width \( w = 1.19 \text{ mm} \), the channel height \( H = 1.78 \text{ mm} \), the diameter of the mixing chamber \( 2R = 6.26 \text{ mm} \) and the outlet diameter \( 2r = 1.40 \text{ mm} \).

The fabrication of the microscale nanoprecipitation reactor is customized such that it has the following features [10, 48]:

- an imaging window that is transparent for the laser beam as well as the fluorescence light to pass through;
- chemical resistance of some sort; at least inert to the materials used in this study;
- leakage prevention to stop the flow field from being altered;
- reasonably precise dimensions, ensuring the correct geometry;
being either able to be opened for cleaning or affordable so that more than enough such devices can be fabricated for this research.

The final design takes the form of a three-piece assembly, the main body made of stainless steel, a piece of quartz and a threaded plastic lid with the center drilled through. The main body is also threaded and can be screwed into the lid with the quartz sandwiched in between. Certainly, to avoid leakage issues, an O-ring is placed between the main body and the quartz. Commercial fittings are fixed to the top of the reactor for connections with tubings.

4.2.2 The Method

The $\mu$-PIV method shares fundamentals with its conventional macroscopic counterpart. Unless special camera setup is adopted, two-dimensional (2D) data will be formed. Such a 2D image is divided into small square areas, called the “interrogation window”. The primary objective of $\mu$-PIV is therefore to find the average displacement of seeding particles in each interrogation windows between lasers pulses with time interval $\Delta t$. By means of cross-correlation of two frames taken at these two distinct time instants, this purpose can be efficiently fulfilled. Laser pulse lasts so short that the turbulent motion is “frozen” onto the grayscale images. The time interval $\Delta t$ must be set to ensure the displacement is noticeable but the majority of the particles remain in a certain interrogation window.

Particle concentration is another key aspect which needs great care. By introducing the concept of “depth of correlation” for $\mu$-PIV:

$$2Z_{corr} = 2 \left[ \frac{1 - \sqrt{\varepsilon}}{\sqrt{\varepsilon}} \left( f^{\#^2} d_p^2 + \frac{5.95(M + 1)^2 \lambda^2 f^{\#^4}}{M^2} \right) \right]^{\frac{1}{2}} \quad (4.1)$$

where $\varepsilon = 0.01$; $d_p$ is the particle diameter; $\lambda$ is the emission wavelength of the particle; $M$ is the magnification of the lens and $f^{\#}$ the focal number, which is related to its...
numerical aperture (NA) by:
\[
f^* = \frac{1}{2\text{NA}},
\]
the minimum particle concentration is then computed by using
\[
C = \frac{N}{2Z_{\text{corr}} \times A}
\]
where \(N\) is the minimum number of particles in each interrogation volume, which is typically taken to be 5–10, and \(A\) is the area of each interrogation window.

Particle size is chosen to meet certain requirement of Stokes number (St) defined as the ratio of particle response time and the flow time scale
\[
St \equiv \frac{\gamma \rho_p d_p^2}{12\mu_f}
\]
where \(\gamma\) is approximated by \(u/R\) with \(u\) being the inlet bulk velocity, \(\rho_p\) is the particle density and \(\mu_f\) is the fluid viscosity. In other words, it should be small so the time lag between the fluid motion and the particle motion can be ignored.

### 4.2.3 The Setup

As shown in Figure 4.2, the experiment setup is consisted of the flow delivery system (upper portion with a solid box) and the imaging facility (lower portion bounded by the dashed line).

A syringe pump with a multi-syringe holder is used a flow generator. The four syringes are filled with seeded working fluids (water in this study) and are connected via soft tubings with the four inlets of the MIVR, which is placed on the stage of the inverted microscope. A small container collects the exiting fluid for refills of syringes when emptied.

The source of illumination in the system is a Nd:YAG laser coupled with a frequency doubler. The resulting wavelength (532 nm) is nearly identical to the optimal excitation wavelength of the seeding particles (535 nm). The laser beam is then expanded to cover
Figure 4.2  Schematic of the experimental setup
as much area of interest as possible. A dichroic mirror (or beam splitter in the schematic) is in place to separate the emission light from the excitation. A 4×0.2 NA objective is used with a 0.45× coupler to give an overall magnification of 1.8× and a depth of correlation of 72.27 µm. A CCD camera is at the other end of the light path, recording data on the computer.

For this setup and \( N = 5 \), the minimum concentration \( C \) of particle (2 µm, 1.05 g/cm\(^3\) Nile red FluoSpheres, Invitrogen Corporation) is found to be \( 2.09 \times 10^7 \) #/ml and \( \text{St} \sim 10^{-7} \ll 1 \). Interrogation windows are chosen to be 32×32 squares with 50% overlap between adjacent windows. Each pixel is also a square of size 3.6 µm and this leads to a vector spatial resolution of 57.6 µm.

Flow rates are equal in all four inlets in this study and we define the Reynolds number \( \text{Re}_j \) in terms of the characteristic inlet velocity (or jet velocity) \( U_j \) by

\[
\text{Re}_j \equiv \frac{d_h U_j}{\nu} \quad (4.5)
\]

where \( d_h \) is the hydraulic diameter of the inlet channel and \( \nu \) is the kinematic viscosity of the fluid. Note that MIVR can be operated in such a way that each of the inlets can have its own flow rate (or even fluid), a more general definition of Reynolds number based on the mixing chamber is given by

\[
\text{Re} \equiv \sum_{i=1}^{4} 2R \frac{U_i}{\nu_i} \quad (4.6)
\]

where \( U_i \) and \( \nu_i \) are the mean inlet velocity and the kinematic viscosity in \( i \)th inlet, respectively. As can be seen, contributions from each inlet are appreciated in this definition. In order to distinguish the two, the first definition is termed as “jet Reynolds number”. Table 4.1 lists the three different jet Reynolds numbers investigated as well as their corresponding \( \text{Re} \)'s. They each represent a flow regime, i.e., laminar at \( \text{Re}_j = 53 \), transitional at \( \text{Re}_j = 93 \) and turbulent at \( \text{Re}_j = 240 \). For each \( \text{Re}_j \), over 1000 realizations are acquired on three planes (shown in the right panel of Figure 4.1, i.e., the quarter-of-
Table 4.1  $Re_j$ and $Re$ at different flow rates

<table>
<thead>
<tr>
<th>Flow rates (ml/min)</th>
<th>$U_j$ (m/s)</th>
<th>$Re_j$</th>
<th>$Re$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.93</td>
<td>0.0369</td>
<td>53</td>
<td>911.40</td>
</tr>
<tr>
<td>8.64</td>
<td>0.0647</td>
<td>93</td>
<td>1,597.27</td>
</tr>
<tr>
<td>22.30</td>
<td>0.1670</td>
<td>240</td>
<td>4,122.58</td>
</tr>
</tbody>
</table>

reactor-height-to-bottom plane, the mid-plane and the quarter-of-reactor-height-to-top plane), from which the mean velocity field is computed.

### 4.3 Simulation Details

Both RANS and LES will be compared with $\mu$-PIV to determine their performance in predicting the velocity field. The open source CFD package OpenFOAM® is chosen to
perform these simulations. It is superior to commercial CFD software in several aspects. First of all, it is free of charge, which is attractive to academic researchers. Also, as it is completely text-based, its speed is faster. More importantly, it provides a set of tools for researcher to develop custom codes with ease. For beginners, it serves as a great learning tool as well due to its open source nature.

The reactor is partitioned into five regions, namely, the four inlet channels and the main mixing chamber. A typical grid of this formulation is shown in Figure 4.3. The grid points are denser in the center where the velocity is greater. For RANS simulations, the mesh has about 200,000 hexahedral cells and the number of cells becomes approximately 6 times more for LES. The standard $k-\varepsilon$ model, implemented in the simpleFoam solver in OpenFOAM, is used in the RANS simulations and the solver pisoFoam with the Smagorinsky model is adopted for LES. For both cases, the velocity profiles at the inlets are simulated in a separate rectangular channel that has the same width and height as the reactor inlets so as to save some computation time. At this stage, the RANS simulations are performed for all three jet Reynolds numbers listed previously, but only the largest jet Reynolds number $Re_j$ has been studied using LES. However, more simulations will be carried out in the near future.

4.4 Results and Discussion

A sample velocity field from the simulations is shown in Figure 4.4. As can be clearly seen, on the mid-plane, the flow field forms a big swirl and the fluid gets accelerated in the center. Their magnitudes are more than 6 times that of the outer velocity vectors. In fact, this observation also extends to all other planes investigated. Another discernible feature of this flow is that the outer fluid barely has a $z$-direction velocity. Owing to this property of the vortex flow, it is more beneficial to look at the radial and tangential components of the velocity vectors instead of $x$ and $y$ components. For this reason, both
Figure 4.4 Sample velocity field on the mid-plane from the simulations. Magnitude is indicated by the color as well as the size of the arrow; the longer and thicker the arrow is, the greater the magnitude is.
experimental and numerical data are transformed from Cartesian coordinates into polar coordinates. The comparisons between the \( \mu \)-PIV results and the simulations are given in Figure 4.6 through Figure 4.11. Details are examined below.

Overall, in accordance with the circular fluid motion, the maximal magnitude of the tangential components are a few time greater than that of the radial components at all Reynolds numbers. This makes it more difficult to measure the radial velocity accurately than the tangential velocity. More evidence is also found to support the fluid acceleration close to the center. For the same reason, the velocity should ideally be zero at \( x = 0 \) mm (see Figures for \( x \) positions).

At \( \text{Re}_j = 53 \), the flow falls in the laminar regime with no turbulent at all. The wall effect is significant in this case. As a result, tangential velocity profiles at different heights are quite distinguishable. On one hand, for \( |x| > 1 \) mm, where both top and bottom walls have impacts on the flow, the flow is fastest on the mid-plane, and symmetry is observed about the mid-plane as expected. On the other hand, for \( |x| < 1 \) mm, where only one wall exists at the bottom, the vortex flow swirls faster as the height increases.
Except for the points close to the center, the radial velocities are negative or nearly zero, indicating the fluids are moving smoothly towards the center of the reactor. Not much collision and redirection of fluids occur at this jet Reynolds number, suggesting poor mixing.

The overall trends predicted by the RANS simulations match those of the $\mu$-PIV experiments with distinct tangential velocity profiles and the crossing between the curves on the mid-plane and the quarter-to-top plane. Unfortunately, the magnitudes from the simulations are only about half of the experimental results. This indicates RANS might just not be the right tool for this case. Indeed, RANS is intended for more turbulent flows with strong kinetic energy dissipation. We therefore proceed to higher jet Reynolds numbers in anticipation of better agreements.

As the $Re_j$ is increased to 93, the flow is more developed indicated by more similar tangential velocity profiles and a larger tangential-to-radial velocity ratio. Nonetheless, the flow is still within the transitional region and flow close to the bottom is more strongly affected by the wall. It thus can be deduced that as the fluids swirl towards the exit, mixing becomes better and better.
Figure 4.7  Tangential velocity comparison of $\mu$-PIV and RANS at $Re_j = 93$.

Figure 4.8  Radial velocity comparison of $\mu$-PIV and RANS at $Re_j = 93$. 
Figure 4.9  Tangential velocity comparison of $\mu$-PIV and RANS at $Re_j = 240$.

Again, the RANS underpredicted the magnitudes of the tangential velocity for this $Re_j$ and surprisingly, the maximal ratio between the simulation and experimental velocity gets even higher, indicating that RANS should not be used for this jet Reynolds number either.

More violent turbulence is observed at $Re_j = 240$ where random motions start to appear in the instantaneous $\mu$-PIV images as well as the LES simulations. In addition, contrary to the other two cases, the tangential velocities close to center of reactor, despite being fairly close, actually increase with the height. This fact suggests that the inertial force has outweighted the viscous force; the wall effect is no longer important for at least the three planes investigated. Consequently, mixing between streams is significantly also improved.

Positive radial velocities are noticed at more points than the previous cases, indicating flow redirection caused by shear stresses due to fluid collision happens more frequently. This is another proof for better mixing.

The RANS predictions somehow once again fail to match the experimental data. The magnitudes of the tangential velocities are far from one another, which could be
Figure 4.10  Radial velocity comparison of $\mu$-PIV and RANS at $Re_j = 240$.

Figure 4.11  Tangential velocity comparison of $\mu$-PIV and LES at $Re_j = 240$. 
because the flow is not fully turbulent and as such, the turbulent kinetic energy and its dissipation rate cannot be simulated accurately. However, rather good agreement is observed between LES and experiments. For $|x| > 0.5$ mm, they almost fall on each other and for $|x| < 0.5$ mm, tangential velocities from LES are slightly smaller than that from the $\mu$-PIV experiments. This gives us enough confidence for future simulations on turbulent mixing in this reactor.

4.5 Conclusion

In this project, two CFD models, the standard $k-\varepsilon$ model for the RANS and the Smagorinsky model for the LES, are applied to the microscale nanoprecipitation reactor, MIVR, and are validated against the $\mu$-PIV experiments. Three jet Reynolds numbers are investigated at three different heights within the reactor. Comparisons between experimental data and numerical predictions illustrate that the RANS simulations might not be suitable for the jet Reynolds numbers studied in this reactor, but good agreement is obtained between LES and experiments for the case of $Re_j = 240$. Therefore, LES will be most likely adopted for turbulent mixing simulations in MIVR.
Fluid dynamics is also examined for all three jet Reynolds numbers. At $\text{Re}_j = 53$, the flow is laminar and mixing is poor in this case. As the $\text{Re}_j$ is increased to 93, the mixing is improved as the flow develops into the transitional range. Wall effect is reduced in this case and fluid redirection starts to show. For the highest jet Reynolds number, which is 240, turbulent flow is observed with many random motions in instantaneous $\mu$-PIV images. Mixing is thus significantly better than the lower two.
CHAPTER 5  CONFOCAL IMAGING OF LAMINAR AND TURBULENT MIXING IN A MICROSCALE MULTI-INLET VORTEX NANOPRECIPITATION REACTOR

This chapter is modified from a paper published in

*Applied Physics Letters*

Yanxiang Shi, Rodney O Fox and Michael G Olsen.

The flow visualization technique that uses the pH indicator phenolphthalein presented previously is able to qualitatively capture the turbulent structures in CIJR. By exerting some threshold on the original RBG images, points with pH > 9.3 (or equivalently the base volume fraction $\xi > 0.5$) can be separated from those < 9.3 (or $\xi < 0.5$). Therefore, the extent of mixing can be evaluated by taking the mean of the binary images. That is, after complete mixing, the local mean should be unity. At $Re_j = 1500$, the streams are still not completely mixed on the macro-scale in CIJR.

Though this technique provides some valuable insights on the turbulent structures as well as useful quantitative data for comparison with the simulations, it lacks the details of the scalar distribution. Also, the threshold brings in some extra experimental er-

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ror. In addition, it has the problem generally associated with conventional microscopes that out-of-focus light interferes with the in-focus light, which greatly reduces the spatial resolution for a micro-scale nanoprecipitation reactor and therefore accuracy. In this chapter, confocal laser scanning microscopy (CLSM) is employed to overcome this difficulty. It is coupled with laser induced fluorescence (LIF) to obtain more accurate results.

5.1 Introduction

Planar laser-induced fluorescence (PLIF) has been one of the primary techniques for studying turbulent mixing at the macroscale [85–87]. By using a fluorescent dye in one or more of the inlet streams, mixing of a measured scalar in a small volume covered by a thin laser sheet can be visualized and quantified.

However, when applied to microscale reactors that are of the same dimensions as the laser sheet, the PLIF technique fails. This difficulty can be overcome with the help of confocal laser scanning microscopy (CLSM) where a pinhole is placed in front of the detector (lower right $h$ component in Figure 5.4) to reject any out-of-focus light [88, 89] such that the axial resolution could be dramatically improved. In this section, an attempt has been put into place for coupling this advanced microscope technology with the laser-induced fluorescence (LIF) method for use in the visualization of turbulent flows in microscale devices.

5.2 Experimental Apparatus and Methodology

5.2.1 Laser-Induced Fluorescence (LIF) method

The laser-induced fluorescence, as a matter of fact, representing a large class of fluorescence imaging, covers a wide range of applications, such as studying structure
of molecules, detection of selective species, recognition of cells or tissues, and so forth. However, when it is associated with flow diagnostics, it is usually used for measurements of scalars, concentration, temperature and pressure, to name a few. Because LIF is such an important and powerful tool for modern scientific investigations, some of its essential aspects are discussed here.

**Fluorescence**

![Illustration of the fluorescence mechanism](image)

**Figure 5.1 Illustration of the fluorescence mechanism**

To put it in simple words, fluorescence is basically a process of light emitting of a molecule after being shined by some incident light. In more details, molecules of a fluorescent dye at ground state can be excited by a light beam of a certain wavelength. After a period of time, named fluorescent lifetime, it returns to its ground state from the excited state, emitting a light of longer wavelength because of some internal energy loss caused by molecular interactions. This mechanism is illustrated in Figure 5.1. The difference in the wavelengths between the exciting light and emitted light is the key that makes possible of the LIF technique because only with this difference can the two light
beams be separated.

**PLIF and \( \mu \text{-LIF} \)**

![Figure 5.2 Typical setup of PLIF experiments](image)

This imaging tool was first introduced to measure scalars in macroscale flows. Due to the fact that the laser beam has to expanded into a thin sheet in order to cover a bigger area in the flow, this method is name as planar laser-induced fluorescence, or PLIF. Thanks to its non-intrusive nature, the PLIF technique has been employed in many studies since its first appearance in the literature. In addition, as opposed to single point measurements as in most probe methods, PLIF captures data on the entire plane at a time, which make feasible of multiple points or spacial statistics calculations. A typical PLIF setup is shown in Figure 5.2. The laser beam passes through a set of optics, of which the most important is the cylindrical lens used as the beam expander, and illuminates the fluorescent dye in the fluid flow. A camera that sits perpendicular to the illuminated plane records the emitted light. A long pass filter is placed in front of the camera to block the exciting light.
In this study, since the experiments serve in part to validate the numerical mixing models, we limit ourselves to only the measurements of concentration field. The theory for the fulfillment this purpose is presented here. Although more detailed description of the relation between the local concentration of the dye and corresponding fluorescence light can be found the literature, as Crimaldi and Koseff [90] pointed out, this relation can be simply given by

\[ F(x, y) = \alpha I(x, y) C(x, y), \]  

(5.1)

provided that the concentration is small enough such that the self-absorption effect can be safely neglected. In the equation above, \( F(x, y) \) denotes the local signal intensity captured by the detector, \( I(x, y) \) the incident light intensity, \( C(x, y) \) the dye concentration and \( \alpha \) a coefficient that is associated with the optical setup and can be found out empirically. The proportional relation between the two quantities, \( C(x, y) \) and \( F(x, y) \), ensures that the final signal output can be mapped back to the original concentration field. In later sections, it can be seen that this requirement is fully satisfied for both the passive scalar mixing and reactive mixing.

Similar to the differences between the conventional PIV method and the \( \mu \)-PIV method, issues arise when applying macroscopic visualization to microscale flows. For one and once again, a laser sheet is not possible to be inserted into the test section, but instead, the entire volume is illuminated. In the case of PLIF, the resolution in the \( z \) direction is precisely controlled by the thickness of the laser sheet which is comparable to the smallest flow structure, the Kolmogorov scale, \( \lambda_K \). Nevertheless, for our system, the depth of microscale nanoprecipitation reactor is on the order of millimeters which is far greater than the smallest flow scale in this case. As a consequence, additional device is necessary to improve the axial resolution. This justifies the use of CLSM. For another, as the reactor volume is shrunk down, the dye concentration that is usually used in PLIF now becomes questionable. In fact, among the others, this is another important issue
that has to be solved for the $\mu$-LIF to perform properly. More details are to follow in the next section.

### 5.2.2 Confocal Laser Scanning Microscopy (CLSM)

The concept of confocal microscopy was explored and brought to the world by Marvin Minsky [88, 91]. The main idea is simple and is explained below.

The light path in a confocal microscope is schematically depicted in Figure 5.3.

The major components that make it different from the conventional epi-fluorescence microscope are the two pinholes equipped in front of the detector and the light source respectively. On the one hand, if the pinhole in front of the light source is removed, light from different points will blur the final image because of the airy disk effect (or the point
spread function, abbreviated PSF). On the other hand, without the pinhole in front of
the detector, as can be seen in the figure, not only the in-focus light (represented by the
solid thin lines between the objective and the detector) but also the out-of-focus light
(represented by the dashed line, which is from below the focal plane, and the dot-dashed
line, which is from above the focal plane) will be captured by the detector. Therefore,
both of the two pinholes are of extreme important in confocal microscopy. The final
result is thus that only a thin slice of the specimen and this effect is termed optical
sectioning' in the literature.

Nevertheless, the confocal microscopy configuration results in the fact that only one
single point is illuminated and thus recorded at a time. As a consequence, two rotating
mirrors, one for the horizontal direction and the other for the vertical direction, are
used to help scan point by point the entire specimen to build a complete image. They
are shown in Figure 5.4 as the component f. For most confocal microscope systems, the
rotation speed of the mirror is a limiting factor. However, with advanced galvanometers,
the scanning frequency has been improved to as fast as over 200 kHz, meaning 200,000
points per second. As will be discussed in more details later, the scanning speed is
crucial for the visualization of turbulent flow.

With all the elements introduced above, that is, the pinholes and therefore the con-
focal, the laser as the illumination source and the rotating mirrors, the confocal laser
scanning microscopy is thus completed. To sum up, confocal microscopes have the fol-
lowing advantages over the conventional epi-fluorescence microscopes:

• less or no at all interference of lateral stray light and hence higher contrast

• rejection of out-of-focus light and hence sharper image and better accuracy (most
  important)

• 3-dimensional (3D) reconstruction of the volume from slices at different heights
Indeed, the confocal microscopy provides a number of attractive features, but they are made available at a price. Due to the reduction in imaging volume and therefore the amount of signal, the final result is highly sensitive to the electronic noise. In addition, as it scans the specimen point by point, it takes some time to build the entire image, which leads to the fact that each point in the image is taken at different instant, make the calculation of spatial multi-point statistics impossible. For biological applications for which the device is initially intended, where specimens are steady or moving relatively slowly, problems mentioned above are not as critical. However, for turbulent flow visualization where structures change rapidly, it could pose some potential difficulties. As such, these limitations have to be taken into consideration when coupling the $\mu$-LIF method with CLSM.

### 5.2.3 Experimental setup

A sketch of the reactor as well as the experimental setup of confocal $\mu$-LIF is schematically illustrated at the top of Figure 5.4. Upper part of the system is the flow delivery system and lower part the imaging system.

The MIVR has a mixing chamber diameter ($2R$) of 6.26 mm and a chamber height ($H$) of 1.78 mm. Other dimensions are outlet channel diameter $2r = 1.40$ mm and inlet channel width $w = 1.19$ mm. Four inlet channels are tangentially attached to the mixing chamber with the outlet channel protruding in the third dimension. Two syringe pumps with double-syringe holders are used to deliver the four inlet streams and a container collects the mixed fluid at the outlet of reactor. The MIVR sits on the stage of the front-end inverted microscope of the confocal system.

The confocal microscope (Leica TCS SP5 X) is located in Room 0117 of Molecular Biology Building at Iowa State University and is available to on-campus as well as off-campus researchers as a public facility. It is equipped with both Argon laser and white light laser (WLL), providing more flexibilities in choosing the excitation light wavelength.
Figure 5.4 Schematic of experimental setup (top) and sketch of the MIVR (bottom, not to scale)
Besides that, an Acousto-Optical Beam Splitter (AOBS) is used to set desired emission wavelength range that is to be captured. In this study, in order to match the maximum excitation wavelength of Rhodamine 6G (525 nm), three laser lines (500 nm 513 nm and 525 nm) of the WLL are used, each outputting at 100%. To cover a wider field of view, an objective with relatively low magnification is used (Leica 506224 HC PL Fluotar 5×/0.15 NA). Also, special to the CLSM, a photomultiplier tube (PMT) is employed to capture and record the low signals.

5.2.4 Operation conditions

Owing to the low solubility of Rhodamine 6G in water, in this study, ethanol is chosen to be the working fluid. As discussed previously, CLSM improves the resolution by sacrificing the amount of signal and this effect results in the vulnerability to noise. Therefore, one of the major preliminary tasks is the fine tune several parameters to min-
imize the electronic noise while keep a good amount of signals. The primary parameters are the pinhole size, the PMT voltage and the dye concentration.

Although increasing the pinhole size could dramatically change the amount of signals that reach the detector, it is the very most important factor that distinguishes the CLSM from the normal epi-fluorescence microscopes. The diameter of the pinhole, with other parameters fixed, exclusively the thickness of the optical slice, as is given by the following estimation

\[ dz = \sqrt{\left(\frac{\lambda_{\text{ex}} \cdot n}{\text{NA}^2}\right)^2 + \left(\frac{\text{AU} \cdot n \cdot \sqrt{2} \cdot 1.22 \cdot \lambda_{\text{ex}}}{\text{NA}^2}\right)^2} \] (5.2)

For this reason, the pinhole size has to be varied within a reasonable region. In this study, it is set to 2.99 AU, or 211.53 µm. In the above equation, \( \lambda_{\text{ex}} \) is the excitation light wavelength, which is taken to be 525 nm, \( n = 1 \) the refractive index of the medium (air in this case), \( \text{NA} \) the numerical aperture of the objective and \( \text{AU} \) the pinhole size in airy unit (AU).

The PMT, designed based on the photoelectric effect and secondary emission, is an extreme light detector. Essentially, it transforms the light signals into electronic signals and more importantly, amplifies it. Due to its high sensitivities to photons, it is able to capture low signals to which ordinary CCD cameras usually fail to respond. This sensitivities can also be controlled by the PMT voltage. However, the higher the PMT voltage is, the noisier the final signal will be. As such, this parameter has to stay as low as possible. In this study, the PMT voltage is set to 499.9 V.

As for the dye concentration, it first needs to meet the requirement of the linear fluorescence response. Within the linear range, according to equation 5.1, it is optimum to have as high concentration as possible in order to obtain a strong output of light. Calibration showed a linear relationship between the fluorescence intensity measured at the detector and dye concentration up to 600 µg/L (see Figure 5.5). Two opposing inlet streams are pure ethanol whereas the other two contain the fluorescent dye Rhodamine
6G with a concentration of 600 µg/L.

To be consistent with previous µ-PIV studies, the confocal µ-LIF data are collected at four inlet stream Reynolds numbers, \( \text{Re}_j = 10 \), \( \text{Re}_j = 53 \), \( \text{Re}_j = 93 \) and \( \text{Re}_j = 240 \), on two different planes, namely, the midplane at half the chamber height and the outlet plane in the outlet channel (see Figure 5.4). The CLSM is able to scan a single measurement volume in 4.88 µs. In other words, forming a 512 × 512 image requires 1.28 s. Consequently, to facilitate rapid collection of data for statistical analysis, the system is operated in line-scanning mode where a specified horizontal line in the imaging zone is scanned repeatedly to form a profile. The horizontal profile presented here is along the center line of the reactor (marked by the white lines crossing the center of the top images in Figs. 5.6–5.9). For each data point in the set, over 10,000 realizations were acquired for statistical analysis. All realizations are normalized against the pure dye signal (which is the local maximum) after the background signal (which is the local minimum) is subtracted. Mean and root mean square (RMS) profiles of this normalized dye concentration are thus plotted and discussed below. In addition to the profile plots, some instantaneous full field images (of the size of 3.10 mm × 3.10 mm marked by the shaded area in Figure 5.4) were also collected. However, due to the finite time required to build an instantaneous image, these images do not represent a true instantaneous ‘snapshot’ of the flow, and unsteady flow can cause a blurring of the full field images. Nevertheless, they do provide a visualization of the flow patterns at lower Reynolds numbers, but are no longer informative when the flow becomes turbulent and unsteady, as in the \( \text{Re}_j = 240 \) case.

### 5.3 Results and Discussion

The results for \( \text{Re}_j = 10 \) are shown in Figure 5.6. At \( \text{Re}_j = 10 \), the flow is laminar and steady. At this low Reynolds number, the fluid has low tangential velocity, and thus,
Figure 5.6  $Re_j = 10$
Figure 5.7  $\text{Re}_j = 53$
Figure 5.8  \( \text{Re}_j = 93 \)
Figure 5.9  \( \text{Re}_j = 240 \)
instead of spiraling towards the reactor exit the fluid enters the reactor and heads nearly directly towards the exit. No large scale stirring takes place at this Reynolds number and mixing occurs only on the short interfaces due to molecular diffusion. Fluid exits the outlet nearly as segregated as it enters the reactor. This is also confirmed by the mean profiles of the normalized concentration. At the midplane, the normalized concentration is nearly binary with values of either zero or one. A similar trend is observed at the outlet plane. The high RMS values that appear where the mean values change most rapidly are due to small unsteady motions of the interfaces.

In the Re\textsubscript{j} = 53 case, the flow begins to exhibit more intricate patterns as shown in Figure 5.7, such as the inner ‘tai-chi’ pattern and the circular streaks around it. At the midplane, the flow spirals towards the center due to the greater tangential velocity resulting in bands that grow thinner and thinner due to the acceleration at the center. In the mean concentration profile, there are smaller local concentration peaks that gradually diminish before becoming larger peaks in the reactor center. The small peaks around the mean value of 0.5 in the outer region of the midplane are not indicative of good mixing. Instead they are an artifact of small unsteady motions in the interfaces which are becoming larger due to the increasing Reynolds number. Indeed, the large variations in the mean profile in the outlet at this Reynolds number demonstrates that the fluid is still poorly mixed. As the flow is still laminar at this Reynolds number [14], velocity fluctuations remain negligible, resulting in poor overall mixing. As the interfaces increase significantly, their movements because of the pumps keep the RMS values relatively high.

Previous research has suggested that Re\textsubscript{j} = 93, as shown in Figure 5.8, in the regions of transition from laminar to turbulent flow in the mixing chamber [92]. However, the confocal \(\mu\)-LIF data indicate that even at this Reynolds number, the mixing is quite poor. At the midplane of the mixing chamber as shown in the top left image in Figure 5.8. The outer part of the flow now is nearly a uniform blur, yet in the center of the reactor, the fluid appears unmixed. This is due to the ‘bands’ of fluid spiraling towards the center.
of the reactor at this Reynolds number being very thin so that unsteady fluctuations in the interfaces smear the resulting images. The poor fluid mixing at \( \text{Re}_j = 93 \) is clearly evident in the results in the reactor outlet. Here, both the planar image and concentration profiles show wildly varying local mean concentrations between nearly pure dyed and undyed fluid.

As the Reynolds number is raised further to 240, the flow becomes truly turbulent and improved mixing is finally observed, as shown in Figure 5.9. Because of the rapidly varying flow field, CLSM fails to capture a meaningful full field image for this case. As it shows, the mean profile is more straightened out as the inner region shrinks down to \((-0.5 \text{ mm}, 0.5 \text{ mm})\) and the values are closer to 0.5 which indicates complete mixing. Based on this, it can be predicted that the mean profile will eventually become a straight line at high enough Reynolds number. Besides that, it takes longer a tube for the turbulence to decay completely. To the point the objective is able to reach, it is still turbulent with no distinct patterns whatsoever. As can be seen, the mean profile on the outlet plane is flatter even. Velocity fluctuations become a crucial factor in this case and they produce high RMS values of the scalar.

5.4 Conclusion

The unique confocal \( \mu \)-LIF technique is developed and applied to the MIVR in this work. It helps to gain a thorough understanding on mixing in such reactors by visualizing the flow field and providing meaningful statistical data. It will also be used to validate computational fluid dynamics (CFD) models in near future.
CHAPTER 6  REACTIVE MIXING VISUALIZATION USING CONFOCAL MICRO-LIF

A paper in preparation

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6.1 Introduction

Numerical simulations of turbulent reacting flows require knowledge of mixing at both macroscale and microscale. It poses unique challenges to the researchers \([93, 94]\). In the combustion community, this topic is equally important as the turbulence modeling because the prediction of the concentration distribution is highly dependent upon the correct simulation of mixing, especially micromixing. The micromixing effects appear in the chemical source terms and have to modeled. While in the gas combustion, where the Schmidt number is moderate (\(\approx 1\)), the smallest scalar fluctuation scale, \(\lambda_B\), is comparable to the velocity fluctuation scale, \(\lambda_K\), for most chemical engineering application, molecular diffusion takes place on a much smaller scale as chemical reagents are normally in the form of liquid or solution whose Schmidt number is high (\(\approx 1000\)). As a consequence, the use of direct numerical simulation (DNS) for scalar field in such flows is less achievable \([22, 95, 96]\) and experiments are thus the only way for the investigation

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of micromixing in fluid flows as well as the validation of micromixing models. [97]

One of the ways of studying the micromixing effects and therefore validating the micromixing models is to use competitive reactions as the "chemical rulers". In this strategy, chemical reactions are carefully chosen such that the conversion is solely dependent upon the difference between the reaction time and micromixing time. Since the reaction time can be found out easily given the chemical kinetics, the micromixing time can be determined by varying the concentration and thus the reaction time. Baldyga [49], Bourne [98] and their colleagues have developed a set of such chemical reactions for this purpose. With these chemical reactions, Johnson et al. [6] and Liu et al. [15] have investigated the micromixing effects in confined impinge-jets reactor and multi-inlet vortex reactor respectively. Later, Liu et al. [39] compared the results from the micromixing models with Johnson et al.'s [6] data and found good agreement. In Liu et al.'s study [15], micromixing simulations results also agreed well with experiment data. Nevertheless, the drawback of the method is also apparent. That is, the concentration distribution inside the reactor is unknown. In this study, a full-field image technique is developed to overcome this difficulty, combining the flexibility of chemical reaction, advanced "optical sectioning" of confocal microscope and the powerfulness of the laser-induced fluorescence technique.

6.2 Experimental apparatus and methodology

6.2.1 Experimental setup

The experimental setup is shown in Figure 6.1. As can be seen, apart from the solutions in the syringes (shown as the c and d components in Figure 6.1), all the other devices are the same as in the confocal-based passive scalar mixing experiments. That is, in order to achieve high resolution in the axial direction, the same CLSM system is employed, and again, two syringe pumps with double-syringe holders are used to
generate steady inflows.

### 6.2.2 Experimental methodology

In passive scalar mixing experiments, the key is to have linear relation between the concentration of dye and the output signal. This way, given a normalized intensity, the corresponding mixture fraction $\xi$ can be inferred. However, this backward mapping is also linear and the results represent mixing on all different scales, i.e., macromixing, mesomixing and micromixing. To reveal the micromixing effects in the MIVR, an acid-base neutralization reaction is employed. A pH-sensitive fluorescent dye, the disodium salt form of fluorescein (a.k.a, uranine or D&C Yellow No. 8), is used to measure the pH change due to mixing. To some extent, the confocal-based reactive mixing experiments are similar to the visualization technique introduced in Chapter 2 that uses phenolphthalein as the tracer.

Analogous to the phenolphthalein method, the relations between dye concentration,
fluorescence signals, pH values and mixture fraction $\xi$ are explored. First, the linear relation between the concentration and the output signals should be ensured to avoid artifact mixing information. The pH dependence of the dye is known and as follows: the radiated light intensity is low at pH $< 4$, increases dramatically over the range $4 < \text{pH} < 8.5$ and stays constant beyond that. Therefore, the calibration of the concentration-intensity relation is carried out at a pH of 9.02 at four planes, namely, the three planes at 1/4, 1/2 and 3/4 reactor height to the bottom and a plane in the outlet tube. The calibration curves shown in Figure 6.2 are respectively close to linear at each plane. From this, the concentration of dye is determined. Second, similar to Chapter 2, defining mixture fraction $\xi = \frac{m_{\text{acid}}}{m_{\text{acid}} + m_{\text{base}}}$, which in turn gives $\xi = 0$ for basic solution and
Figure 6.3  Relation between mixture fraction $\xi$ and the fluorescence intensity at dye concentration of 1 mg/L for all planes given initial acid and base pH values $pH_{a0} = 2.55$ and $pH_{b0} = 10.55$

$\xi = 1$ for acidic solution, the $\xi$–pH relation is written

$$
\xi = \begin{cases} 
\frac{C_{a0} - 10^{-pH}}{C_{a0} + C_{b0}} & \text{pH} < 7 \\
10^{-14-pH} + C_{a0} & \text{pH} \geq 7 
\end{cases} \tag{6.1}
$$

where $m_{\text{acid}}$ and $m_{\text{acid}}$ are mass flow rates of acid and base respectively, and $C_{a0}$ and $C_{b0}$ are concentrations of H$^+$ and OH$^-$ at the inlets respectively, which are fixed given initial acid and base pH values, $pH_{a0}$ and $pH_{b0}$. With this and known relation between pH and the fluorescence intensity, the latter quantity can be related to the mixture fraction $\xi$. A set of solutions with a dye concentration of 1 mg/L and pH values varying from 2.14 to 11.05 is tested and the $\xi$–intensity plot with fixed pH values in the inlet streams is shown in Figure 6.3. As can be seen, the intensity stays low ($10 \pm 4$) until $\xi$ reaches around 0.88 after which it soars from approximately 10 to over 170 within a mere $\xi$
range of 0.01. Although differences in intensity between different planes are present, at each plane, the values remain more or less constant at $\xi \geq 0.89$. The sudden jump of the intensity within a small range of $\xi$ indicates that in the final images, more dark color will be observed.

### 6.2.3 Experimental parameters

![Figure 6.4](image)

**Figure 6.4** Field of view covered by the objective (left) and measurement planes (right)

To ensure the chemical reaction is instantaneous and irreversible, strong acid (hydrochloric acid, HCl) and base (sodium hydroxide, NaOH) are used. The initial pH values in the inlets are set to 2.55 and 10.55 respectively. Both acidic and basic solutions contain the fluorescent dye, sodium fluorescein, to avoid the dye concentration difference and the concentration is 1 mg/L.

As for the illumination, the Argon laser is employed outputting at 100% the light with a wavelength of 488 nm, which matches pretty well with the optimal excitation wavelength (490 nm) of the fluorescent dye. The objective is once again Leica HCX PL FLUOTAR 5.0×/0.15NA DRY. The sketch to the left in Figure 6.4 shows the field of view covered by this objective is highlighted by the shade area. The side length of the square is 3.10 mm. The final image has a spatial resolution of 512 × 512 pixels, resulting
in the pixel size of 6 µm. The scan rate is 400 Hz, or in other words, 400 horizontal lines per second, giving a scan time of 4.88 µs per pixel. The PMT voltage is set to 524.9 V. Given these operating conditions, the RMS-to-mean noise ratio is less than 5% at the maximum fluorescence signal.

The experiments are performed for four jet Reynolds number as in previous chapters, Re\(_j\) = 10, 53, 93 and 240. The data acquisition planes are shown on the right of Figure 6.4. However, results are only presented for the midplane and the plane in the outlet. As in the passive scalar mixing experiments, both full-field images and line-scan images are recorded. Line-scan images are taken along the center line (crossing the center of the reactor, as shown in the left sketch of Figure 6.4) at each plane. To ensure the statistical accuracy, over 10,000 lines are obtained for each case.

6.3 Results and discussion

In this section, results at the midplane and the plane in the outlet obtained for all four Reynolds numbers from the reactive mixing experiments are examined closely and discussed below. In addition to full-field images and line-scan images, mean and root mean square (RMS) profiles at the center line are also presented.

6.3.1 Full-field and line-scan patterns

The full-field results from the midplane and the plane in the outlet are shown in Figures 6.5 and 6.6 respectively. Arrangements of the panels are described in the caption of Figure 6.5. Overall, as mentioned previously, more dark color than bright color is observed because the fluorescence is “turned off” at ξ < 0.88.

At Re\(_j\) = 10, the flow is laminar and no large vortex is formed. Four big blobs of fluid meet at the center of the reactor and exit as it is. However, when compared to the passive scalar mixing where the four streams meeting point is exactly at the
center, the reactive mixing experiments shows more dark at the center for the “switch” effect. Distinct interfaces are observed between the bright and dark region. Instead of four straight lines connecting the four corners to the center, the interfaces are curved, suggesting that the fluid field is already twisted even at the low Reynolds number. As it enters the outlet tube, the twisting effect of the vortex flow is stronger due to the contraction of cross section and thus an increase in velocity. In this case, mixing only occurs on the interfaces and therefore pH values are not changed in the bulk dark and bright regions.

At Re\textsubscript{j} = 53, the flow develops into some pattern. From its comparison with the passive scalar mixing at the same Reynolds number, the conclusion can be drawn that at this plane the fluid between the outer ring (see the four corners in the image) and the inner pattern is mixed to some extent despite the alternating rings observed in the passive mixing experiments. At the center, however, the fluid remain largely segregated and the “tai-chi” pattern is still clear. What is worth noting is that, unlike in the Re\textsubscript{j} = 10 case where the interfaces are mostly sharp throughout the entire image, blurry regions are present in this case. Note that the intensity changes abruptly with the mixture fraction in a very small range, this means in these regions, the mixture fraction varies from 0.88 to 0.89. In the outlet, the three zones are distinguishable from each other, that is, the inner “tai-chi” pattern, the four separate stripes close to wall and the complete ring in between. They are formed from fluid different height in the mixing chamber because of the wall effects. It can be expected, if the reactor is scaled up, that the complete ring in between the segregated zones will grow with respect to the height of the reactor.

Since at Re\textsubscript{j} = 93, the flow falls in the same regime as with Re\textsubscript{j}, the flow patterns are very similar. However, because of the higher velocity, the inner “tai-chi” region is squeezed at the midplane. At the plane in the outlet, areas of the three zones are about the same as in the Re\textsubscript{j} case, but more detailed structures are developed at the center.
At the highest Reynolds number, 240, the flow becomes unsteady and no discernible pattern can be observed in this case. Due to the limitation of the scan speed, CLSM is no longer able to capture meaningful full-field images. However, statistical analysis is performed, whose results are discussed in the following section. In this case, dark and bright bits are distributed nearly uniformly over the whole image, with more bright color concentrated at the center. This distribution is more apparent in the line-scan images, as is discussed below.

Line-scan results are shown in Figures 6.7 and 6.8. Since the first three cases are all laminar and steady, the flow pattern on a certain line should be approximately the same from time to time, even considering the mechanical noise caused by the syringe pumps. As a result, different colors are now separated by the (nearly) straight lines. As the Reynolds number increases, more lines are developed, which are also thinner, indicating finer structures. At Re\textsubscript{j} = 240, where the flow is turbulent, the line-scan images are both still noisy. However, as pointed out earlier, at the center of the midplane, more bright color is observed. Again, at this Reynolds number, only does statistical analysis reveal more meaningful information and this is presented below.

### 6.3.2 Mean and fluctuation profiles

Mean and root-mean-square (RMS) profiles are plotted in Figures 6.9 to 6.14. Note that the chemical reaction is a switch that “turns on/off” the fluorescence and therefore the statistical results presented here are similar to those in Chapter 2, which represent the local probabilities of the fluorescence.

As can be seen, at Re\textsubscript{j} = 10, along the center line, the fluorescence is constantly off close to the center and constantly on to each side. The fluctuations is the highest at the interfaces due to the mechanical noise. The same behavior is observed on both planes. At Re\textsubscript{j} = 53, the probability of fluorescence or equivalently $\xi > 0.88$ at the midplane is reduced because of the slight traverse motions. However, the flow in the outlet is more
steady and higher probabilities are observed. Again, more fluctuations take place where the interfaces are. The $Re_j = 93$ case behaves very similarly to the previous case only with more and narrower peaks, especially close to the center.

Since the flow regime is completely different at $Re_j = 240$, both mean and RMS profiles shape differently in this case. As discussed in the previous section, more fluorescence is found close to center, which reflected on mean profile are higher values in the center region. Because more large scale convection occurs at this Reynolds number, more basic solution is transported such that the probability of fluorescence is non-zero at any of the location on the center line. Nevertheless, lower mean values indicate better mixing and when the mixing is complete the fluorescence should be off which corresponds to low intensity. With that in mind, it can be concluded that the mixing is by no means complete at this Reynolds number judging by the high mean values (around 0.2 across the entire center line) in the outlet. In addition, the fluctuations remain high, which is another strong indicative of incomplete mixing.

## 6.4 Conclusion

In this study, reactive mixing is visualized using the previously developed confocal-based microscopic laser induced fluorescence (confocal $\mu$-LIF) technique. An instantaneous and irreversible acid-base neutralization chemical reaction is employed with a pH-sensitive fluorescent dye, sodium fluorescein. Due to chemical reaction occurs only through diffusion of chemical species, this method is carried out the quantify the micromixing. Full-field and line-scan images are recorded for examining the large scale structures as well as the statistics. Based on the analysis, it is concluded that the mixing is far from complete even at the high Reynolds number investigated.
Figure 6.5  Full-field images at midplane for all fours Reynolds numbers, $Re_j = 10$ (top left), $Re_j = 53$ (top right), $Re_j = 93$ (bottom left) and $Re_j = 240$ (bottom right)
Figure 6.6  Full-field images at the plane in the outlet for all fours Reynolds numbers. Arrangements of panels are the same as in Figure 6.5
Figure 6.7  Line-scan images at midplane for all fours Reynolds numbers. Arrangements of panels are the same as in Figure 6.5
Figure 6.8  Line-scan images at plane in the outlet for all fours Reynolds numbers. Arrangements of panels are the same as in Figure 6.5
Figure 6.9 Mean profiles (top row) and RMS profiles (bottom row) for $Re_j = 10$ at the midplane (left column) and the plane in the outlet (right column)
Figure 6.10  Mean profiles and RMS profiles for Re<sub>j</sub> = 53. Arrangement of panels are the same as in Figure 6.9
Figure 6.11  Mean profiles and RMS profiles for Re$_j$ = 93. Arrangement of panels are the same as in Figure 6.9
Figure 6.12 Mean profiles and RMS profiles for $Re_j = 240$. Arrangement of panels are the same as in Figure 6.9
Figure 6.13  Mean profiles and RMS profiles for Re_j = 93. Arrangement of panels are the same as in Figure 6.9
Figure 6.14  Mean profiles and RMS profiles for Re$_j$ = 240. Arrangement of panels are the same as in Figure 6.9
CHAPTER 7 SUMMARY AND FUTURE WORK

This chapter summarizes the sub-projects and their corresponding findings described in previous chapters, based on which, some light is shed on the direction of the future work.

7.1 Summary and major findings

On the whole, laminar and turbulent mixing in microscale nanoprecipitation reactors, i.e, the CIJR and the MIVR, is investigated in this project in order to assist understanding the physics involved in the Flash Nanoprecipitation process. The goals of the project include the validation of CFD models for use in the CIJR and the MIVR and the development of sophisticated experimental methods for visualization and characterization of microscale flows.

The microscale flow visualization technique using phenolphthalein developed in this project was applied to the CIJR. Two inlet streams were fed with acid and base solutions respectively, both containing phenolphthalein. With the help of the flash lamp whose pulse duration is extremely short, the turbulent motions created by the impingement of the two inlet streams were frozen onto instantaneous images. Stunning turbulent structures were observed. By applying an image processing technique, different colors were separated, representing pH greater or less than a certain threshold pH value, which hereby was taken to be 9.3. The resulting grayscale images were ensemble averaged for the three jet Reynolds numbers studied, 25, 1000 and 1500. As the local average
value indicates the pH probability, which can be related to a mixture fraction quantity, mixing was thus found not to be complete even at the highest jet Reynolds number we could achieve. In addition to that, two-point spatial auto-correlation analysis and POD analysis were carried out as well to study the flow structures. Both methods suggested major flapping motions around the impingement point at higher Reynolds numbers, to which the mixing can be mainly attributed.

The well-developed velocity field measurement technique, μ-PIV is applied to the MIVR as the first step of the CFD model validation because of the strong dependence of the mixing on the turbulence field. Three jet Reynolds numbers of interest here are 53, 93, 240. They each represents the laminar flow regime, the transitional flow regime and the turbulent flow regime respectively. As the flow spirals towards the center, Cartesian velocity vectors were transformed into polar coordinates with tangential and radial components. The vortex flow was found to be greatly affected by the geometry. Velocities close to the center of the reactor are several times greater than those far away from the center, where the center is the stagnation point with zero velocity at low Reynolds numbers, namely, steady and laminar flow. At high Reynolds number, the wall effects are relatively attenuated. Tangential-to-radial velocity ratio increases with the Reynolds number, indicating more violent vortex flow. Comparisons between experiments and simulations showed that the RANS underpredicted the velocities at all Reynolds numbers. LES, on the other hand, found good agreement with the experiments at the highest Reynolds number, from which great confidence is achieved. Therefore, LES will be chosen primarily for simulating the mixing in these reactors.

Lastly, the confocal-based μ-LIF technique is developed and applied to the MIVR. Passive scalar mixing was accomplished at this stage. Two opposing streams of the total four inlets were dyed with Rhodamine 6G whereas the other two were not. Mixing between streams can thus be visualized. Due to the fact that the CLSM scans in a point-by-point manner, it was run in the line-scanning mode to rapidly obtain sufficient
realizations for statistical analysis. Full-field ‘snapshots’ illustrated the interesting mixing patterns at different Reynolds numbers. Of the four Reynolds number investigated, only the highest one exhibited apparent unsteadyness. Mixing is quantified by the normalized concentration and the value of 0.5 indicates good mixing at the macroscale. Mean profile of the normalized concentration was examined in conjunction with the RMS profile. At lower Reynolds number, poor mixing was observed. At $Re_j = 240$, mixing is well improved, yet not complete still.

7.2 Future Work

In terms of the experimental techniques, more adjustments have yet to be made to improve the accuracy of the results. For example, in order to increase the scan speed in the confocal-based $\mu$-LIF, a spinning-disk confocal system can be used.

From the comparison between the RANS and $\mu$-PIV data in the MIVR, we conclude that the $k-\varepsilon$ is definitely not suitable for the swirling flow in this type of the reactor. Therefore, an appropriate RANS model has to be found to predict the velocity field correctly.

While the LES simulations with the Smagorinsky model predicted well the velocity fields, the scalar field predictions are not satisfactory due to numerical diffusion. As a consequence, a better model is necessary to account for the scalar field.
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