Computational and experimental investigation of turbulent mixing in multiscale reactors for CFD model validation

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CHAPTER 1. INTRODUCTION

1.1 Motivation and objectives

With the advances in computing technology, computational fluid dynamics (CFD) has found its wide application in commercial chemical reactor design and optimization. By simulating a chemical reactor of interest using the best suited CFD models, the engineers are informed of the performance, such as the stability, yield and selectivity, of the reactor with variety in operating conditions, feed configuration and heat transfer, for example, with no need to carry out the time-consuming experiments. In theory, by employing a computational approach, based on CFD for turbulent reacting flows, experiment-free design and scale-up of chemical reactors should be possible. Nevertheless, before such an approach can be used with confidence in industry, it must first be demonstrated that CFD predictions for a carefully designed and executed laboratory experiment are accurate and reliable.

The turbulent reacting flows are fundamentally governed by the conservation of momentum, chemical species and energy. A CFD approach is expected to be able to account for the reactor flow patterns, the interaction between turbulence and the chemistry, given chemical kinetics. In the cases where the reaction time scales are much larger than the turbulence time scales or vice versa, the interaction between turbulence and the chemistry can be safely ignored. However, for a system comprising a wide range of time scales of the reactions, these two factors are required to be accurately formulated at the same time. Thus, it is not surprising that the turbulent mixing draws increasing attention from the academic and industrial communities.

This work consists of my research in two categories. The first category is the computational study of multi-scale reactors. CFD models including the two-layer $k-\varepsilon$ model and the mixing models such as the interchange-with-th-mean (IEM) model, Eulerian minimum span
of tree (EMST) and the direct-quadrature-method-of-moments (DQMOM) - IEM model were employed to investigate the turbulent mixing in several chemical reactors including a lab-scale confined planar reactor, a thermo-chlorination reactor and a microscale confined impinging-jets reactor (CIJR). The CFD predictions including the statistics of the flow field and scalar field were compared with the experimental data available for model validation and evaluation. The second category is the experimental study of the fluid dynamics in a microscale planar CIJR using micron-resolution particle image velocimetry (micro-PIV) techniques. The experimental data were used to validate the CFD models for microscale turbulence.

1.2 Outline

This work is comprised of ten chapters. Chapter 2 provides a review of turbulence models and scalar mixing models reported in the literature. The transported PDF method and the major closures applied in our Reynolds-Average Navier-Stokes (RANS) numerical studies are explained. Chapter 3 contains a detailed description of the flow solver CHEM3D and the Lagrangian PDF code that have been successfully applied to simulate the confined planar reactor and thermo-chlorination reactor with various feed configurations. Chapters 4 and 5 demonstrate the model validation against experimental data of turbulent mixing in a confined reactor – a confined planar jet and a rectangular wake, respectively, taken by PIV and planar laser-induced fluorescence (PLIF) techniques. The flow statistics such as the mean velocity, turbulent kinetic energy, dissipation rate, scalar mean and variance, and the probability density function (PDF) of the a scalar is discussed in details. The scale up of the gas-phase chlorination reactors using CFD is presented in Chapter 6. The dependence of the behaviors of the reactors on the feed configurations and dimensions are analyzed in detail. The optimized operating conditions are proposed accordingly. The two-layer \( k - \varepsilon \) model satisfactorily predicts the fields of mean velocity and turbulence in the confined planar reactors and is then employed to model a microscale CIJR with a mixing-sensitive chemistry in Chapter 7. The CIJR is widely used in the pharmaceutical industry to produce nanoparticles. With the predicted mixing time scale and shear rate of the CIJR, the effects of mixing on the particle size distribution in a
plug-flow reactor were investigated by solving the population balance equation (PBE) using the DQMOM-IEM model. Details can be found in Chapter 8. So far, no experimental data of the fields of velocity and turbulence in the CIJR are available for CFD model validation. We were therefore motivated to exam those flow statistics experimentally using the micro-PIV techniques and the initial results are presented and discussed in Chapter 9. Chapter 10 summarizes the major conclusions and discusses possibilities and recommendation for future work.
CHAPTER 2. LITERATURE REVIEW

2.1 Laws of conservation

For a flow with a constant density $\rho$ and a modified pressure $p$, the mass and velocity field $U$ are governed by a set of hydrodynamic equations known as the Navier-Stokes equations:

$$\nabla \cdot U = 0, \tag{2.1}$$

$$\frac{\partial U_i}{\partial t} + U_j \frac{\partial U_i}{\partial x_j} = \nu \frac{\partial^2 U_i}{\partial x_j \partial x_i} - \frac{1}{\rho} \frac{\partial p}{\partial x_i}, \tag{2.2}$$

and the reacting scalar is governed by

$$\frac{\partial \phi_\alpha}{\partial t} + U_j \frac{\partial \phi_\alpha}{\partial x_j} = \Gamma \frac{\partial^2 \phi_\alpha}{\partial x_j \partial x_i} + S_\alpha (\phi). \tag{2.3}$$

$\nu$ represents the kinematic viscosity. The repeated indices indicate summation over the range of the indices. $\Gamma$ is the molecular diffusivity or the thermal conductivity of the scalar $\phi_\alpha$ that can be the concentration of a chemical species $\alpha$ or enthalpy. $S_\alpha (\phi)$ is the source term of $\phi_\alpha$ due to the $N_r$ elementary reactions involving $N$ species:

$$S_\alpha (\phi) = \sum_{i=1}^{N_r} \left[ (v^{f}_{\alpha i} - v^{r}_{\alpha i}) \left( k^{f}_{i} (T) \prod_{\beta=1}^{N} \phi^{v^{f}_{\beta i}}_{\beta} - k^{r}_{i} (T) \prod_{\beta=1}^{N} \phi^{v^{r}_{\beta i}}_{\beta} \right) \right], \tag{2.4}$$

where $v^{f}_{\beta i}$ is the stoichiometric coefficient of the species $\beta$ in the $i$th forward reaction the rate constant of which is $k^{f}_{i} (T)$ and $v^{r}_{\beta i}$ and $k^{r}_{i}$ are their counterparts in the reverse reaction.

Equation 2.2 can be alternatively written as

$$\frac{\partial U_i}{\partial t} + U_j \frac{\partial U_i}{\partial x_j} = \frac{\partial \tau_{ij}}{\partial x_i} + g \tag{2.5}$$

by defining a stress tensor $\tau_{ij}$ as

$$\tau_{ij} = \nu \left( \frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right) - P \delta_{ij}. \tag{2.6}$$
In Eq. 2.5, \( g \) denotes the acceleration of gravity. \( P \) in Eq. 2.6 is the pressure.

The turbulent flow is characterized by the fluctuations in the fields of the instantaneous velocity, pressure and scalar. The instantaneous velocity may then be written as the sum of the time-smoothed velocity \( \langle U \rangle \) and a velocity fluctuation \( u' \):

\[
U_i = \langle U_i \rangle + u'_i. \tag{2.7}
\]

with the restriction that \( \langle u'_i \rangle = 0 \). A similar expression can be written for the modified pressure and the reacting scalar

\[
p = \langle p \rangle + p', \tag{2.8}
\]
\[
\phi_\alpha = \langle \phi_\alpha \rangle + \phi'_\alpha, \tag{2.9}
\]

where \( \langle p' \rangle = 0 \) and \( \langle \phi'_\alpha \rangle = 0 \)

By substituting Eqs. 2.7, 2.8 and 2.9 into Eqs. 2.1, 2.2 and 2.3, the Reynolds-averaged equations are obtained

\[
\nabla \cdot \langle U \rangle = 0, \tag{2.10}
\]
\[
\frac{\partial \langle U_i \rangle}{\partial t} + \langle U_j \rangle \frac{\partial \langle U_i \rangle}{\partial x_j} = \nu \frac{\partial^2 \langle U_i \rangle}{\partial x_j \partial x_i} - \frac{1}{\rho} \frac{\partial \langle p \rangle}{\partial x_i}, \tag{2.11}
\]
\[
\frac{\partial \langle \phi_\alpha \rangle}{\partial t} + \langle U_j \rangle \frac{\partial \langle \phi_\alpha \rangle}{\partial x_j} = \Gamma \frac{\partial^2 \langle \phi_\alpha \rangle}{\partial x_j \partial x_i} - \frac{\partial \langle u'_j \phi_\alpha \rangle}{\partial x_j} + \langle S_\alpha (\phi) \rangle. \tag{2.12}
\]

The Reynolds stress \( \langle u'_i u'_j \rangle \) in Eq. 2.11, the scalar flux \( \langle u'_j \phi_\alpha \rangle \) and the Reynolds-averaged chemical source term \( \langle S_\alpha (\phi) \rangle \) (\( \langle S_\alpha (\phi) \rangle \neq S_\alpha (\langle \phi \rangle) \)) except for first-order reactions) in Eq. 2.12 are unclosed and this is where the turbulence closure problem originates. Modeling a turbulent reacting flow is thus quantitatively equivalent to modeling these three unknowns.

Closure is not a problem when performing a direct numerical simulation (DNS) in which we numerically produce the instantaneous motions using exactly Eqs. 2.10, 2.11 and 2.12. Unfortunately we are not able to perform such simulations for real engineering problems so far due to its computational cost. As a consequence, those terms are usually modeled rather than being resolved.
2.2 Turbulent-viscosity models

The RANS turbulence models determine the Reynolds stresses either via a turbulent-viscosity model or more directly, from modeled Reynolds-stress transport equation. The following discussion will be concentrated on the turbulent-viscosity models.

The base of all the turbulent-viscosity models is the turbulent-viscosity hypothesis proposed by Boussinesq in 1877, which introduces the concept the turbulent viscosity $\nu_T$:

$$
\langle u'_i u'_j \rangle = \frac{2}{3} k \delta_{ij} - \nu_T \left( \frac{\partial \langle U_i \rangle}{\partial x_j} + \frac{\partial \langle U_j \rangle}{\partial x_i} \right).
$$

Mathematically, Eq. 2.13 is analogous to the stress-rate-of-strain relation for a Newtonian fluid (Eq. 2.6). Here, $k$, the turbulent kinetic energy, is defined as

$$
k = \frac{1}{2} (u'^2 + v'^2 + w'^2).
$$

Now, all that remains is to evaluate $\nu_T$. For simplicity, $\nu_T$ can be assume to be a constant or estimated by a zero-equation model among which is the well-known Prandtl mixing length model [Prandtl, L. (1926)]:

$$
\nu_T = l_m^2 \left| \frac{\partial \langle U \rangle}{\partial y} \right|,
$$

where $l_m$ is the mixing length. Many approaches have been suggested to evaluate $l_m$ for simple viscous flows and flows with "complicating" features, the Cebeci-Smith model [Cebeci, T. and Smith, A. M. O. (1967)] and the Baldwin-Lomax model [Baldwin, B. S. and Lomax, H. (1978)], for example. More details can be found elsewhere [Pope, S. B. (2000); McEligot, D. M. et al (1970); Tannehill, J. C. et al., (1997)]. The application of these models are extremely limited since that the algebraic models do not account for the effects of upstream on the turbulence structure downstream. People therefore are motivated to develop more complex models: one-half-equation, one-equation and two-equation models.

In one-half-equation models, model parameter ($\nu_T$, $\mu_T$ or $l_m$) varies with the primary flow direction in a manner governed by an ordinary differential equation (ODE). McDonald and Camerata, Chan, Adams and Hodge [McDonald, H. and Camerata, F. J. (1968); Chan,
Y. Y. (1972); Adams Jr. J. C. and Hodge, B. K. (1977) proposed models in which the mixing length is determined by the ODE based on the transport equation of the turbulent kinetic energy. Shang and Hankey, Reyhner, et al. [Shang, J. S. and Hankey Jr., W. L. (1975); Reyhner, T. A. (1968)] deduced the empirical ODE for $\mu_T$. In order to treat the non-equilibrium conditions present in transonic separated flows, Johnson and King [Johnson, D. A. and King, L. S (1985)] developed an empirical ODE for the maximum shear stress $\tau_{\text{max}}$.

A one-equation model is one in which an additional partial differential equation (PDF) is solved for a turbulence quantity. Independently, Kolmogorov [Kolmogorov, A.N. (1942)] and Prandtl [Prandtl, L. (1945)] suggested a model transport equation for the turbulent kinetic energy which is related to $\nu_T$ by

$$\nu_T = C_k l_m (k)^{1/2}. \quad (2.16)$$

The model transport equation of $k$ is

$$\frac{\partial k}{\partial t} + (U_j) \frac{\partial k}{\partial x_j} = \nabla \cdot \left( \frac{\nu_T}{\sigma_k} \nabla k \right) + \left( 2 \nu_T S_{ij} - \frac{2}{3} k \delta_{ij} \right) \frac{\partial \langle U_i \rangle}{\partial x_j} - C_D \frac{k^{3/2}}{l_m}. \quad (2.17)$$

In fact, the exact transport equation of $k$ is

$$\frac{\partial k}{\partial t} + (U_j) \frac{\partial k}{\partial x_j} = -\nabla \cdot T' + P - \varepsilon, \quad (2.18)$$

where the flux $T'$ is

$$T'_i = \frac{1}{2} (u_i u_i u_j) + (u_i u'_j) / \rho - \nabla k. \quad (2.19)$$

$P$ and $\varepsilon$ are the production and dissipation rate of $k$, respectively.

$$P \equiv -\langle u_i u_j \rangle \frac{\partial \langle U_i \rangle}{\partial x_j} \quad (2.20)$$

$$\varepsilon \equiv -\nu_T (u_i \frac{\partial u_i}{\partial x_j} \frac{\partial u_j}{\partial x_j}). \quad (2.21)$$

By comparing Eqs. 2.17 and 2.18, it can be found that in the former, $P$ is closed by the turbulent-viscosity hypothesis (Eq. 2.13). $T'$, and $\varepsilon$ are approximated by:

$$T' = -\frac{\nu_T}{\sigma_k} \nabla k, \quad (2.22)$$

$$\varepsilon = C_D \frac{k^{3/2}}{l_m}. \quad (2.23)$$
Although this one-equation model has more accuracy than the mixing-length models, the mixing length that must be specified limits its application.


The two model equations are

$$\frac{\partial k}{\partial t} + \langle U_j \rangle \frac{\partial k}{\partial x_j} = \nabla \cdot \left( \frac{\nu_T}{\sigma_k} \nabla k \right) + \mathcal{P} - \varepsilon, \quad (2.24)$$

$$\frac{\partial \varepsilon}{\partial t} + \langle U_j \rangle \frac{\partial \varepsilon}{\partial x_j} = \nabla \cdot \left( \frac{\nu_T}{\sigma_\varepsilon} \nabla \varepsilon \right) + C_{\varepsilon 1} \frac{P\varepsilon}{k} - C_{\varepsilon 2} \frac{\varepsilon^2}{k}, \quad (2.25)$$

with $C_\mu = 0.09$, $C_{\varepsilon 1} = 1.44$, $C_{\varepsilon 2} = 1.92$, $\sigma_k = 1.0$ and $\sigma_\varepsilon = 1.3$. Then the specification of the eddy viscosity is

$$\nu_T = C_\mu \frac{k^2}{\varepsilon}. \quad (2.26)$$

One of the main shortcomings of the standard $k-\varepsilon$ model is its poor behavior in the viscous sublayer. Improvement can be achieved by using wall functions of a form described by Launder and Spalding [Launder, B. E. and Spalding, D. B. (1974)] or a traditional damped mixing-length algebraic model. A frequently used alternative is to employ a low Reynolds number $k-\varepsilon$ model [Jones, W. P. and Launder, B. E. (1972); Launder, B. E. and Sharma, B. I. (1974); Lam, C. K. G. and Bremhorst, K. A. (1981); Chien, K.-Y. (1982)] in which the "low" $Re$ is the $Re$ of turbulence defined by $Re = k^2/\varepsilon \nu$. More details can be found elsewhere [Patel, V. C. et al. (1985); Shih, T. H. and Mansour, N. N. (1990); Rodi, W. and Mansour, N. N. (1993); Wilcox, D. C. (1998)]. However, the wall-function method is not satisfactory when the law of the wall assumption is questionable, for example, in separated flows and in three-dimensional flows. On the other hand, low-Reynolds-number $k-\varepsilon$ models are not able to accurate predict the flow close to a solid wall even in the relatively simple case of two-dimensional flows [Chen, H. C. and Patel, V. C. (1988)]. For this reason, Chen and Patel
[Chen, H. C. and Patel, V. C. (1988)] proposed a two-layer, near-wall turbulence model which is more accurate and computational efficient. They defined a turbulence Reynolds number as

$$Re_y = \frac{k^{1/2}y}{\nu},$$

(2.27)

where $y$ is the distance from the nearest wall. The model divides the domain into two regions: the fully turbulent region (I) where $Re_y \geq 200$ and the viscosity-affected near-wall region (II) where $Re_y < 200$. In region I, the standard $k - \varepsilon$ model is employed. In region II, the one-equation model of Wolfshtein [Wolfshtein, M. (1969)] is used to account for the wall proximity effects. The one-equation model requires the solution of only the turbulent kinetic energy in region II. The rate of energy dissipation in this region is specified by

$$\varepsilon = \frac{k^{3/2}}{l_\varepsilon},$$

(2.28)

where the length scale is given by the expression

$$l_\varepsilon = C_l y [1 - \exp (-Re_y/A_\varepsilon)].$$

(2.29)

The eddy viscosity is obtained from the equation

$$\nu_T = C_\mu k^{1/2}l_\mu,$$

(2.30)

where

$$l_\mu = C_l y [1 - \exp (-Re_y/A_\mu)].$$

(2.31)

The constants in the length-scale formulas are

$$C_l = KC_\mu^{3/4}, A_\mu = 70, A_\varepsilon = 2C_l,$$

(2.32)

where the von Kármán constant $K$ is 0.41. The turbulence Reynolds number depends only on the local turbulence intensity. It does not vanish at separation, and remains well defined in regions of flow reversal. Therefore this two-layer approach is applicable in complex flows, and we have adopted this model in all our simulations.
The second most widely used two-equation is the $k-\omega$ model by Wilcox [ Wilcox, D. C. (1998)]. In this model, the expression for $\nu_T$ and $k$ are the same as those in the standard $k-\varepsilon$ model but the second turbulent quantity modeled is $\omega \equiv \frac{k}{\varepsilon}$ rather than $\varepsilon$. 

\[
\frac{\partial \omega}{\partial t} + (U_j) \frac{\partial \omega}{\partial x_j} = \nabla \cdot \left( \frac{\nu_T}{\sigma_\omega} \nabla \omega \right) + C_{\omega1} \frac{P_\omega}{k} - C_{\omega2} \omega^2. \tag{2.33}
\]

The standard model constants are $C_{\omega1} = 5/9$, $C_{\omega2} = 5/6$, $\sigma_\omega = \sigma_k = 2$ and $C_\mu = 0.09$. As discussed in detail by Wilcox [ Wilcox, D. C. (1998)], the $k-\omega$ model is superior both in its treatment of the viscous near-wall region, and in its accounting for the effects of streamwise pressure gradients for boundary-layer flows. However, this model has spurious sensitivity to free-shear conditions.

### 2.3 RANS models for scalar mixing

Similarly, the scalar flux $\langle u_j' \phi_\alpha \rangle$ can be closed either via a turbulent-viscosity-based model or more directly from modeled scalar-flux transport equation. Mathematically, the turbulent-viscosity-based model is analogous to Fourier’s law of heat conduction and Fick’s law of molecular diffusion. It can be expressed as [ Taylor, G. I. (1921)]

\[
\langle u_j' \phi_\alpha \rangle = -\Gamma_T \frac{\partial \langle \phi \rangle}{\partial x_j}, \tag{2.34}
\]

with the turbulent diffusivity, $\Gamma_T$, is related to the turbulent viscosity through $\Gamma_T = \nu_T / \text{Sc}_T$, where $\text{Sc}_T$ is the turbulent Schmidt number. This model is also known as the gradient-diffusion model and is used in our CFD codes. It assumes that the scalar flux is aligned with the gradient of the scalar mean and only strictly holds for isotropic turbulence [ Biferale, L. et al. (1995)]. General accuracy can be expected by solving the modeled transport equation of the scalar flux at the cost of extra complexity.

For very fast, non-premixed reactions, the reactants can not coexist at the same spatial location. Thus, the reaction rate is exclusively determined by the rate of turbulent mixing that can often be quantified by the variance $\langle \phi'^2 \rangle$ of an inert scalar $\phi$ (for example, the mixture
fraction). The transport equation of $\langle \phi'^2 \rangle$ is

$$\frac{\partial \langle \phi'^2 \rangle}{\partial t} + \langle U_j \rangle \frac{\partial \langle \phi'^2 \rangle}{\partial x_j} = \Gamma \frac{\partial^2 \langle \phi'^2 \rangle}{\partial x_j \partial x_i} - \frac{\partial \langle u_j \phi' \rangle}{\partial x_j} + \mathcal{P}_\phi - \varepsilon_\phi. \quad (2.35)$$

$\mathcal{P}_\phi$, the scalar-variance-production term, is defined by $\mathcal{P}_\phi \equiv -2\langle u_j \phi \rangle \frac{\partial \langle \phi \rangle}{\partial x_j}$ and is closed with Eq. 2.34 in this study. $\langle u_j' \phi'^2 \rangle$ is the scalar-variance flux which is closed by invoking the gradient-diffusion model [Taylor, G. I. (1921)]:

$$\langle u_j' \phi'^2 \rangle = -\Gamma \frac{\partial \langle \phi'^2 \rangle}{\partial x_j} \quad (2.36)$$

$\varepsilon_\phi$ is the scalar dissipation rate defined by $\varepsilon_\phi \equiv 2\Gamma (\frac{\partial \phi'}{\partial x_j} \frac{\partial \phi'}{\partial x_j})$. The “equilibrium” model [Spalding, D. B. (1971)] which assumes the proportionality of the scalar time scale to the mechanical time scale is the most frequently used closure

$$\varepsilon_\phi = C_{\phi} \varepsilon \langle \phi'^2 \rangle. \quad (2.37)$$

Equation 2.37 is actually a model for the scalar spectral energy transfer rate through the inertial-convective sub-range in homogeneous turbulence. It does not account for the turbulent anisotropy and the mean shear rate [Fox, R. O. (2003)]. These effects are incorporated in the modeled transport equation of the scalar dissipation rate.

### 2.4 Closures for the chemical source term

To close the chemical source term $\langle S_\alpha (\phi) \rangle$, one needs to know the shape of the joint composition PDF. The joint scalar PDF can be computed directly from its transport equation (transported PDF method) or be assumed directly (for example, presumed PDF methods) or indirectly (for example, moment closures).

The moment closures in which the joint scalar PDF is represented by its moments is the simplest closure for $\langle S_\alpha (\phi) \rangle$. In the first-order moment closures, $\langle S_\alpha (\phi) \rangle = S_\alpha (\langle \phi \rangle)$ by assuming zero scalar covariance. Unfortunately, this assumption is only valid for cases where the micromixing is so fast that the composition scalars can reach their equilibrium values. If the reaction rates are controlled by micromixing (mixing sensitive reactions), the first-order moment closures fail. This dilemma has motivated the development of higher-order moment
closures [Dutta, A. and Tarbell, J. M. (1989); Shenoy, U. V. and Toor, H. L. (1990)]. The closures in this category relate the covariances of reactive scalars to the mixture-fraction variance or obtain the covariances by solving their transport equations. They have difficulty with multiple-step chemistry or higher-order reactions.

The conditional-moment closures are based on the experimental and computational observation that the fluctuation of the reactive scalar is relatively small around the mean conditioned on a given value of the mixture-fraction \( \xi \). By assuming \( \langle \phi'_\alpha|\xi \rangle = 0 \), \( \langle S_\alpha (\phi)|\xi \rangle = S (\langle \phi_\alpha |\xi \rangle) \).

Then modeling \( \langle S_\alpha (\phi) \rangle \) is converted to modeling the conditional mean \( \langle \phi_\alpha |\xi \rangle \) given a presumed PDF of the mixture fraction \( \xi \). The conditional moments can be found either by a linear interpolation procedure [Baldyga, J. (1994)] or by solving its transport equation that depends explicitly on turbulent transport and chemical reactions [Bilger, R. W. (1993)]. The prediction yielded by this type of closures for inhomogeneous reacting flows is questionable [Cha, C. M. et al. (2001)].

The multi-environment presumed PDF models assume that the joint composition PDF is the summation of \( N_e \) probability-weighted delta functions:

\[
f_\phi (\psi; \mathbf{x}, t) = \sum_{n=1}^{N_e} p_n (\mathbf{x}, t) \prod_{\alpha=1}^{N} \delta [\psi_\alpha - \langle \phi_\alpha \rangle_n (\mathbf{x}, t)],
\]

(2.38)

where \( p_n \) is the probability of the \( n \)th environment and \( \langle \phi \rangle_n (\mathbf{x}, t) \) is the mean composition vector in the \( n \)th environment. By employing the DQMOM method, the transport equations of the model variables including the probability and the probability-weighted scalars can be deduced. A two-environment presumed PDF model was employed to simulate the mixing-sensitive reactions in a confined impinging-jet reactor. More details will be presented in Chapter 7. It should be noted that the chemical source term in the transport equations of the probability-weighted reactive scalars is in closed form and needs no modeling. However, the presumed form of the joint scalar PDF in terms of a finite collection of delta functions may be inadequate for complex chemistry [Fox, R. O. (2003)].

In the transported PDF methods, the shape of the joint scalar PDF is computed from its transport equation. Methods of this type treat the effect of chemical reactions on the joint scalar PDF exactly, thus describe the interaction between turbulence and reactions with more
accuracy and details. Theoretically, the number of reactive scalars treated by the transported PDF methods could be arbitrary. Nevertheless, the computational cost of the transported PDF simulations is intensive. In practice, solving the transport equation of the joint scalar PDF using standard discretization methods is intractable due to the large number of dimensions. Pope [Pope, S. B. (1976, 1985)] proposed Lagrangian PDF methods to express the transport equation in terms of stochastic differential equations for "notional" particles. With this strategy, a flow solver is required to supply the PDF code with a solution to the flow statistics such as the mean velocity, turbulent kinetic energy and dissipation rate if the Reynolds stresses are closed by the $k - \varepsilon$ model. In this study, a finite-volume RANS code and a Lagrangian PDF code are coupled and work together to investigate the scalar mixing in single-phase turbulent flows (Chapters 4, 5 and 6). More details about the finite-volume RANS/transported PDF method can be found in the following chapter.
CHAPTER 3. FINITE-VOLUME RANS/TRANSPORTED PDF METHOD

3.1 CHEM3D – code overview

CHEM3D is a parallel, multi-block chemical reacting flow solver developed at Dow [Harvey, A. D. (2003)]. It solves the RANS equations using the finite-volume (FV) method.

Using standard notation for mean flow quantities ($\bar{\rho}$, $\bar{p}$, $\bar{T}$, $\bar{h}$, $\bar{\phi}_\alpha$, $\bar{p}_\alpha$, $\alpha = 1, \cdots, N$ and $\bar{U}$, $\bar{V}$ and $\bar{W}$ are the mean density and pressure, and Farve-averaged temperature, enthalpy, species mass fractions, species partial pressure and Cartesian velocity components, respectively), the generalized transport equations solved are

$$\frac{\partial}{\partial t}Q + \frac{\partial}{\partial x}(E - E_v) + \frac{\partial}{\partial y}(F - F_v) + \frac{\partial}{\partial z}(G - G_v) = S,$$

(3.1)

where the primary variable vector is

$$U = \left[\bar{\rho}_1, \ldots, \bar{\rho}_N, \bar{U}, \bar{V}, \bar{W}, \bar{T}\right]^T,$$

(3.2)

the conserved variable is

$$Q = \left[\bar{\rho}\bar{\phi}_1, \ldots, \bar{\rho}\bar{\phi}_N, \bar{p}\bar{U}, \bar{p}\bar{V}, \bar{p}\bar{W}, \bar{E}_t\right]^T,$$

(3.3)

the inviscid fluxes are

$$E = \left[\bar{p}\bar{U}\bar{\phi}_1, \ldots, \bar{p}\bar{U}\bar{\phi}_N, \bar{p}\bar{U}^2 + \bar{p}, \bar{p}\bar{U}\bar{V}, \bar{p}\bar{U}\bar{W}, (\bar{E}_t + \bar{p})\bar{U}\right]^T,$$

(3.4)

$$F = \left[\bar{p}\bar{V}\bar{\phi}_1, \ldots, \bar{p}\bar{V}\bar{\phi}_N, \bar{p}\bar{U}\bar{V}, \bar{p}\bar{V}^2 + \bar{p}, \bar{p}\bar{V}\bar{W}, (\bar{E}_t + \bar{p})\bar{V}\right]^T,$$

(3.5)

$$G = \left[\bar{p}\bar{W}\bar{\phi}_1, \ldots, \bar{p}\bar{W}\bar{\phi}_N, \bar{p}\bar{U}\bar{W}, \bar{p}\bar{V}\bar{W}, \bar{p}\bar{W}^2 + \bar{p}, (\bar{E}_t + \bar{p})\bar{W}\right]^T.$$

(3.6)
The viscous fluxes are
\[
E_v = \left[ q_{x1}, \ldots, q_{xN}, \tau_{xx}, \tau_{xy}, \tau_{xz}, \tilde{U} \tau_{xx} + \tilde{V} \tau_{xy} + \tilde{W} \tau_{xz} + q_{xe} \right]^T, \quad (3.7)
\]
\[
F_v = \left[ q_{y1}, \ldots, q_{yN}, \tau_{yx}, \tau_{yy}, \tau_{yz}, \tilde{U} \tau_{yx} + \tilde{V} \tau_{yy} + \tilde{W} \tau_{yz} + q_{ye} \right]^T, \quad (3.8)
\]
\[
G_v = \left[ q_{z1}, \ldots, q_{zN}, \tau_{zx}, \tau_{zy}, \tau_{zz}, \tilde{U} \tau_{zx} + \tilde{V} \tau_{zy} + \tilde{W} \tau_{zz} + q_{ze} \right]^T \quad (3.9)
\]
and the source term is
\[
S = \left[ S_1, \ldots, S_{N_r}, 0, 0, 0 \right]^T, \quad (3.10)
\]
where \( S_\alpha \) is the combined mass production rate of the species \( \alpha \) in a system containing \( N_r \) reactions (Eq. 2.4). \( E_t \) is the total energy expressed by
\[
E_t = \rho \left[ \frac{1}{2} \left( \tilde{U}^2 + \tilde{V}^2 + \tilde{W}^2 \right) \right], \quad (3.11)
\]
where \( e \) is the specific internal energy. \( q_{x\alpha}, q_{y\alpha} \) and \( q_{z\alpha} \) are the diffusion fluxes of the species \( \alpha \) given by
\[
q_{x\alpha} = \rho \left( D_{\alpha m} + \frac{\nu_t}{S_{ct}} \right) \partial_x \tilde{\phi}_\alpha, \quad (3.12)
\]
\[
q_{y\alpha} = \rho \left( D_{\alpha m} + \frac{\nu_t}{S_{ct}} \right) \partial_y \tilde{\phi}_\alpha, \quad (3.13)
\]
\[
q_{z\alpha} = \rho \left( D_{\alpha m} + \frac{\nu_t}{S_{ct}} \right) \partial_z \tilde{\phi}_\alpha, \quad (3.14)
\]
where \( D_{\alpha m} \), the binary molecular diffusivity of species \( \alpha \) in the gas mixture is
\[
D_{\alpha m} = \frac{(1 - X_\alpha)}{\sum_{\beta=1,\beta\neq i}^N X_\beta / D_{\alpha \beta}}. \quad (3.15)
\]
\( X_\alpha \) is the molar fraction of the species \( \alpha \). \( q_{xe}, q_{ye} \) and \( q_{ze} \) are the energy diffusion fluxes given by
\[
q_{xe} = k_e \partial_x \tilde{T} + \rho \sum_{\alpha=1}^N h_i D_{\alpha m} \partial_x \tilde{\phi}_\alpha, \quad (3.16)
\]
\[
q_{ye} = k_e \partial_y \tilde{T} + \rho \sum_{\alpha=1}^N h_i D_{\alpha m} \partial_y \tilde{\phi}_\alpha, \quad (3.17)
\]
\[
q_{ze} = k_e \partial_z \tilde{T} + \rho \sum_{\alpha=1}^N h_i D_{\alpha m} \partial_z \tilde{\phi}_\alpha. \quad (3.18)
\]
where \( k_e \) represents the effective thermal conductivity. \( \tau_{ij} \) are the stress components. In a generalized frame of reference with coordinate directions denoted by \( \xi, \eta \) and \( \zeta \), the vector equation is of the form

\[
\frac{\partial}{\partial t} \mathbf{Q} + \frac{\partial}{\partial x}(\mathbf{E} - \mathbf{E}_v) + \frac{\partial}{\partial y}(\mathbf{F} - \mathbf{F}_v) + \frac{\partial}{\partial z}(\mathbf{G} - \mathbf{G}_v) = \mathbf{S},
\]

where

\[
\mathbf{Q} = \frac{1}{J} \mathbf{Q},
\]

\[
\mathbf{E} = \frac{1}{J}(\xi_x \mathbf{E} + \xi_y \mathbf{F} + \xi_z \mathbf{G}),
\]

\[
\mathbf{F} = \frac{1}{J}(\eta_x \mathbf{E} + \eta_y \mathbf{F} + \eta_z \mathbf{G}),
\]

\[
\mathbf{G} = \frac{1}{J}(\zeta_x \mathbf{E} + \zeta_y \mathbf{F} + \zeta_z \mathbf{G})
\]

and

\[
\mathbf{S} = \frac{1}{J} \mathbf{S},
\]

\[
\mathbf{E}_v = \frac{1}{J}(\xi_x \mathbf{E}_v + \xi_y \mathbf{F}_v + \xi_z \mathbf{G}_v),
\]

\[
\mathbf{F}_v = \frac{1}{J}(\eta_x \mathbf{E}_v + \eta_y \mathbf{F}_v + \eta_z \mathbf{G}_v),
\]

\[
\mathbf{G}_v = \frac{1}{J}(\zeta_x \mathbf{E}_v + \zeta_y \mathbf{F}_v + \zeta_z \mathbf{G}_v).
\]

Second-order backward 3-point differencing, Euler differencing, second-order low diffusion flux-splitting scheme and second-order central differencing are used for physical time, pseudo-time, convective terms and viscous terms, respectively. In this FV RANS code, the Reynolds stresses can be closed by the two-layer \( k-\varepsilon \) model, \( k-\omega \) model, or \( v^2-f \) model. The two-layer \( k-\varepsilon \) model is used in the simulations presented in this report.

### 3.2 Transported PDF code

Given the solution to the flow statistics, the PDF code solves the stochastic differential equations for each “notional” particles in the computational domain. Denoting the position and composition of a notional particle by \( \mathbf{X}^* \) and \( \phi^* \), respectively, the particles are governed
by equations [Fox, R. O. (2003)]

\[
d\mathbf{X}^* = \left[ (U)(\mathbf{X}^*, t) + \nabla \Gamma_T(\mathbf{X}^*, t) \right] dt + \sqrt{2\Gamma_T(\mathbf{X}^*, t)} d\mathbf{W}(t) \tag{3.28}
\]

and

\[
d\phi^* = \frac{C_{\phi \varepsilon}}{2k} \left( \langle \phi \rangle (\mathbf{X}^*, t) - \phi^* \right) dt + S(\phi^*)dt, \tag{3.29}
\]

where \( d\mathbf{W}(t) \) is a multi-variate Wiener process, and \( S(\phi^*) \) is the chemical source term. \( \langle U \rangle (\mathbf{X}^*, t) \) and \( \langle \phi \rangle (\mathbf{X}^*, t) \) are the mean velocity and the estimated scalar mean at the particle location. The composition vector of each particle consists of \( N + 1 \) scalars: the mass fractions of \( N - 1 \) species, the temperature \( T \) and the mixture fraction \( \xi \). The mass fraction of the \( N \)th species is given by \( 1 - \sum_{\alpha=1}^{N-1} \phi_\alpha \). Initially, each grid cell has \( N_p \) uniformly distributed particles the mass of which is \( \frac{m}{N_p} \). Here, \( V \) is the volume of the grid cell. In many computations, smaller grid-cell volumes are required at areas where the flow quantities change quickly. Particles in those grid cells thus weigh less than particles elsewhere, for a constant-density system, leading to a ununiform particle distribution throughout the computational domain but the total mass of each grid cell always remains constant. In contrast, the density of a compressible flow may change with the reactions. In this case, once the chemical source term is treated, the PDF code updates the density of each grid cell and return it to the flow solver in which the temperature field and other flow quantities are consequently updated. The FV-RANS code and the PDF code run iterations alternately until the global convergence is achieved.

Equation 3.29 is solved by a fractional time-stepping method [Fox, R. O. (2003)]. The left-hand side of Eq. 3.29 and the chemical source term form an ODE system. In order to minimize the statistical error, a large number of notional particles need to be adopted in the PDF code. However, solving the ODE system for so many particles is computational prohibitive with traditional stiff ODE solvers. As in our earlier works [Raman, V. et al. (2001, 2003, 2004)], the in-situ adaptive tabulation (ISAT) [Pope, S. B (1997)] is employed to improve computational efficiency.
CHAPTER 4. INVESTIGATION OF TURBULENT MIXING IN A
CONFINED PLANAR-JET REACTOR

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abstract

The velocity and concentration fields in a liquid-phase confined planar-jet reactor were measured using particle image velocimetry (PIV) and planar laser-induced fluorescence (PLIF). Measurements were taken at downstream distances from the jet splitter plates of 0, 1, 4.5, 7.5, 12, and 15 jet widths for a Reynolds number of 50,000 based on the distance between two sidewalls of the test section. The velocity and concentration field data were analyzed for such flow statistics as mean velocity, Reynolds stresses, turbulent kinetic energy, and scalar mean and variance. The turbulence dissipation rate was also estimated based on a large-eddy PIV approach using the strain-rate tensors computed from velocity fields and the sub-grid scale (SGS) stress obtained from the Smagorinsky model. Computational fluid dynamics (CFD) models including a two-layer $k - \varepsilon$ turbulence model, gradient-diffusion models and a scalar dissipation rate model were validated against experimental data collected from this facility. The experimental and computational results were found to be in good agreement.

4.1 Introduction

Because of their ability to transport and mix chemical species, momentum, and energy much faster than molecular diffusion, turbulent flows are widely used in the chemical process industry. For example, most chemical reactors are designed to operate in the turbulent regime
in order to maximize throughput. It follows that a detailed understanding of turbulent mixing is necessary for the proper design and optimization of chemical reactors, making turbulent mixing the topic of numerous experimental and computational studies over the years [Mehta, R. V. and Tarbell, J. M. (1987); Pipino, M. and Fox, R. O. (1994); Baldyga, J. A. and Pohorecki R. (1995); Baldyga, J. A. and Bourne, J. R. (1999)]. One objective in studying turbulent mixing is to develop computational fluid dynamics (CFD) models for turbulent reacting flows [Fox, R. O. (2003)]. By virtue of its potential for quickly generating flow field predictions in complex geometries at a relatively low cost, CFD can be a useful tool in reactor design and analysis [Ranade, V. V. (2002)]. One key component of a successful CFD model is the model used to characterize turbulent mixing at the microscale [Jimenez, J. et al. (1997); Vreman, B. et al. (1997); Langford, J. A. and Moser, R. D. (1999); Fox, R. O. (2003)]. Both the development and validation of sub-grid scale models require comparison with experimental data [Sohankar, A. et al. (1999); Friberg, P. C. and Hjertager, B. H. (1999)]. Accordingly, experimental studies can be of great importance in both advancing turbulence theory and in the development and validation of CFD micromixing models. The primary objective of this work is to implement state-of-the-art experimental techniques in order to validate CFD models for turbulent mixing in a well-defined flow geometry: a confined planar-jet reactor. In the present study, velocity and concentration fields in a turbulent flow have been measured using two non-intrusive optically based techniques: particle image velocimetry (PIV) and planar laser induced fluorescence (PLIF). After their rapid development in the recent years, both PIV and PLIF have been proven to be capable of providing high-quality measurements. Aanen et al. [Aanen, L. et al. (1999)] tested the reliability and precision of the techniques of PIV and PLIF. They measured the mixing of fluorescein emitted from a point source placed in the center of a fully developed turbulent flow in a smooth pipe and found that the experimental results agreed well with those of a direct numerical simulation (DNS) and the analytical results. In their paper on the mixing in a self-preserving axisymmetric turbulent jet, Fukushima et al. [Fukushima, C. et al. (2000)] compared their results obtained from PIV and PLIF techniques with not only the results from DNS, but also with point velocity measurements and
combined PIV, particle tracking velocimetry (PTV), or laser Doppler velocimetry (LDV) with laser induced fluorescence (LIF) measurements, and found satisfactory agreement between the DNS simulations and the data collected using each technique. Meyer et al. [Meyer, K. E. et al. (2000)] also measured the velocity field and concentration field using PIV and PLIF. They considered the mixing of a jet in a crossflow in a square duct and compared their results with measurements in the same setup by the use of pointwise LIF and laser Doppler anemometry (LDA). They found that PIV and PLIF gave results in good agreement with those from single-point techniques. Furthermore, as whole-field measurement techniques, both PIV and PLIF have distinct advantages over single-point measurement techniques, especially in their ability to give instantaneous spatial information. For this reason, PIV and PLIF have been employed to investigate the spatial structure of turbulent velocity and concentration fields [Kawaguchi, Y. et al. (2002); Olsen, M. G. and Dutton, J. C. (2002); Crimaldi, J. P. and Koseff, J. R. (2001)]. In collecting experimental data to develop or validate computational models, one would like to perform experiments with enough spatial resolution to accurately determine flow quantities such as Reynolds stresses and dissipation rates. According to classical turbulence theory [Kolmogorov, A.N. (1941)], the smallest spatial scales of motion in the flow are set by the Kolmogorov scale, which is defined by

\[ \eta = \left( \frac{\nu^3}{\varepsilon} \right)^{1/4}, \]  

(4.1)

where \( \nu \) is the molecular kinematic viscosity and \( \varepsilon \) is the rate of dissipation of turbulent kinetic energy per unit mass. Mixing layer growth and fluid entrainment are dominated by large-scale turbulent structures [Brown, G. L. and Roshko, A. (1974); Mankbadi, R. R. (1992); Lesieur, M. et al. (1995)]. Large-scale structures absorb energy from the mean flow and are usually flow-dependent, while small-scale structures mainly dissipate the energy provided by larger eddies and are more universal than the large scales [Pope, S. B. (2000)]. For high Reynolds number flows, only the large-scale turbulent structures need to be resolved to determine the Reynolds stresses and turbulent kinetic energy since they are the energy containing structures. For example, Law and Wang [Law, A. W. and Wang, H. (2000)] studied turbulent mixing using PIV with a spatial resolution of about 16\( \eta \) and obtained turbulence intensities in good
agreement with results from fine scale measurements. Smaller scales must be resolved if one desires to measure or estimate turbulence dissipation. Tennekes and Lumley [Tennekes, H. and Lumley, J. L. (1972)] suggested that the spatial resolution of the velocity measurement be no more than $5\eta$ where the dissipation of the turbulence has a maximum. Tsurikov and Clemens [Tsurikov, M. S. and Clemens, N. T. (2002)] found that kinetic energy dissipative structures have thicknesses ranging from approximately $1\eta$ to $10\eta$ and a mean thickness of $4\eta$ after processing the PIV data at a few different resolutions. In homogeneous and isotropic turbulence, the mean turbulence dissipation rate, $\varepsilon$, can be approximated by

$$\varepsilon \simeq A \frac{u_0^3}{l},$$

where $u_0$ is the characteristic fluctuating velocity, $l$ represents the integral length scale of turbulence, and $A$ is a constant [Batchelor, G. K. (1953); Tennekes, H. and Lumley, J. L. (1972)]. Antonia et al. [Antonia, R. A. et al. (1980)] found that the value of $A$ is approximately equal to one if Eq. diss appro is applied to planar jets. In practice, the integral length scale is not a constant and varies throughout the flow field so that Eq. diss appro cannot be used to describe the local dissipation rate. Numerous methods have been suggested to estimate the local dissipation rate from hot wire or laser Doppler anemometry data [Browne, L. et al. (1987); Elsener, J. W. and Elsner, W. (1996)]. However, these methods are limited due to their being single-point velocity techniques. Because of the planar nature of the collected data, PIV offers the possibility of estimating the distribution of the dissipation rate over a large flow region. Based on a large-eddy PIV approach, Sheng et al. [Sheng, J. et al. (2000)] showed that the turbulence dissipation rate could be approximated by computing the Reynolds averaged sub-grid-scale (SGS) dissipation rate

$$\varepsilon \simeq -2\langle \tau_{ij} \bar{S}_{ij} \rangle$$

where $\bar{S}_{ij}$ is the filtered rate-of-strain tensor defined by

$$\bar{S}_{ij} = \frac{1}{2} \left( \frac{\partial \bar{U}_j}{\partial x_i} + \frac{\partial \bar{U}_i}{\partial x_j} \right),$$

where $\bar{U}$ is the filtered velocity field. To close the SGS stress, various SGS models have been proposed. The Smagorinsky model [Smagorinsky, J. (1963)] is one of the simplest models,
which gives

$$\tau_{ij} = -C_s^2 \Delta^2 |\mathbf{S}| \mathbf{S}_{ij}, \quad (4.5)$$

where $C_s = 0.17$ is the Smagorinsky constant, $\Delta$ is the filter width, and $|\mathbf{S}| = (2\mathbf{S}_{ij}\mathbf{S}_{ij})^{1/2}$.

Although a large body of experimental data exists for turbulent flows, no detailed experimental data for both the turbulent flow field and concentration field inside of a liquid-phase, confined planar jet are available for model validation. The objective of the present study is to investigate turbulent mixing in a confined planar jet using both PIV and PLIF. The velocity and concentration fields are analyzed to provide insight into the characteristics of turbulent mixing and to validate the results of CFD models.

4.2 Experimental apparatus and methodology

4.2.1 Flow facility

The experimental setup is shown in Figs. 4.1 and 4.2. The flow system is designed to provide a shear flow for Reynolds numbers, based on the distance between two sidewalls, in the range 5,000-100,000. The measurements are carried out in a Plexiglas test section (Fig. 4.2) with a rectangular cross-section of 60 mm by 100 mm and an overall length of 1 m. The test section is mounted in an adjustable cage so that it can be moved up and down to change the interrogation region without moving the lasers and cameras. The width of each of the three inlet channels is 20 mm. Three feedback control systems (Fieldvuc DVC6000, Fisher Controls International Inc.) with flow accuracy of 0.5% are used to supply constant flow rates to the inlet channels.

Before they enter the test section, uniform flow and reduced free-stream turbulence intensities are imparted on the incoming flow by flow conditioning consisting of a packed bed, turbulence reducing screens, and a 16:1 contraction. For the present study, the flow rates of each inlet channel were 1.0, 2.0 and 1.0 liter/sec, thus the free-stream velocities were 0.5 m/s, 1 m/s and 0.5 m/s, respectively. The Reynolds number based on the distance between two sidewalls was 50,000. The coordinate system in plots presented here is such that $x$- is in the
downstream direction and y- is in the transverse direction. The cross-stream direction (z-) is assumed to be nearly homogeneous (except near the front and back walls), and no data were taken in that direction.

### 4.2.2 Velocity measurements

PIV was used to measure the instantaneous velocity field in a planar cross section of the observed flow. A schematic depicting the PIV (and also the PLIF) experimental setup is shown in Fig. 4.3. The flow was seeded with hollow glass spheres (Sphericel, Potters Industries Inc.) with a nominal diameter of 11.7 $\mu$m and a density of 1.1 g/cm$^3$. The particles were added to the feed tanks and mixed until they were distributed homogeneously. About 120 grams of seed particles were added to the total reservoir volume of 3500 liters. Illumination was provided by a New Wave Research Gemini PIV laser. The Gemini is a double-pulsed Nd:YAG laser that emits two independent 532 nm light pulses at a frequency of 15 Hz. The maximum pulse energy is 120 mJ and the pulse duration is about 5 ns. A time delay between the two laser pulses of 600 $\mu$s was used in the present study. Using a series of mirror and cylindrical and spherical lenses, the laser beam was formed into a thin light sheet with a thickness of about 0.5 mm passing through the reactor at the centerline of the cross-stream direction. The waist of the light sheet was located near the centerline in the y- direction. Images of the seeded flow were obtained at a frame rate of 8 images/sec using a 12-bit LaVision Flowmaster 3S CCD camera with a resolution of 1280 $\times$ 1024 pixels. The laser and cameras were connected to a host computer that controlled the timing of laser illumination and image acquisition. Two images were captured per realization, and the corresponding velocity field was computed using a cross-correlation technique [Westerweel, J. (1993); Kompenhans, J. et al. (1998)]. A multi-pass interrogation scheme with decreasingly smaller window sizes was used with a final interrogation spot size measuring 16 by 16 pixels, corresponding to 0.9 mm on a side. With 50% overlap between adjacent interrogation spots, the spatial resolution was 0.45 mm in both the and directions. The only post-processing performed on the vector fields was the removal of bad vectors. No smoothing of vector fields was performed. At each observed location, 2500
image pairs were taken and then analyzed. Using the exit width of the jet as the characteristic length scale, the Kolmogorov scale in the present study was estimated to be approximately 75 μm based on Eqs. 4.1 and 4.2. The spatial resolution of the PIV measurements is about 6η; therefore, the measurements cannot adequately resolve the smallest scales of the flow. However, since the primary interest in this study is in the determination of the first- and second-order flow statistics such as mean velocity and turbulence intensity, the loss of the fine-scale information should not affect the results.

Uncertainties in the velocity measurements include errors introduced during the recording of the images and bias introduced by large velocity gradients [Keane, R. D. and Adrian, R. J. (1992)]. The maximum uncertainty of the measurements can be estimated as one-tenth of the particle image diameter [Prasad, A. K. et al. (1992)]. The centerline free-stream velocity corresponds to a displacement of 600 μm and the side free-stream velocities correspond to a displacement of 300 μm; thus, the maximum experimental uncertainty is ±1.3% for the center free-stream and ±2.7% for the side free streams.

4.2.3 Concentration measurements

A similar optical setup was used for the PLIF measurements, except the camera was placed closer to the reactor than in the PIV measurements, giving a smaller field of view. Based on the area imaged per pixel, the spatial resolution for PLIF measurements was 0.026 mm. However, the diffraction-limited spot size for the lens was 0.035 mm; this is a better estimate of the PLIF spatial resolution. Rhodamine 6G was used as the passive scalar. In the center stream, the source concentration of Rhodamine 6G was 45 μg/liter, whereas the other two streams were pure water. Rhodamine 6G emits broadband fluorescence with a peak emission around 555 nm when excited by light from an Nd:YAG laser [Penzkofer, A. and Leupacher, W. (1987)]. To ensure that reflected or scattered laser light does not interfere with the fluorescence measurements, the camera lens was fitted with a long-pass (i.e., low pass for frequency) optical filter that blocked light below 555 nm. The concentration field images were captured at a frame rate of 8 images/sec. Since the flow could not be re-circulated during PLIF
measurements, the number of images that could be collected per run was limited by the volume of feed tanks. For the data presented here, 1500 images were taken at each observed location. Nd:YAG lasers have a Gaussian energy distribution, so it is impossible to obtain a uniform energy distribution throughout the entire light sheet. This drawback can be significant for PLIF that is based on light intensity [Law, A. W. and Wang, H. (2000)]. Furthermore, the intensity of a laser beam decays as it passes through the dye solution due to absorption. Crimaldi and Koseff [Crimaldi, J. P. and Koseff, J. R. (2001)] that under appropriate experimental conditions, the local intensity of the fluoresced light, \( F \), is proportional to the local intensity of the excitation source, \( I \), and to the local concentration of the dye, \( C \), so that \( F \) is given by

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

where \( \alpha \) is a constant that can be determined empirically. In the present study, we found that this relationship was valid for dye concentrations up to 100 \( \mu \)g/liter with our experimental setup. To eliminate any variation of the local intensity of the excitation source, we employed the following procedure for the calibration of the concentration measurements. A series of 1000 dark images were taken and averaged at each pixel to measure the gray offset value distribution in the interrogation field, and this was used to remove the dark field component from each PLIF image. Variations in illumination intensity were accounted for by filling up the test section with the source dye solution and recording a series of 200 in-situ calibration images at each measurement location. The instantaneous PLIF images at each measurement location were then normalized for illumination variations using the ensemble mean of the calibration images.

### 4.3 Overview of CFD models

Turbulent flows are governed by conservative equations of mass, momentum and energy [Pope, S. B. (2000)]. In most applications of CFD models, the Reynolds equations are closed either by turbulent-viscosity models or by Reynolds-stress models. In this work, we adopt a turbulent-viscosity-based model that is widely used in industry, that is, the \( k - \varepsilon \) model [Jones, W. P. and Launder, B. E. (1972)]. All the model constants adopt their standard values [Launder, B. E. and Sharma, B. I. (1974)]. The model is generally regarded as being
easy to implement and computationally inexpensive [Pope, S. B. (2000)]. However, $k - \varepsilon$ calculations in the near-wall region can be computational intensive due to two principal difficulties: (i) sharp gradients in $k$ and $\varepsilon$, and (ii) source terms becoming very large. In order to obtain the desired accuracy with reasonable computational cost, a two-layer $k - \varepsilon$ model (see Appendix for details) has been implemented in our finite-volume Reynolds-averaged Navier-Stokes (RANS) code [Wilcox, D. C. (1998); Harvey, A. D. (2003)]. The performance of this model is evaluated by comparing predicted single-point turbulence statistics with time-averaged PIV data. While turbulent transport of an inert scalar can be successfully described by a small set of statistical moments, the same is not true for reactive scalar fields, which are strongly coupled through the chemical-source term [Fox, R. O. (2003)]. According to how they treat the sub-grid-scale concentration fluctuations in the closure for the chemical source term, CFD models for liquid-phase turbulent reacting flows can be roughly classified into four general categories: moment methods, conditional moment methods, multi-environment presumed probability density function (PDF) methods and transported PDF methods [Fox, R. O. (1996, 1998, 2003)]. In the moment methods, the sub-grid-scale fluctuations are represented by a mean-field approximation involving low-order moments. No attempt is made to represent the entire PDF that is present at the mesoscopic level. In general, these models are insufficient for predicting byproduct selectivity in chemical reactors [Chakrabarti, M. et al. (1997)]. Conditional moment methods use a presumed PDF model to account for the sub-grid-scale fluctuations of the mixture fraction. The reaction progress variables are modeled in terms of their mean values conditioned on the value of the mixture fraction. The conditional moments can be found either by a linear interpolation procedure [Baldyga, J. (1994)] or by solving a transport equation [Bilger, R. W. (1993)]. Multi-environment presumed PDF methods assume that the joint PDF of the sub-grid-scale fluctuations can be represented by a small number of environments, each of which is parameterized by its probability and its chemical composition [Fox, R. O. (1998, 2003); Wang, L. and Fox, R. O. (2004)]. In this work, we will validate both a moment model for the mean and variance of an inert scalar and a transported PDF model for the scalar PDF. Although the transported PDF model is not strictly required
to describe mixing of inert scalars, it will be needed in our future work with reacting scalars.

4.3.1 Scalar moment transport model

Turbulent mixing encountered in chemical process equipment is almost always inhomogeneous. The most frequently employed inert scalar statistics are the scalar mean and the scalar variance, where \( \phi \) represents an inert scalar and is its fluctuation. Denoting the Reynolds average velocity and the fluctuation velocity as \( \langle U \rangle \) and \( u' \), respectively, the transport equations of an inert scalar mean and variance are \[ \frac{\partial \langle \phi \rangle}{\partial t} + (U_j) \frac{\partial \langle \phi \rangle}{\partial x_j} = \Gamma \nabla^2 \langle \phi \rangle - \frac{\partial \langle u'_j \phi \rangle}{\partial x_j} \] (4.7)

and

\[ \frac{\partial \langle \phi'^2 \rangle}{\partial t} + (U_j) \frac{\partial \langle \phi'^2 \rangle}{\partial x_j} = \Gamma \nabla^2 \langle \phi'^2 \rangle - \frac{\partial \langle u'_j \phi'^2 \rangle}{\partial x_j} + P_{\phi} - \varepsilon_{\phi}, \] (4.8)

where \( \Gamma \) is the molecular diffusivity and repeated indices imply summation. The scalar-variance-production term \( P_{\phi} \) is defined by

\[ P_{\phi} \equiv -2\langle u'_j \phi \rangle \frac{\partial \langle \phi \rangle}{\partial x_j}. \] (4.9)

Thus, Eqs. 4.7 and 4.8 have three unclosed terms: the scalar flux \( \langle u'_j \phi \rangle \), the scalar-variance flux \( \langle u'_j \phi'^2 \rangle \), and the scalar dissipation rate \( \varepsilon_{\phi} \), which is defined by

\[ \varepsilon_{\phi} \equiv 2\Gamma \langle \frac{\partial \phi'}{\partial x_i} \frac{\partial \phi'}{\partial x_i} \rangle. \] (4.10)

To be consistent with the \( k - \varepsilon \) model used to close the Reynolds stresses, the scalar and scalar-variance fluxes in this study are closed by invoking a gradient-diffusion model \[ \text{[ Taylor, G. I. (1921)]}, \] resulting in

\[ \langle u'_j \phi \rangle = -\Gamma \frac{\partial \langle \phi \rangle}{\partial x_j} \] (4.11)

and

\[ \langle u'_j \phi'^2 \rangle = -\Gamma \frac{\partial \langle \phi'^2 \rangle}{\partial x_j}, \] (4.12)
with $\Gamma_T = \nu_T/Sc_T$. $\nu_T$ is the eddy viscosity and $Sc_T$ is the turbulent Schmidt number that equals 0.7 in this study unless specified elsewhere. The scalar dissipation rate is related to the turbulent frequency $\varepsilon/k$ by the equation [Spalding, D. B. (1971)]

$$\varepsilon_\phi = C_\phi \frac{\varepsilon}{k} \langle \phi'^2 \rangle$$

(4.13)

with the empirical constant $C_\phi$ taken to be 2.0 throughout this work unless specified otherwise.

The RANS code solves Eqs. 4.7 and 4.8 with closures Eqs. 4.11, 4.12 and 4.13, the accuracy of which is validated by comparing the simulated scalar mean and variance fields with PLIF data.

### 4.3.2 Transported PDF model

Transported PDF methods simulate a transport equation for the joint PDF of the sub-grid-scale fluctuations of all concentrations [Pope, S. B. (1985)]. They are the most computationally intensive of the PDF models. However, they offer the distinct advantage that chemical source terms appear in closed form and require no modeling. Therefore, transported PDF methods are powerful methods for treating the complex (finite-rate) chemistry that is often associated with minor species formation. With the development of detailed chemical kinetics based on molecular-level simulations [Tirtowidjo, M. (1997)], transported PDF methods are an attractive macroscopic simulation technique for probing turbulence-chemistry interactions. Moreover, transported PDF simulations can be employed to validate the assumptions made in simpler closures, and to suggest alternative closures for particular kinetic schemes [Wang, L. and Fox, R. O. (2004)].

Taking the molecular transport coefficients for all species to be equal, the transport equation of the joint scalar PDF denoted by $f_\phi$ is [Pope, S. B. (1985)]

$$\frac{\partial f_\phi}{\partial t} + \frac{\partial}{\partial x_j} \left( \langle U_j \rangle f_\phi \right) + \frac{\partial}{\partial x_j} \left[ \langle u'_j | \psi \rangle f_\phi \right] = -\frac{\partial}{\partial \psi_\alpha} \left[ \langle \Gamma \nabla^2 \phi'_\alpha | \psi \rangle f_\phi \right] - \frac{\partial}{\partial \psi_\alpha} \left\{ [\Gamma \nabla^2 \phi_\alpha + S_\alpha (\psi)] f_\phi \right\}$$

(4.14)

where $\phi$ and $\psi$ represent the composition vector and the composition field, respectively. $S_\alpha (\psi)$ is the chemical source term of species $\alpha$. $\langle \cdot | \psi \rangle$ denotes the Reynolds average conditioned on
The scalar-flux term $\langle u'_j \phi' \rangle$ can be closed by the gradient-diffusion model [ Pope, S. B. (1985)] as

$$\langle u'_j | \psi \rangle f_\phi = -\Gamma_T \frac{\partial f_\phi}{\partial x_j} \quad (4.15)$$

The micromixing term $\langle \nabla^2 \phi_\alpha | \psi \rangle$ may be represented by a micromixing model [ Pope, S. B. (1985)]. The interaction-by-exchange-with-the-mean (IEM) model [ Villermaux, J. and Devillon, J. C. (1972)] is used in this study. For our case, that of an inert scalar, only one composition variable $\phi$ is needed, and the chemical source term $S_\alpha (\psi)$ is null. However, we retain $S_\alpha (\psi)$ for future reference. In our Lagrangian PDF code [ Raman, V. et al. (2001, 2003, 2004)], Eq. 4.14 is expressed in terms of stochastic differential equations for notional particles. The position and composition of a notional particle are given by $X^*$ and $\phi^*$, respectively, the particles are governed by equations [ Fox, R. O. (2003)]

$$dX^* = [\langle U \rangle (X^*, t) + \nabla \Gamma_T (X^*, t)] dt + \sqrt{2}\Gamma_T (X^*, t)dW (t) \quad (4.16)$$

and

$$d\phi^* = \frac{C_\phi \varepsilon}{2k} (\langle \phi \rangle (X^*, t) - \phi^*) dt + S (\phi^*) dt, \quad (4.17)$$

where $dW (t)$ is a multi-variate Wiener process, and $S (\phi^*)$ is the chemical source term. $\langle U \rangle (X^*, t)$ and $\langle \phi \rangle (X^*, t)$ are the mean velocity and the estimated scalar mean at the particle location. The scalar mean and variance are estimated from the compositions of the particles. In the non-reacting flow investigated in this study, $S (\phi^*)$ is null. The turbulence statistics appearing in Eqs. 4.16 and 4.17 are taken from the RANS code. Details on the coupling between the flow field and the particle fields in the Lagrangian PDF code can be found elsewhere [ Fox, R. O. (2003)]. The turbulent transport closure defined by Eq. 4.15 can be validated by agreement of the scalar mean and variance predicted by the PDF code with PLIF data.

### 4.4 Simulation conditions

The performance of the confined planar-jet reactor was simulated using the RANS and PDF models described above. Since no chemical reactions occur, the scalar is inert. The
distribution of the experimental data was found to be slightly asymmetric with respect to
the centerline due to the jet growing slightly towards one of the walls of the test section. To
provide inlet boundary conditions for the simulations, the experimental data of mean velocity
and turbulent kinetic energy at the entrance plane of the jet were made symmetric with respect
to $y/d = 0$ by averaging and then interpolated linearly between data points. The PIV data
for the mean velocity and turbulent kinetic energy at the jet exit and the corresponding inlet
boundary conditions for the RANS code are shown in Fig. 4.4. In this study, the PIV data
for the turbulent kinetic energy were derived from the streamwise and transverse velocity
fluctuations, $u'$, $v'$, through Eq. 4.18

$$k = \frac{\langle u'^2 \rangle + \langle v'^2 \rangle}{2}. \quad (4.18)$$

More details can be found in the discussion of the CFD predictions for turbulent kinetic energy.
The inlet values of dissipation rate were estimated by

$$\varepsilon = A \frac{k^{3/2}}{l_m}, \quad (4.19)$$

where $l_m$ is a characteristic length scale. The length scales $l_m$ were set equal to 0.0035 m for
the inner jet and 0.002 m for the outer jets after trial and error investigation that produced a
turbulent kinetic energy at $x/d = 0.5$, which agreed with the PIV measurements. Note that
these values are smaller than the jet widths, as expected, adopting the value suggested by
Antonia, et al. [Antonia, R. A. et al. (1980)]. By comparing Eqs. 4.2 and 4.19, it is known
that $l_m/l = (3/2)^{3/2}$.

Because the flow statistics at the centerline of the channel are only slightly affected by the
front and back walls, all simulations were performed on a two-dimensional grid by neglect-
ing gradients in the spanwise direction. An $81 \times 121$ Cartesian grid was generated for the
computational domain. The grid has non-uniform cells with denser grid points near stream
interfaces and walls to capture more details associated with sharp gradients. The grid was
chosen fine enough to ensure a grid-independent solution. However, its resolution is lower than
the spatial resolution in the PIV/PLIF measurements. Thus, the inlet boundary conditions
shown in Fig. 4.4 effectively cut off the high gradients measured in the shear layers due to the
difference in resolution. This was found to have no impact on the predicted flow statistics. A fixed time step that equals 0.005 s was used in the transported PDF code.

4.5 Results and discussion

A typical velocity field from PIV measurements is shown in Fig. jet instant velocity. To aid in the visualization of turbulent structures, a convective velocity of 0.75 m/s has been subtracted from each vector in this figure. As a reminder, the coordinate system used in Fig. 4.5 is such that the tips of the splitter plates are located at $x = 0$ and $y = \pm 10$, and the centerline between two side walls is along $y = 0$. Similarly, Fig. 4.6 shows an instantaneous concentration field. The contour levels represent mixture fraction, which is the concentration normalized by the concentration of the dye in the inner feed stream $C_0$. In Figs. 4.7-4.12, $\langle U \rangle$ and $\langle V \rangle$ denote the streamwise and transverse mean velocity components, respectively.

4.5.1 Experimentally measured mean velocities and Reynolds stresses

The ensemble averaged streamwise velocity profiles for six representative downstream locations are shown in Fig. 4.7. The mean velocity components are normalized by $U_c = 0.5$ m/s, which is the difference between the inlet free-stream velocities of the center and side streams. The $y$-axis has been normalized by the inlet jet width, $d = 20$ mm. This normalization of the transverse coordinate is used throughout the presented work. As Fig. 4.7 shows, at the inlet level ($x/d = 0$), the velocity profile is fairly symmetric with two mixing layers growing from the tips of the splitter plates, and this symmetry is maintained in each of the downstream velocity profiles. However, these mixing layers are short lived, and they quickly grow together as the flow convects downstream. Indeed, the potential core in the center jet has completely disappeared at $x/d = 4.5$. As the flow progresses downstream, the potential cores in the outer streams also disappear, and the flow continues its development towards channel flow. Reynolds stress profiles, normalized by $U_c^2$, for the same six locations are shown in Figs. 4.8-4.10. At all six measurement locations, $\langle u'v' \rangle$ (Fig. 4.8) is approximately twice as large as the $\langle v'v' \rangle$ (Fig. 4.9), and both are approximately symmetric about the jet centerline. The stresses are
highest just downstream of the tip of the splitter plates, just after the incoming boundary layers have merged to form the initial mixing layers, and the stresses decay as the mixing layers grow. After the two mixing layers have grown together, the peak values remain almost constant while the valley between the two peaks fills up. However, the two peaks in the Reynolds stress profiles remain distinct even at the farthest downstream measurement location, $x/d = 15$. Also note that because of the boundary layers developing along the sidewalls of the test section, the values of the Reynolds normal stresses increase as the observation point moves towards the wall. The Reynolds shear stress, $\langle u'v' \rangle$, shown in Fig. 4.10, is asymmetric around the centerline, positive where the mean flow shear stress is negative, and negative where the mean flow shear stress is positive. Along the centerline of the reactor, which is a plane of symmetry, the Reynolds shear stress is zero. Due to the turbulent boundary layers, the values of shear stress in the regions near walls are nonzero. Moreover, the boundary layers developing along both sides of the splitter plate cause the sign change of Reynolds shear stress in the mixing layers at locations near the tips (such as $x/d = 0$ and $x/d = 1$). The peak Reynolds shear stress is highest just downstream of the splitter plate tips, and decreases with increasing downstream distances.

4.5.2 CFD predictions for mean velocity

The mean streamwise velocity predicted by the RANS code with the two-layer $k - \varepsilon$ model is compared with PIV measurements in Fig. 4.11. Comparisons are shown for downstream locations $x/d = 4.5, 7.5$ and 15. The comparisons are good, although the spreading rate of the jet is slightly lower than that measured by PIV, and this characteristic becomes more pronounced as the downstream distance increases. This smaller spreading rate in the RANS calculations is most likely due to a lower diffusion rate of the turbulent kinetic energy, as discussed in the next section.
4.5.3 CFD predictions for turbulent kinetic energy

The PIV velocity fields are 2-D measurements, containing only streamwise and transverse velocity components. In order to obtain the turbulent kinetic energy from the 2-D PIV measurements, the spanwise (that is, out-of-plane) velocity fluctuation must be estimated based on the measured \( x \)- and \( y \)-fluctuations. The spanwise fluctuation was assumed to be equal in magnitude to the cross-stream fluctuation (Eq. 4.18). This assumption is expected to be valid near the inlet since the flow there resembles a pair of mixing layers, and turbulence in mixing layers has this characteristic [Pope, S. B. (2000)]. Fully developed turbulent channel flow also has this characteristic, so the assumption of comparable transverse and spanwise velocity fluctuations is expected to yield reasonable results. Also recall that PIV measures a filtered velocity field due to the measurement volume being larger than the Kolmogorov scale. However, since the larger energy containing eddies are fully resolved, errors from the filtered velocity field should not significantly affect the measured turbulent kinetic energy. Turbulent kinetic energy predicted by the RANS code with a two-layer \( k - \varepsilon \) model is compared with PIV measurements in Fig. 4.12 for downstream locations \( x/d = 1, 4.5, 7.5 \) and 15. The RANS code predicts a slightly higher turbulent kinetic energy than that measured by PIV, but in general, the agreement between the two is excellent at all downstream locations.

4.5.4 Experimentally measured scalar mean and scalar variance

Figure 4.13 shows the transverse profiles of the ensemble-averaged mixture fraction across the channel at four downstream locations: \( x/d = 1, 4.5, 7.5, \) and 15. The mean mixture fraction at \( x/d = 1 \) is very nearly a top-hat function, with all of the dye located in the center stream. However, as the downstream distance increases, the mean mixture fraction in the center stream decreases and the mean mixture fractions in the outer streams increase because of mass transport of the dye due to both turbulent mixing and molecular diffusion. As in the mean velocity profiles, the plots are slightly asymmetric due to the jet growing slightly towards one of the walls of the test section. The mixture-fraction variance is shown in Fig. 4.14. Note that as the mixing layers develop and begin to grow into one another, the peaks of the variance
move towards the walls. Also, the experimentally measured peak value of the variance initially increases with increasing distance from the tip of the splitter plate, but after \( x/d = 7.5 \), it begins to decrease. Since a fully mixed fluid would have a mixture-fraction variance of zero, this behavior after \( x/d = 7.5 \) is expected. Note also that just as for the Reynolds stresses, two distinct peaks remain in the plots of mixture-fraction variance even at the farthest downstream measurement location.

### 4.5.5 CFD predictions for mean mixture fraction

The mean mixture-fraction fields predicted by the RANS and transported PDF codes are compared with the experimental results at various downstream locations in Fig. 4.13, and they agree quite well with the PLIF data. The results indicate that the gradient-diffusion model (Eqs. 4.11 and 4.15) accurately predicts the scalar flux for this flow geometry. The lower spreading rate of the mean mixture fraction in the simulations suggest that the turbulent Schmidt number required in Eqs. 4.11 and 4.15 is slightly less than the typical value of 0.7. By adopting \( Sc_T = 0.5 \) the agreement between the CFD simulations and PILF data improves as shown in Fig. 4.13.

### 4.5.6 CFD predictions for mixture-fraction variance

The profiles of the mixture-fraction variance as predicted by the RANS and the transported PDF codes are compared with experimental data at various downstream locations in Fig. 4.14. The RANS code and the PDF code yield similar results except at \( x/d = 1 \), where the PDF code predicts a higher variance than the RANS code. In theory, grid-independent solutions for the mean and variance should be exactly the same for both codes. Thus, the higher values observed near the inlet with the PDF code are an indication that a much smaller time step is required in that region where turbulent mixing is slow. In general, both codes predict a higher mixture-fraction variance in the shear layers, where the variance peaks in value, than was measured experimentally. As seen in Fig. 4.14, the agreement cannot be improved by reducing the turbulent Schmidt number to 0.5. Instead, due to the higher turbulent diffusivity, the
mixture-fraction variance at each streamwise position reaches a maximum value that is even higher than that given by $Sc_T = 0.7$ at a cross-section position that is further from the centerline. If the scalar dissipation term, $\varepsilon_{\phi}$, is set to zero (this is equivalent to turning off the micromixing model in the PDF code), the analytical solution to Eq. scalar variance becomes

$$\langle \phi'^2 \rangle = (1 - \langle \phi \rangle) \langle \phi \rangle.$$  \hspace{1cm} (4.20)

The numerical simulation results show (Fig. 4.15) that the PDF code and the RANS code predict this analytical solution accurately. Thus, the scalar-variance flux (Eq. 4.12) was correctly implemented in the RANS code and the grid density at downstream locations was fine enough to ensure that both codes predict consistent results. Figure 4.13 shows that the mixture-fraction mean (and thus the production of mixture-fraction variance defined by Eq. 4.9) is accurately predicted. Therefore, the discrepancies of the model predictions and experimental results observed in Fig. 4.14 indicate either inaccuracy in the closure for the scalar dissipation rate (Eq. 4.13), which is determined by the mixing timescale $k/\varepsilon$, or experimental limitations (due to finite resolution of PLIF at high $Sc$), or both. Near walls, $k \sim O(y^2)$ and $\varepsilon \sim O(1)$ as $y \rightarrow 0$. This results in a very small mixing timescale and thus a scalar dissipation rate that is so large that the mixture-fraction variance is forced to zero in the near-wall regions. Therefore, in the near-wall regions the predicted mixture-fraction variance shows insufficient diffusion. In fact, Eq. 4.13 is actually a model for the scalar spectral energy transfer rate through the inertial-convective sub-range in homogeneous turbulence, and thus cannot be expected to be accurate in the near-wall regions. For inhomogeneous turbulence, it can be expected that $\varepsilon_{\phi}$ depends on the degree of turbulent anisotropy and the mean shear rate. Near the reactor entrance ($x/d = 1$) where the turbulence is neither fully developed nor isotropic, this closure cannot represent the entire energy transfer rate from large to small scales. Nevertheless, this closure is valid in fully developed turbulence when the dissipation scales are in spectral equilibrium with the energy-containing scales. With the development of the flow, the performance of the model improves gradually resulting in better agreement of the predicted variance and PLIF data (Figs. 4.14(b) and (c)). The insufficient diffusion at near-wall regions is overshadowed by the more uniform scalar concentration indicated by the PLIF data at those downstream
locations. At $x/d = 15$, where the non-zero near-wall mixture-fraction variance shown by PLIF data indicates that the scalar concentration is not uniform near walls, the underestimation by the model is significant. Therefore the performance of the model does not improve in the near-wall region at downstream locations (Fig. 4.14(d)). Further work will be required to improve the closure for the scalar dissipation rate for this region. Another factor that must be considered is that the PLIF measurements underestimate the scalar variance due to the spatial resolution being insufficient to resolve the smallest mixing scales. By definition, the scalar variance can be found directly from the scalar energy spectrum $E_\phi(\kappa, t)$ by integrating over the space of the wavenumber $\kappa$:

$$\langle \phi'^2 \rangle = \int_0^\infty E_\phi(\kappa) \, d\kappa. \quad (4.21)$$

The spatial resolution of the PLIF measurements is limited by the thickness of the laser sheet. The laser-sheet thickness represented by $L^*$ ($L^* = 5 \times 10^{-4}$ m in this study) determines a cut-off wavenumber

$$\kappa^* = \frac{1}{L^*}. \quad (4.22)$$

Consequently, the scalar variance measured by PLIF decreases to

$$\langle \phi'^2 \rangle^* = \int_0^{\kappa^*} E_\phi(\kappa) \, d\kappa. \quad (4.23)$$

Using the model scalar spectrum [Fox, R. O. (2003)], Table 4.1 shows the percentage of scalar variance missed by the PLIF measurements, defined as $1 - \langle \phi'^2 \rangle^*/\langle \phi'^2 \rangle$, at each downstream location. The missing variance decreases from 12.68% at $x/d = 1$, to about 5.98% at the furthest downstream distance where the Kolmogorov scale of the turbulence is largest, and thus less of the scalar energy spectrum is cut-off. This may account for some of the discrepancies between the experimental results and the simulations. Nevertheless, even after accounting for the PLIF resolution, Fig. 4.14 indicates that the missing mixture-fraction variance is larger than expected. For example, the maximum variance predicted and measured at $x/d = 4.5$ are 0.048 and 0.035, respectively. Thus, the scalar variance missed by the PLIF measurement is 27%, rather than 9.36%, if the exact scalar variance is 0.048. We are therefore motivated to
investigate the effect of $C_\phi$ on the mixture-fraction variance prediction. From direct numerical simulations [Yeung, P. K. et al. (2002)], it is known that $C_\phi$ can vary in the range of 2.0-2.5 for inert scalar mixing in stationary turbulence. Moreover, at large Reynolds numbers, $C_\phi$ will approach a Schmidt number-independent limiting value of 2.43 [Fox, R. O. (2003)], which is the ratio of the Kolmogorov and the Obukhov-Corrsion constants. By taking $C_\phi = 2.5$, the predicted mixture-fraction variance (Fig. 4.16) matches the PLIF data much better at all downstream locations except for $x/d = 1$. This result is quite interesting because it is usually assumed that $C_\phi$ in liquid-phase flows should be smaller than in gas-phase flows due to the larger Schmidt number effects [Fox, R. O. (2003)]. Under these flow conditions, however, it appears that the Reynolds number is high enough to make Schmidt-number effects negligible.

4.5.7 Dissipation Rate

One of the primary advantages of PIV over pointwise velocity measurement techniques is the capability of measuring vorticity and rate-of-strain fields [Adrian, R. J. (1991)]. This enables us to evaluate the dissipation rate in the flow field. However, in 2D-PIV measurements, the out-of-plane component of velocity is not measured. Therefore only four terms of velocity gradient, $\partial \bar{U}/\partial x$, $\partial \bar{U}/\partial y$, $\partial \bar{V}/\partial x$ and $\partial \bar{V}/\partial y$, can be computed directly. Another term, $\partial \bar{W}/\partial z$, may also be determined by using the incompressible continuity equation. Here, $\bar{U}$, $\bar{V}$ and $\bar{W}$ are the $x$, $y$ and $z$ components of filtered velocity. Since the other four terms are still missing, some researchers have computed only the so-called 2-D dissipation rate [Saarenrinne, P. and Piirto, M. (2000); Tsurikov, M. S. and Clemens, N. T. (2002)]. To estimate the turbulence energy dissipation rate using 2D-PIV data, Sharp et al. [Sharp, K. V. et al. (1998)] assumed that the unknown terms were statistically isotropic and thus derivable from the known ones. For a complicated 3-D flow in a stirred vessel, Sheng et al. [Sheng, J. et al. (2000)] applied a similar assumption that approximated the dissipation rate by multiplying the sum of the known components of Eq. 4.3 by a factor of $9/5$. In the present study, two methods were used to estimate the dissipation rate: 1) Sheng’s method; 2) assuming $w = v$ and $\partial / \partial z = \partial / \partial y$ to obtain nine terms. Because of the nature of the flow (i.e., shear layers and wall-bounded
flow), we expect that the second method most closely corresponds to our conditions. The results of the estimations at five downstream locations can be seen in Fig. 4.17. Notice that the dissipation rates calculated using Shengs method are smaller than those from the second method. However, both methods show that the distribution of the dissipation rate in the reactor is highly inhomogeneous. These graphs also indicate the general trend that the profile of dissipation rate becomes more uniform in the $y$-direction as the observation location moves downstream, and the peak values in dissipation decay very quickly at positions nearer the inlet. In comparing with the distributions of energy dissipation rate and turbulent kinetic energy, it is also seen that regions of high values of these quantities coincide, implying a strong correlation between these two properties. The dissipation rate predicted by the $k-\varepsilon$ model is compared with that estimated from PIV measurements in Fig. 4.18. The predicted dissipation rate agrees better with that calculated using nine terms (that is, method 2) than with that found using Shengs method.

4.6 Conclusions

In the present study, velocity and concentration measurements were made for turbulent mixing in a confined planar-jet reactor using PIV and PLIF techniques. The measurements were carried out at six downstream locations with a Reynolds number of 50,000 based on the distance between sidewalls. Statistics of mean velocity, Reynolds stresses, turbulent kinetic energy, mixture-fraction mean and mixture-fraction variance were calculated. It was observed that two mixing layers grow symmetrically about the centerline of the reactor from the tips of the splitter plates, but these merged together very quickly, and the flow continued its development towards channel flow. It was also noticed that the values of turbulent kinetic energy and Reynolds stress are nonzero in regions near the walls, which indicates that unlike free jets, the boundary layer developing along sidewalls in the confined jet plays a significant role in the mixing, especially after the potential cores in the outer streams disappear. The planar velocity data from PIV measurements were also used for estimating the turbulence dissipation rate by computing the Reynolds-averaged SGS dissipation rate. Because the out of
plane component of velocity fluctuations is unachievable in the present study, some terms of the velocity gradient were not measured. Therefore, two methods were tested to approximate the missing terms using known ones. The results of the dissipation rate from the two methods were compared and showed that the dissipation rate decayed rapidly close to the tips of the splitter plates. It was noted that the distribution of the dissipation rate was symmetric around the centerline and inhomogeneous in the reactor. As expected, the distribution of the dissipation rate also suggested strong correlation with the turbulent kinetic energy. CFD models were validated against the experiments by comparing computed mean velocity and turbulence fields, and the mixture-fraction mean and variance with PIV/PLIF data. The Reynolds stresses were closed by a two-layer $k-\varepsilon$ model that predicted the turbulent kinetic energy and dissipation rate successfully with reasonable computational cost even in near-wall regions. The scalar fluxes were closed by gradient-diffusion models. The accurately computed mixture-fraction mean indicates that the scalar flux was well represented by the gradient-diffusion model. The analytical solution to the transport equation of mixture-fraction variance with no dissipation was predicted exactly by both scalar transport models, illustrating that the solutions were grid independent. The scalar dissipation rate was over-predicted by the equilibrium closure in near-wall regions, suggesting that this quantity might be better approximated by solving its transport equation. Elsewhere, $\varepsilon_\phi$ was underpredicted by the equilibrium model with $C_\phi = 2$, but well predicted with $C_\phi = 2.5$. In general, the overall agreement between the CFD models and the experimental data is excellent for this rather complex flow.

Acknowledgements

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graduate researchers.
Table 4.1  Estimated Error of PLIF Variance Measurements

<table>
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<th>$x/d$</th>
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<th>4.5</th>
<th>7.5</th>
<th>12</th>
<th>15</th>
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</thead>
<tbody>
<tr>
<td>Error(%)</td>
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<td>9.36</td>
<td>8.01</td>
<td>7.75</td>
<td>5.98</td>
</tr>
</tbody>
</table>
Figure 4.1 Flow facility used in the PIV and PLIF experiments.

Figure 4.2 Confined planar-jet test section.
Figure 4.3 Top view of the optical setup for the PIV and PLIF experiments.

Figure 4.4 (a) Mean streamwise velocity and (b) turbulent kinetic energy at the entrance plane of the confined planar jet. —, Simulations; •, PIV data.
Figure 4.5  Sample instantaneous velocity field.

Figure 4.6  Sample instantaneous concentration field.
Figure 4.7  Normalized mean streamwise velocity at various downstream locations as measured by PIV. $\times$, $x/d = 0$; ■, $x/d = 1$; $\Delta$, $x/d = 4.5$; ▼, $x/d = 7.5$; ◆, $x/d = 12$; ○, $x/d = 15$.

Figure 4.8  Streamwise Reynolds normal stress at various downstream locations as measured by PIV. $\times$, $x/d = 0$; ■, $x/d = 1$; $\Delta$, $x/d = 4.5$; ▼, $x/d = 7.5$; ◆, $x/d = 12$; ○, $x/d = 15$. 
Figure 4.9  Cross-stream Reynolds normal stress at various downstream locations as measured by PIV. ×, $x/d = 0$; ■, $x/d = 1$; ∆, $x/d = 4.5$; ▼, $x/d = 7.5$; ♦, $x/d = 12$; ◦, $x/d = 15$.

Figure 4.10  Reynolds shear stress at various downstream locations as measured by PIV. ×, $x/d = 0$; ■, $x/d = 1$; ∆, $x/d = 4.5$; ▼, $x/d = 7.5$; ♦, $x/d = 12$; ◦, $x/d = 15$.
Figure 4.11 Comparison of the mean streamwise velocity profiles measured by PIV (symbols) and calculated from the RANS code (solid line) for (a) $x/d = 1$, (b) $x/d = 4.5$, (c) $x/d = 7.5$, (d) $x/d = 15$. 
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Figure 4.13 Comparison of mean mixture fraction profiles for (a) $x/d = 1$, (b) $x/d = 4.5$, (c) $x/d = 7.5$, (d) $x/d = 15$. ●, PLIF; —, RANS, $Sc_T = 0.7$; - - -, RANS, $Sc_T = 0.5$; ▲, PDF, $Sc_T = 0.7$; △, PDF, $Sc_T = 0.5$. 
Figure 4.14  Comparison of mixture-fraction variance profiles (a) $x/d = 1$, (b) $x/d = 4.5$, (c) $x/d = 7.5$, (d) $x/d = 15$. •, PLIF; —, RANS, $Sc_T = 0.7$; - - -, RANS, $Sc_T = 0.5$; ▲, PDF, $Sc_T = 0.7$; △, PDF, $Sc_T = 0.5$. 
Figure 4.15  Comparison of analytical solution to mixture-fraction variance and calculated mixture-fraction variance. - - -, Analytical solution; ◯, RNAS; △, PDF at $x/d = 7.5$; —, analytical solution; •, RANS; ▲, PDF at $x/d = 15$. 
Figure 4.16 Effect of $C_\phi$ ($C_\phi = 2.5$) on the prediction of mixture-fraction variance profiles at (a) $x/d = 1$, (b) $x/d = 4.5$, (c) $x/d = 7.5$, (d) $x/d = 15$. •, PLIF; —, RANS, $Sc_T = 0.7$; -, -, -, RANS, $Sc_T = 0.5$; ▲, PDF, $Sc_T = 0.7$; Δ, PDF, $Sc_T = 0.5$. 
Figure 4.17 Turbulence dissipation rate at various downstream locations measured by PIV: (a) estimated by Sheng’s method; (b) estimated with nine terms. ■, $x/d = 1$; △, $x/d = 4.5$; ▼, $x/d = 7.5$; ◆, $x/d = 12$; ○, $x/d = 15$. 
Figure 4.18 Comparison of dissipation profiles measured Sheng’s method (●), method 2 (○), and calculated from the RANS code (—) for (a) $x/d = 1$, (b) $x/d = 4.5$, (c) $x/d = 7.5$, (d) $x/d = 15$. 
CHAPTER 5. TURBULENT MIXING IN A CONFINED RECTANGULAR WAKE

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Abstract

Liquid-phase turbulent transport in a confined rectangular wake was investigated for a Reynolds number of 37,500 based on bulk velocity and the hydraulic diameter of the test section and a Schmidt number of 1,250 using particle image velocimetry (PIV) and planar laser-induced fluorescence (PLIF). The velocity and concentration field data were analyzed for flow statistics such as the mean velocity, Reynolds stresses, turbulent kinetic energy, turbulent dissipation rate, mixture-fraction mean, mixture-fraction variance and one-point composition PDF. Computational fluid dynamics (CFD) models, including a two-layer $k$–$\epsilon$ turbulence model, a scalar gradient-diffusion model and a scalar dissipation rate model were validated against PIV and PLIF data collected at six downstream locations. Low-Reynolds-number effects on turbulent transport were taken into consideration through the mechanical-to-scalar time-scale ratio. The experimental and computational results were found to be in satisfactory agreement.

5.1 Introduction

Turbulent mixing is crucial in processes in the chemical process industry that require rapid mixing and transport of species, momentum and energy. Thus, it is imperative to have a detailed understanding of turbulent mixing for the design and optimization of chemical reac-
tors. Although computational fluid dynamics (CFD) models have great potential for studying turbulent flows and designing reactors, these models need to be validated against experimental data to avoid costly design mistakes on scale up. Therefore, experimental studies of mixing in turbulent shear flows (e.g., wakes, jets and mixing layers) are of great importance not only in advancing turbulence theory, but also in the development and validation of CFD models. The primary objective of the work presented here is to obtain detailed experimental data for both the velocity field and concentration field in a liquid-phase turbulent confined, rectangular wake and to use these data to validate CFD models.

A wake is formed when a uniform stream flows over an obstacle, resulting in the formation of a region downstream with a velocity deficit. The flow in a wake may be divided into three regions: a near-wake, an intermediate wake and a far wake [Kiya, M. and Matsumura, M. (1985); Tritton, D. J. (1988)], although it is difficult to quantify the boundaries between these regions since they depend on many parameters [Mi, J. et al. (2004)]. The near wake is a critical region as it determines the dominant instability in the flow [Triantafyllou, G. et al. (1986); Unal, M. and Rockwell, D. (1988); Ma, X. et al. (2000)]. Due to the difficulty of obtaining accurate experimental data in the near wake, only a few measurements have been reported for this region. Cantwell and Coles [Cantwell, B. and Coles, D. (1983)] investigated transport processes in the near wake of a circular cylinder using an X-array of hot wire probes for a Reynolds number of 140,000. Ong and Wallace [Ong, L. and Wallace, J. (1996)] also conducted hot-wire measurements in the very near wake of a circular cylinder at a Reynolds number of 3900. They noticed that measurements of the streamwise velocity component were inaccurate for such flow fields and the very near wake region was pre-dominantly 2-dimensional. Using laser Doppler velocimetry (LDV), Nakagawa et al. [Nakagawa, S. et al. (1999)] measured the unsteady turbulent near wake of a rectangular cylinder in channel flow and found that the turbulent intensities on the centerline of the channel reached their maxima near the rear stagnation point of the recirculation region. More recently, in their numerical study on the dynamics of a turbulent near wake behind a circular cylinder, Ma et al. [Ma, X. et al. (2000)] argued that the very near wake (characterized by downstream distances of less than three
diameters) was dominated by shear layer dynamics and was very sensitive to disturbances and cylinder aspect ratio, whereas farther downstream the flow was dominated by the vortex shedding dynamics and was not as sensitive to the aforementioned factors.

As the wake evolves, the profile of the mean streamwise velocity becomes asymptotically self-similar in the far wake [Wygnanski, I. et al. (1986)]. Self-similarity essentially indicates that the wake has reached a dynamical equilibrium. The local centerline velocity defect, $U_s(x)$, is defined as

$$U_s(x) \equiv U_0 - \langle U(x, 0, 0) \rangle,$$  \hspace{1cm} (5.1)

where $U_0$ is the free-stream velocity. The half-width, $y_{1/2}(x)$, is defined such that

$$\langle U(x, \pm y_{1/2}(x), 0) \rangle = U_0 - \frac{1}{2} U_s(x).$$  \hspace{1cm} (5.2)

Then with $\xi \equiv y/y_{1/2}(x)$ being the scaled cross-stream variable, the self-similar velocity defect $f(\xi)$ in a plane wake is defined by

$$f(\xi) = \frac{[U_0 - \langle U(x, y, 0) \rangle]}{U_s(x)}.$$  \hspace{1cm} (5.3)

However, it has been found that the wakes from the different generators do not reach the same self-similar state [Pope, S. B. (2000)]. Instead, the self-similar state retains information about how the wake was generated [George, W. K. (1989)].

The magnitude of the turbulent kinetic energy determines the quality and the efficiency of many industrial mixing processes. Therefore, the local turbulent dissipation rate, $\varepsilon$, is one of the fundamental parameters for the process designer. With the data collected from PIV measurements, it is possible to study the distribution of the dissipation rate over a large flow region. Based on the classical turbulence theory [Kolmogorov, A.N. (1941)], the characteristic scale of the smallest turbulent motions is the Kolmogorov scale, which is defined by

$$\eta = (\nu^3 / \varepsilon)^{1/4}$$

where $\nu$ is the molecular kinematic viscosity. However, Tennekes and Lumley [Tennekes, H. and Lumley, J. L. (1972)] suggested that the spatial resolution of the velocity measurement could be as large as $5\eta$ and still resolve the turbulent dissipation rate. Tsurikov
and Clemens [Tsurikov, M. S. and Clemens, N. T. (2002)] also argued that kinetic energy
dissipative structures have thickness ranging from approximately $1\eta$ to $10\eta$ and a mean thick-
ness of $4\eta$. In terms of the gradients of the instantaneous velocity, the turbulent dissipation
rate can be evaluated by Eq. 5.4, provided that such gradients are measured with sufficient
resolution [Sharp, K. V. and Adrian, R. J. (2001)]:

$$
\varepsilon = \nu \left\{ 2 \left[ \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial v}{\partial y} \right)^2 + \left( \frac{\partial w}{\partial z} \right)^2 \right] \right. \\
\quad + \left. \left( \frac{\partial v}{\partial x} \right)^2 + \left( \frac{\partial w}{\partial y} \right)^2 + \left( \frac{\partial w}{\partial z} \right)^2 + \left( \frac{\partial u}{\partial y} \right)^2 + \left( \frac{\partial u}{\partial z} \right)^2 + \left( \frac{\partial v}{\partial z} \right)^2 \right) \\
\quad + 2 \left( \frac{\partial u}{\partial y} \frac{\partial v}{\partial x} + \frac{\partial u}{\partial z} \frac{\partial w}{\partial x} + \frac{\partial w}{\partial y} \frac{\partial v}{\partial z} \right) \right\} 
$$

(5.4)

where $u, v$ and $w$ are the three components of instantaneous velocity and $\nu$ is the kinematic viscosity. The overline denotes an ensemble-averaged quantity.

The study of turbulent mixing has benefited greatly from developments in laser-based flow
diagnostic techniques. In the present study, velocity and concentration fields have been mea-
sured using two such techniques, particle image velocimetry (PIV) and planar laser induced
fluorescence (PLIF). As non-intrusive techniques, both PIV and PLIF have distinct advantages
over intrusive techniques and have been proven capable of providing high-quality measurements
on turbulent flows [Aanen, L. et al. (1999); Fukushima, C. et al. (2000); Meyer, K. E. et
al. (2000)]. Moreover, because of their planar, rather than pointwise, nature, they are be-
coming the methods of choice for many experimental fluid mechanics investigations requiring
velocity vector field or scalar field data.

Although numerous studies have been reported on turbulent planar wakes, experimental
data for both the turbulent velocity field and concentration field in a liquid-phase, confined
rectangular wake are scarce. To address this deficiency, in the present study turbulent mixing in
a confined rectangular wake is investigated using both PIV and PLIF. Although the traditional
method to form the wake is to place a circular cylinder in a freestream, in the present study the
wake is produced by a plate (a characteristic of using a plate is the absence of a wake producing
blunt body with the inevitable local separation and large pressure gradients [Ali, S. F. and
The velocity and concentration fields in the wake are analyzed to provide insight into the characteristics of turbulent mixing and to validate the predictions of CFD models.

5.2 Experimental apparatus and methodology

5.2.1 Flow facility

The experimental flow system, shown in Fig. 5.1, is designed to provide a shear flow with a Reynolds number of up to 100,000, based on the channel hydraulic diameter. The reactor is mounted in an adjustable cage that can be raised or lowered in order to change the measurement location without moving the optics of the measurement system. As Fig. 5.2 shows, the reactor consists of a vertical Plexiglas test section and a flow conditioning section. The test section is 60 mm by 100 mm and 1 m in length. The width of each of the inlet channels is 20 mm. The slope of the surface of the splitter plates is 3 degrees along the side channels and 1 degree along the center channel. Three Fisher control valves and feedback control systems with flow accuracy of 0.5% are used to supply constant flow rates to the three inlet channels.

A flow-conditioning section consisting of a packed bed of 1 cm diameter spheres, turbulence reducing screens, and a pair of 4:1 contractions creates a uniform flow with reduced free-stream turbulence intensities. For the present study, the volumetric flow rate of each of the inlet channels was 1.0 liters/s, corresponding to a free-stream velocity \( U_0 \) of 0.5 m/s. The Reynolds number based on the hydraulic diameter of the test section and the bulk velocity was 37,500.

In the coordinate system used in this study, \( x \) represents the streamwise direction and \( y \) represents the transverse direction. All planar images are acquired in the center plane between the front and back walls of the test section. More details of the experimental apparatus and methodology can be found in [Feng, H. et al. (2005)].
5.2.2 Velocity measurements

The optical setup for the PIV measurements is shown schematically in Fig. 5.1. The flow tracer particles were hollow glass spheres (Sphercel, Potters Industries, Inc.) with a nominal diameter of 11.7 µm and a density of 1.1 g/cm³. Before performing the measurements, approximately 24 grams of seed particles were added to the total reservoir volume of 3500 liters and mixed until the particles were distributed homogeneously.

A double-pulsed Nd:YAG laser (New Wave Research Gemini PIV laser) was used as the light source, providing two independent 532 nm light pulses with a maximum pulse energy of 120 mJ and a pulse duration of approximately 5 ns. The time delay between the two laser pulses was set to 700 µs for the present experiments. The laser beam was formed into a sheet and focused along the center line (in the y direction) of the test section. The minimum sheet thickness was approximately 0.5 mm in the measured flow field region.

10,000 PIV image pairs were collected at each observation location at a frame rate of 8 images/s using a 12-bit LaVision Flowmaster 3S CCD camera with a resolution of 1280×1024 pixels. A multi-pass interrogation scheme with decreasingly smaller window sizes was used with a final interrogation spot size measuring 16×16 pixels, corresponding to 0.9 mm on a side. With 50% overlap between adjacent interrogation spots, the velocity vector spacing was 0.45 mm in both the x and y directions. The image magnification was about 0.12, and the numerical aperture was 8. The experimental uncertainty for velocity was ±3% [Prasad, A. K. et al. (1992)]. Peak locking [Christensen, K. T. (2004)] is a potential problem in PIV experiments in which measured particle displacements can become biased towards integer pixel displacements. The peaking-locking effect can be quantified by determining the peak-locking coefficient [Stanislas, M. et al. (2005)]. For the results presented here, this coefficient was found to be 0.04, indicating an acceptable low degree of peak locking.

Table 5.1 shows the Kolmogorov scales and the spatial resolution of the PIV measurements in terms of these Kolmogorov scales at the five observation locations in this work. To estimate the Kolmogorov scale, the following equation [Tennekes, H. and Lumley, J. L. (1972)] was used to approximate ε:
where $A$ is a constant of order 1. $u'_0$ denotes the characteristic fluctuating velocity, which was assumed to be the square root of $2/3$ of the maximum turbulent kinetic energy at each downstream location. The width of the wake was used as the integral length scale, $l$. As Table 5.1 shows, the spatial resolution of PIV measurements in terms of the Kolmogorov scale was $8.7\eta$ at $x/d = 1.0$ and continuously improved with downstream distance. At $x/d = 15$, the spatial resolution was $4.1\eta$.

### 5.2.3 Concentration measurements

The instantaneous concentration field was measured with PLIF using the same optical setup as in the PIV measurements. The fluorescent dye Rhodamine 6G was used as a passive scalar. Rhodamine 6G has $Sc \approx 1,250$ in water [Crimaldi, J. P. and Koseff, J. R. (2001)], and emits broadband fluorescence with a peak emission around 555 nm when excited by the light from an Nd:YAG laser [Penzkofer, A. and Leupacher, W. (1987)]. A long-pass (low pass for frequency) optical filter that blocked light with wavelengths shorter than 555 nm was attached on the camera lens so that reflected or scattered laser light did not interfere with the fluorescence measurements. In the center stream, the source concentration of Rhodamine 6G was 45 $\mu$g/liter, while the outer two streams were pure water.

Preliminary PLIF experiments were performed to calculate the fluorescent dye and to determine if the shot-to-shot variability of the laser was a concern. This was done by performing PLIF measurements on fixed concentrations of dye in a small Plexiglas tank with identical cross-sectional area to the test section. Since the dye concentration in each measurement was constant, any measured concentration fluctuations could only be due to a combination of shot-to-shot laser variation and camera noise. In these experiments, the measured variation in dye concentration was approximately 2%, indicating that the shot-to-shot laser power was remarkably steady. Thus, it was deemed unnecessary to monitor the shot-to-shot laser power variations during the PLIF experiments.
The image magnification of the PLIF measurements was about 0.12, and the numerical aperture was 5.6. The diffraction-limited spot size for the PLIF optical system was 8.1 µm. However, the spatial resolution was limited instead by the area viewed per pixel, which was 56 µm. The smallest length scale of turbulent mixing is known as the Batchelor scale [Batchelor, G. K. (1953)], which is defined by \( \eta_B = \eta/\sqrt{Sc} \). As Table 5.2 shows, the resolution of PLIF measurements is much larger than the Batchelor scale in all directions, therefore the smallest concentration scale cannot be resolved in the presented study.

At each observation location, 10,000 PLIF images were captured at a frame rate of 8 images/s. The local intensity of the fluorescent light is proportional to the local intensity of the excitation source and the local concentration of the fluorescent dye [Crimaldi, J. P. and Koseff, J. R. (2001)]. In the present study, we found that this relationship was valid for dye concentrations up to 100 µg/liter with our experimental setup. Each PLIF image was individually calibrated for the non-uniform energy distribution throughout the entire laser sheet and laser absorption across the illuminated field. The procedure to calibrate the concentration measurements is described by [Feng, H. et al. (2005)].

5.3 Overview of CFD models

Turbulent transport is described mathematically by the Reynolds-averaged Navier-Stokes (RANS) equations which need closures. Alternatively, one could use direct numerical simulation (DNS) [Rogallo, R. S. and Moin, P. (1984); Moin, P. and Mahesh, K. (1998)] or large-eddy simulation (LES) [Akselvoll, K. and Moin, P. (1996); Hughes, T. J. R. et al. (2001)]. Though DNS can provide extremely detailed information (beyond what is possible in experimental measurements), its application is limited by its prohibitive computational costs. Similarly, LES, although it attempts to reduce computational costs by resolving only the largest turbulent scales, is also computationally expensive. RANS simulations are more cost-effective, and thus these were adopted in this work. Here, a two-layer \(k-\varepsilon\) model is employed to close the Reynolds stresses. This model was proposed by [Chen, H. C. and Patel, V. C. (1988)] and solves the near-wall effect [Wilcox, D. C. (1998); Durbin, P. A. and Pettersson Relif, B. A. (2001)]
satisfactorily at reasonable cost even for complex flows. More details of the RANS code used in this study can be found elsewhere [Liu, Y. et al. (2004)]. The performance of this model is evaluated by comparing predicted single-point turbulence statistics with ensemble-averaged PIV data (which is equivalent to time-averaged data for this stationary flow).

5.3.1 Inert scalar moment transport model

Closure problems are also frequently encountered when solving the Reynolds-averaged scalar (which is the mixture fraction in this study) transport equations. In these models, an inert scalar $\phi$ can be successfully described by a small set of statistical moments, the scalar mean $\langle \phi \rangle$ and the scalar variance $\langle \phi^2 \rangle$, for example. Denoting the mean velocity and fluctuation velocity by $\langle U_j \rangle$ and $u_j$, respectively, the RANS transport equation of an inert scalar mean can be written as (repeated indices imply summation)

$$\frac{\partial \langle \phi \rangle}{\partial t} + \langle U_j \rangle \frac{\partial \langle \phi \rangle}{\partial x_j} = \Gamma \nabla^2 \langle \phi \rangle - \frac{\partial \langle u'_j \phi \rangle}{\partial x_j},$$

(5.6)

where $\Gamma$ is the molecular diffusivity, and repeated indices imply summation. The only unclosed term in Eq. 5.6 is the scalar flux $\langle u'_j \phi \rangle$ representing turbulent transport. In order to be consistent with the Reynolds stress closure, a two-layer $k-\varepsilon$ model is used in this work where $\langle u'_j \phi \rangle$ is modeled by invoking the gradient-diffusion hypothesis [Taylor, G. I. (1921)]:

$$\langle u'_j \phi \rangle = -\Gamma_T \frac{\partial \langle \phi \rangle}{\partial x_j},$$

(5.7)

where $\Gamma_T$, the turbulent diffusivity, is related to the turbulent viscosity $\nu_T$ by $\Gamma_T = \nu_T/Sc_T$. $Sc_T$ is the turbulent Schmidt number and has a typical value of 0.7 in this study.

The transport of an inert scalar variance is governed by

$$\frac{\partial \langle \phi^2 \rangle}{\partial t} + \langle U_j \rangle \frac{\partial \langle \phi^2 \rangle}{\partial x_j} = \Gamma \nabla^2 \langle \phi^2 \rangle - \frac{\partial \langle u'_j \phi^2 \rangle}{\partial x_j} + P_\phi - \varepsilon_\phi.$$  

(5.8)

Here $P_\phi$, the scalar-variance production term, is defined by

$$P_\phi \equiv -2\langle u'_j \phi \rangle \frac{\partial \langle \phi \rangle}{\partial x_j},$$

(5.9)
and represents the rate at which scalar energy is transferred from mean flow to turbulent fluctuations. The last term on the right-hand side $\varepsilon_\phi$ is the scalar dissipation rate defined by

$$\varepsilon_\phi = 2\Gamma \left\langle \frac{\partial \phi'}{\partial x_j} \frac{\partial \phi'}{\partial x_j} \right\rangle.$$  (5.10)

This term is responsible for dissipation of scalar variance due to molecular diffusion.

Since Eq. 5.9 is closed by Eq. 5.7, the remaining unclosed terms in Eq. 5.8 are the scalar-variance flux $\langle u'_j \phi'^2 \rangle$ and the scalar dissipation. Again, by invoking the gradient-diffusion hypothesis, the scalar-variance flux is modeled by

$$\langle u'_j \phi'^2 \rangle = -\Gamma_T \frac{\partial \langle \phi'^2 \rangle}{\partial x_j}.$$  (5.11)

By assuming proportionality between the scalar time scales and the turbulent time scales, [Spalding, D. B. (1971); Beguier, C. I. et al. (1978)] the scalar dissipation can be related to the turbulent frequency $\varepsilon/k$ by

$$\varepsilon_\phi = C_\phi \frac{\varepsilon}{k} \langle \phi'^2 \rangle,$$  (5.12)

with the mechanical-to-scalar time-scale ratio $C_\phi$ taking a Reynolds-number-dependent value determined by [Liu, Y. and Fox, R. O. (2006)]

$$C_\phi = \sum_{n=0}^{6} a_n (\log_{10} Re_T)^n$$  (5.13)

where, for $Sc = 1250$, $a_0 = 0.4093$, $a_1 = 0.6015$, $a_2 = 0.5851$, $a_3 = 0.09472$, $a_4 = -0.3903$, $a_5 = 0.1461$, $a_6 = -0.01604$, and the turbulent Reynolds number is defined by

$$Re_T = \frac{k}{\sqrt{\nu \varepsilon}}.$$  (5.14)

The RANS code solves Eqs. 5.6 and 5.8 closed by Eqs. 5.7, 5.11 and 5.12. These models are then validated against the inert scalar mean and variance measured by PLIF.
5.3.2 Transported PDF model

The transport equation of the composition PDF, denoted by \( f_\phi \), for an incompressible fluid is

\[
\frac{\partial f_\phi}{\partial t} + \frac{\partial}{\partial x_j} \left( \langle U_j \rangle f_\phi \right) + \frac{\partial}{\partial x_j} \left[ \langle u'_j | \psi \rangle f_\phi \right] = -\frac{\partial}{\partial \psi} \left[ \langle \nabla^2 \phi | \psi \rangle f_\phi \right]
\]

(5.15)

where \( \phi \) and \( \psi \) represent the composition and the composition state space, respectively, and \( \langle \cdot | \psi \rangle \) denotes the Reynolds average conditioned on \( \phi = \psi \). The scalar-flux term \( \langle u'_j | \psi \rangle f_\phi \), which denotes the scalar-conditioned velocity fluctuations (i.e., mesomixing), is closed by the gradient-diffusion model as

\[
\langle u'_j | \psi \rangle f_\phi = -\Gamma_T \frac{\partial f_\phi}{\partial x_j}.
\]

(5.16)

The term on the right-hand side of Eq. 5.15, representing transport in composition space due to molecular diffusion, is approximated in this study by a micromixing model - the interaction-by-exchange-with-the-mean (IEM) model and the Euclidean minimum spanning tree (EMST) model [Subramaniam, S. and Pope, S. B. (1998)], which are described later in this section.

The numerical discretization of Eq. 5.15 is intractable due to its high dimensionality. In our Lagrangian PDF code [Raman, V. et al. (2001, 2003, 2004)], Eq. 5.15 is expressed in terms of stochastic differential equations for so-called “notional” particles. [Pope, S. B. (1976, 1985)]. Denoting the position of a notional particle by \( X^{(n)} \), transport in physical space with Eq. 5.16 is governed by the following equation:

\[
dX^{(n)} = \left[ \langle U \rangle \left( X^{(n)}, t \right) + \nabla \Gamma_T \left( X^{(n)}, t \right) \right] dt + \sqrt{2\Gamma_T \left( X^{(n)}, t \right)} dW(t),
\]

(5.17)

where \( dW(t) \) is a multi-variate Wiener process with a mean of zero and \( \langle U \rangle \left( X^{(n)}, t \right) \) is the mean velocity vector at the particle location. The evolution equation for the particle composition \( \phi^{(n)} \) can be written as

\[
\frac{d\phi^{(n)}}{dt} = \Theta^{(n)},
\]

(5.18)
where $\Theta$ represents the micromixing model. For the IEM model, Eq. 5.18 is characterized by

$$d\phi^{(n)} = \frac{C_{\Theta} \varepsilon}{2k} \left( \langle \phi \rangle \left( X^{(n)}, t \right) - \phi^{(n)} \right) dt,$$

(5.19)

where $\langle \phi \rangle \left( X^{(n)}, t \right)$ is the estimated scalar mean at the particle location. In the EMST model, which is local in composition space, composition interactions only occur between neighbor pairs of particles, $m_e$ and $n_e$, connected by the edge $e$:

$$d\phi^{(n)} = \alpha \sum_{e=1}^{N_T-1} B_e \left\{ \left( \phi^{(m_e)} - \phi^{(n)} \right) \delta_{nm_e} + \left( \phi^{(n_e)} - \phi^{(n)} \right) \delta_{nn_e} \right\} dt,$$

(5.20)

where $N_T$ denotes the number of particles chosen for mixing from the ensemble of $N$ particles within a grid cell and $B_e$ is the edge-weight. $\delta$ represents the Kronecker delta function. The parameter $\alpha$ is determined by requiring that the scalar variance decays exponentially with $C_{\Theta}/k$. More details can be found in [Subramaniam, S. and Pope, S. B. (1998, 1999)].

The flow statistics appearing in Eqs. 5.17, 5.19 and 5.20 are known from the RANS code [Fox, R. O. (2003); Raman, V. et al. (2001)]. Given the composition of the notional particles, the scalar mean and variance, which are assumed to be independent of the particle locations within a grid cell, are estimated as

$$\langle \phi \rangle = \frac{\sum_{n=1}^{N} W^{(n)} \phi^{(n)}}{\sum_{n=1}^{N} W^{(n)}},$$

(5.21)

$$\langle \phi^2 \rangle = \frac{\sum_{n=1}^{N} W^{(n)} \left( \phi^{(n)} - \langle \phi \rangle \right)^2}{\sum_{n=1}^{N} W^{(n)}},$$

(5.22)

where $W^{(n)}$ is the weight of the $n$th particle. Equation 5.15 is validated by comparing the inert scalar statistics predicted by the transported PDF method with PLIF data.

5.3.3 Simulation conditions

The wake flow was simulated using the RANS and PDF models described above. All simulations were performed on a two-dimensional (2-D) grid by assuming that gradients in the spanwise direction are negligible. The computational grid consists of $80 \times 120$ Cartesian cells with denser grid cells near stream interfaces and walls to resolve sharp gradients. This methodology ensures a grid-independent solution.
The inlet boundary conditions of the streamwise mean velocity \( \langle U \rangle \), the turbulent kinetic energy \( k \) and the turbulent dissipation rate \( \varepsilon \) for the RANS simulations were extracted from the experimental data measured at the entrance plane of the reactor. The distribution of the experimental data was found to be slightly asymmetric with respect to the centerline (Fig. 5.3). By averaging the experimental data with respect to \( y/d = 0 \) and then interpolating linearly between data points, the symmetric inlet boundary conditions for \( \langle U \rangle, k \) and \( \varepsilon \) were obtained (Fig 5.3). Due to the difference in resolution mentioned above, the inlet boundary conditions effectively cut off the large gradients appearing in the interfaces of streams. However this was found to have no impact on the calculated flow statistics. Note that the PIV data are 2-D measurements, containing no information on the out-of-plane velocity component. The PIV data for the turbulent kinetic energy were estimated from the streamwise and transverse velocity fluctuations, \( u' \) and \( v' \), as

\[
{k} = \frac{\langle u'^2 \rangle + 2\langle v'^2 \rangle}{2}. \tag{5.23}
\]

The spanwise velocity fluctuation was assumed to be equal in magnitude to the cross-stream velocity fluctuation. By further assuming \( \partial/\partial z = \partial/\partial y \), the turbulent dissipation rate was derived from the 2-D PIV data. More details can be found in Sec. 5.4.4.

### 5.4 Results and discussion

Figure 5.4 displays a sample instantaneous velocity field from PIV measurements with a convective velocity subtracted from each vector. A system of double roller-like counter-rotating large eddies are observed in the wake region just downstream of the tips of the splitter plates. An instantaneous concentration field at this same location as measured by PLIF is illustrated in Fig. 5.5. The contour levels represent the concentration normalized by the source concentration, or mixture fraction. Note that the velocity and concentration fields shown in Figs. 5.4 and 5.5 are uncorrelated with each other, as the PIV and PLIF measurements in this study were not performed simultaneously. By themselves, instantaneous velocity and concentration fields such as those shown in Figs. 5.4 and 5.5 provide only anecdotal data
concerning the flow field. In order to be useful in validating the computational results, the PIV and PLIF data sets must be analyzed statistically.

### 5.4.1 Mean velocities and Reynolds stresses

The ensemble-averaged streamwise velocity profiles measured by PIV for six representative downstream locations are shown in Fig. 5.6, where the $y$-axis has been normalized by the inlet channel width, $d = 20$ mm. This normalization of the transverse coordinate is used throughout the present work. The mean velocity has been normalized by the bulk velocity, $U_0 = 0.5$ m/s, i.e., the mean velocity as determined from the volumetric flow rate. As Fig. 5.6 shows, two wake regions appear just downstream of the tips of the splitter plates as the boundary layers on the splitter plate surfaces merge downstream of the tips. Also note that the velocity profiles are nearly symmetric about the centerline of the reactor at each downstream location. The wake velocity defect diminishes quickly at the lower downstream locations. The two wake regions meet at $x/d = 4.5$ near the channel centerline, as seen by the potential core in the center stream disappearing at this position. At $x/d = 30$ the velocity profile begins to look like a fully developed turbulent channel flow, with the wakes no longer observed.

The mean streamwise velocity predicted by the RANS code with the two-layer $k-\varepsilon$ model is compared with PIV measurements in Fig. 5.6. The spreading rate of the wake predicted by the RANS code is slightly lower than that measured by PIV, and this characteristic becomes more obvious further downstream. However, the agreement in Fig. 5.6(f) is good, and at $x/d = 30$ the RANS code also predicts the complete decay of the wakes. The smaller spreading rate in the RANS calculation is most likely caused by a lower diffusion rate of the turbulent kinetic energy, as discussed later.

The PIV measured Reynolds stresses, normalized by $U_0^2$, for seven streamwise locations are plotted in Fig. 5.7. Just downstream of the splitter plate tips, the longitudinal Reynolds stress, $\langle u'u' \rangle$, in each wake displays two peaks. This is due to the two boundary layers along the splitter plates coming together to form the wakes. Each of these boundary layers has its own peak in Reynolds stress, and these peaks remain distinct for some distance downstream.
of the splitter plate tip. However, at further downstream locations these two peaks become
indistinct, and only a single peak is observed in each wake.

The disparate boundary layer development along the surfaces of the splitter plate gives
rise to a slight asymmetry in the wakes such that \( \langle u'u' \rangle \) is higher in the left wake. Also, at
the first downstream location \( \langle u'u' \rangle \) is 8 times larger than the lateral Reynolds stress, \( \langle v'v' \rangle \).
However, \( \langle u'u' \rangle \) decays much more rapidly at lower downstream locations than \( \langle v'v' \rangle \), and both
normal stresses become almost identical in magnitude at \( x/d = 7.5 \) and further downstream.
After the initial convergence of the two boundary layers forming each wake, both \( \langle u'u' \rangle \) and
\( \langle v'v' \rangle \) initially increase near the centerline at \( x/d = 1.0 \), but then show a marked decrease at
\( x/d = 4.5 \). Thereafter, the Reynolds normal stresses continually decrease to very small values
as the results at \( x/d = 30 \) show.

The Reynolds shear stress, \( \langle u'v' \rangle \), is antisymmetric around the center line of the channel:
positive where the mean shear is negative, and negative where the mean shear is positive. The
Reynolds shear stress also changes sign at the center of each wake, and along the center line
of the channel the Reynolds shear stress is zero. Due to the boundary layers along the side
walls, the Reynolds shear stress near the side walls is nonzero. At \( x/d = 30 \), after the wakes
have completely disappeared, the Reynolds shear stress decreases to zero in the region near
the center line of the channel.

5.4.2 Self-similarity of the rectangular wake

Using Eqs. 5.1, 5.2, and 5.3, the self-similar velocity defect \( f(\xi) \) in the wake downstream
of the left splitter plate was calculated. It should be noted that the free-stream velocity \( U_c \)
used in these calculations is taken to be 0.56 m/s which is the maximum local inlet velocity.
The profiles at five downstream locations are shown in Fig. 5.8 for both the PIV and RANS
simulation data. These results indicate that the mean velocity profile in the wake tends to
reach an equilibrium state. However, unlike in a free wake, the distribution of the velocity
defect at the edges of the wake is very different due to the interaction of the two wakes and the
effect of boundary layers growing along the side walls. Moreover, since the potential core in the
center stream disappears faster than that in the side stream, the velocity defect corresponding
to the positive scaled cross-stream variable ($\xi$) departs from the self-similar profile faster than
that for negative $\xi$. Additionally, due to the different slopes of both surfaces of the splitter
plate, the pressure gradients on both sides are slightly different. As a result, the profile of the
self-similar velocity is not perfectly symmetric about the center line of the wake.

5.4.3 Turbulent kinetic energy

The turbulent kinetic energy predicted by the RANS code is compared with PIV data for
downstream locations $x/d = 1, 4.5, 7.5, 12, 15$ and $30$ in Fig. 5.9. The RANS code captures
all the essential behavior of the turbulent kinetic energy, though the diffusivity in the central
channel is slightly lower than expected based on comparisons with the PIV results. Figure 5.9
also indicates that the PIV measurements missed sharp gradients of the turbulent kinetic
energy, especially near the walls where the mean and variance of the velocity are changing
quickly. This is not surprising if we recall that PIV measures a filtered velocity field, given
that the measurement resolution is lower than the Kolmogorov scale. The spatial resolution
of PIV is limited by the interrogation spot size, $l_{\text{PIV}}^*$ ($l_{\text{PIV}}^* = 9 \times 10^{-4}$ m in this study).
In the boundary layers formed near the walls and at the stream interfaces, the size of the
largest energy-containing eddies, which scales with the thickness of the boundary layers, is
much smaller than $l^*$. Therefore, portions of the turbulent kinetic energy is cut off by the
measurements at those regions. On the other hand, the RANS computation involves a grid the
resolution of which is higher than the spatial resolution in the PIV measurements near stream
interfaces and walls, capturing more local details of the turbulent kinetic energy.

5.4.4 Turbulent dissipation rate

Notice the spatial resolution of the PIV measurements in the present work was good enough
to resolve the turbulent dissipation rate [Tennekes, H. and Lumley, J. L. (1972); Tsurikov,
M. S. and Clemens, N. T. (2002)], Eq. 5.4 was therefore used to compute the turbulent
dissipation rate. However the out-of-plane component of velocity ($w$) is not available in 2-D
PIV measurements, only four terms of the velocity gradient, i.e., $\partial u/\partial x$, $\partial u/\partial y$, $\partial v/\partial x$ and $\partial v/\partial y$, can be computed directly using PIV data. By using the incompressible continuity equation, $\partial w/\partial z$ can also be determined. To estimate the dissipation rate, the following assumptions were made to obtain the four unknown terms in Eq. 5.4: (1) $w = v$; and (2) $\partial/\partial z = \partial/\partial y$.

The results of the turbulent dissipation rate at six downstream locations computed by Eq. 5.4 are shown in Fig. 5.10 and compared with those predicted by the two-layer $k-\varepsilon$ model. The dissipation rate in the flow is highly inhomogeneous. Initially, the profile of dissipation rate has two distinct peaks in each wake (due once again to the two boundary layers along each splitter plate coming together at the splitter plate tip). However, the dissipation rate decreases very quickly with increasing downstream distance, and the two peaks are indistinct at farther downstream locations. The dissipation rate at the center of the channel starts to increase after the two mixing layers meet and the potential core disappears. At $x/d = 30$, the wakes have collapsed, and the dissipation rate decreases to small values. Comparing the profiles of the dissipation rate and turbulent kinetic energy, it is noticed that there exists strong correlation between these two properties.

The dissipation rate predicted by the two-layer $k-\varepsilon$ model agrees well with that estimated from the PIV data (Fig. 5.10), even in the near-wall regions, indicating that the performance of the turbulence model is satisfactory.

### 5.4.5 Mixture-fraction mean and variance

The profiles of ensemble-averaged mixture-fraction mean and variance at the six streamwise locations as measured by PLIF are presented in Figs. 5.11 and 5.12, respectively, and compared with those predicted by the RANS and the micromixing models. The profile of mixture-fraction mean is symmetric about the center line of the channel. At $x/d = 1$, the mixture-fraction mean resembles a top-hat shape. As $x$ increases, the mixture-fraction mean in the center stream decreases and the mixture-fraction mean in the side streams increases due to mass transport of the dye. After the two wakes meet at $x/d = 4.5$ (i.e., after the potential core in the center
stream disappears), the profile of mixture-fraction mean becomes bell-shaped. At the farthest observed downstream location, $x/d = 30$, the profile still remains bell shaped, indicating that even at this far downstream location, the fluid is not fully mixed. As Fig. 5.12 shows, the mixture-fraction variance profiles are also nearly symmetric. The magnitudes of the peaks of variance increase with $x$ initially but then remain almost unchanged at $x/d = 4.5, 7.5$ and $12$, before decreasing slowly at $x/d = 15$ and beyond. After the potential core between the two wakes disappears, the mixture-fraction variance in the center of the channel becomes nonzero and increases with increasing downstream distance. At the farthest location investigated in this work, the two peaks in mixture-fraction variance are still distinct. Note also that at $x/d = 1.0$, the measured mixture-fraction variance at $y/d = 0$ is nearly zero. Since the measured variance at this location is primarily due to shot-to-shot variations in laser intensity, this demonstrates the consistency of the lasers used in these experiments.

The RANS code and the micromixing models yield similar profiles for the mixture-fraction mean at all locations. This is expected since the mean conservation property of the IEM model and the EMST model guarantees a mixture-fraction mean that is exclusively determined by the flow statistics given the inlet boundary condition of the mixture-fraction mean. In general, the predicted mixture-fraction mean agrees well with the PLIF data, though the former shows a lower spreading rate, which is consistent with observations in Figs. 5.6 and 5.9. It was also found that the spreading rate was insensitive to the value of the turbulent Schmidt number, indicating that it is the mean velocity rather than the gradient-diffusion model (Eqs. 5.7 and 5.16) that most likely causes the discrepancy in the spreading rate. The mixture-fraction mean near the wall becomes non-zero by $x/d = 30$.

The mixture-fraction variances predicted by the micromixing models are similar and agree closely with the results given by the RANS code except at $x/d = 1$, where the models predict a higher variance in the stream interfaces than the RANS code. The time step for the PDF calculations, which is 0.002 s in this study, is the key factor that initiates the overpredicted variance [Feng, H. et al. (2005)]. Both codes predict a higher peak value for the variance, and the agreement cannot be improved by reducing the value of the turbulent Schmidt number.
This is consistent with discussion concerning the mixture-fraction mean, which reveals that the slower diffusion predicted by the two-layer \( k - \varepsilon \) model leads to the smaller spreading rate. Meanwhile, the gradient of the mixture-fraction mean overpredicted by the RANS code and the micromixing models (Figs. 5.11e and f) results in a higher mixture-fraction variance production term. A overpredicted mixture-fraction variance is consequently expected. It should be noted that the variance decays at an identical rate in the IEM and EMST models, although how the particles interact is distinct.

The performance of the closure for the scalar dissipation rate is worth further investigation. Equation 5.12 is a model for the rate at which the scalar spectral energy transfers through the inertial-convective subrange in homogeneous turbulence. In the stream interfaces near the reactor entrance \((x/d = 1)\), where the turbulence is highly inhomogeneous, the energy transfer rate from large to small scales cannot be represented completely by the closure. Therefore the scalar dissipation rate is underestimated, leading to a higher variance (Fig. 5.12a). The model can be expected to be more accurate as the flow develops except in the near-wall regions where the inhomogeneity persists (Fig. 5.9) [Feng, H. et al. (2005)]. Figure 5.6 shows that the turbulence is still developing up to \(x/d = 30\). The same tendency is indicated by Figs. 5.12a-d: the agreement of the predicted variance and PLIF data improves gradually from \(x/d = 1\) to \(x/d = 15\). The insufficient spreading rate and sharper mixture-fraction mean gradient affect the variance prediction more significantly after \(x/d = 15\) (Figs. 5.12e and f).

Meanwhile, the PLIF measurements tend to underestimate the mixture-fraction variance since the spatial resolution of the PLIF measurements is insufficient to resolve the smallest mixing scales. The scalar variance can be found directly from the scalar energy spectrum \(E_\phi(\kappa)\) by integrating over the space of the wavenumber \(\kappa\):

\[
\langle \phi'^2 \rangle = \int_0^\infty E_\phi(\kappa) d\kappa. \tag{5.24}
\]

The thickness of the laser sheet used in the PLIF experiments, \(l_{PLIF}^*\), determines a cut-off wavenumber

\[
\kappa^* = \frac{1}{l_{PLIF}^*}. \tag{5.25}
\]
where \( l_{PLIF}^* = 5 \times 10^{-4} \) m. Consequently, the mixture-fraction variance that can be measured by PLIF is limited to

\[
\langle \phi'^2 \rangle^* = \int_0^{\kappa^*} E_\phi(\kappa) d\kappa.
\]

(5.26)

By using a model scalar spectrum [Fox, R. O. (2003)], the percentage of mixture-fraction variance “missed” by the PLIF measurements, represented by \( 1 - \langle \phi'^2 \rangle^*/\langle \phi'^2 \rangle \), is estimated at points where the predicted variance peaks in value for each downstream location (Table 5.3). This “missing” variance decreases from 24.44% at \( x/d = 1 \) to 8.3% at \( x/d = 30 \). This tendency is expected since more of the scalar energy spectrum is resolved as the Kolmogorov length scale increases in the streamwise direction.

### 5.4.6 One-point composition PDF

The evolution of the probability density function (PDF) of mixture fraction was studied using the PLIF data. Designating the midpoint of the peaks in mixture-fraction variance at each downstream location as position “0” and the left peak of mixture-fraction variance as “\( \delta \)”, eight points along the transverse direction were chosen as positions of interest. In the transported PDF code, the \( N \) particles within the grid cells centered on the selected points were sorted into 20 equal-spaced bins between 0 to 1 by their composition. Denoting the number of particles in each bin by \( N_i \), the PDF of the mixture fraction was approximated by \( 20N_i/N \). Figures 5.13 - 5.18 show the one-point composition PDF extracted from the PLIF data, the beta-PDF characterized by the measured mixture-fraction mean and variance, as well as the one-point composition PDF predicted by the IEM model and the EMST model at the points of interest for selected downstream locations.

The experimentally observed mixture-fraction PDF is well approximated by the beta PDF. This is partly because that the experimental values of the mixture-fraction mean and variance were used to define the beta PDF. At the lowest observed downstream location \( (x/d = 1) \), the PDF approximates a delta function at positions “0” and “3/2\( \delta \)” (Figs. 5.13a and h) since very little mixing has occurred at regions far from the stream interface. When the observation position moves towards the point “\( \delta \)” (i.e., towards the peak in mixture-fraction variance),
the PDF extracted from the PLIF data shows a tendency towards becoming bell-shaped while the IEM model and the EMST model predict a saddle-shaped curve and a relatively flat line, respectively (Fig. 5.13d). The discrepancy can be well understood if we recall that the PLIF measures a mixture-fraction field averaged over a finite measurement volume. As a result, the experimentally observed PDF reaches its maximum value at $\phi = 0.5$ at the point “δ”.

The spatial resolution of the PLIF measurements is much lower than the Batchelor scale (i.e., the PLIF measurement volume is much larger than the Batchelor scale), especially at near-entrance areas where the Batchelor scale is small. Therefore, scalar eddies smaller than the spatial resolution are filtered by averaging.

Unlike the mixture-fraction mean which was not affected by the spatial resolution, the PDF of the mixture fraction is expected to be more uniform than reality in the neighborhood of the point “δ”. On the other hand, two peaks near $\langle \phi \rangle = 0.2$ and $\langle \phi \rangle = 0.8$ (Fig. 5.13d) are predicted by the IEM model, revealing one of the properties of that model: two peaks initially formed by the delta functions at $\phi = 0$ and $\phi = 1$ persist until they merge at $\phi = \langle \phi \rangle$. In contrast, the EMST model predicts a relatively flat PDF (Fig. 5.13d) as a result of localness: a stochastic particle mixes preferentially with particles that are close to it in composition.

As the downstream distance increases, mixing does begin to take place at points far from point “3/2δ” since more interface stream fluid has been entrained into the channel steams, and the PDF curves become flatter but remain skewed (Figs. 5.13 - 5.18), indicating the persistence of high concentrations of fluorescent dye at these positions. A Gaussian distribution can be expected at a position far downstream from the entrance. The discrepancy between the experimentally observed PDF and the calculated PDF decreases gradually (Figs. 5.13 - 5.16) mainly due to two reasons. First, the Batchelor scale increases, leading to an improved resolution of the PLIF measurements. Second, the modeled PDFs relaxed towards a Gaussian gradually along the streamwise direction. However, the agreement of the measured PDF and calculated PDF does not improve from $x/d = 15$ to $x/d = 30$ since the insufficient spreading rate and the higher mixture-fraction gradient begin to play an important role in the PDF prediction. The insufficient spreading rate can be clearly observed at the point
“0” (Figs. 5.15h and 5.17h). We attribute the discrepancy shown in these two figures to the insufficient spreading rate since the spatial resolution is comparable to the Batchelor scale and the scalar variance production is zero at the point “0”. At all locations, the PDF predicted by the EMST model agrees with the experimental observation much better than does that predicted by the IEM model.

5.5 Conclusions

In this study, PIV and PLIF were employed to investigate a rectangular wake flow in a confined reactor with a Schmidt number of 1,250 and a Reynolds number of 37,500 based on bulk velocity and hydraulic diameter. Measurements were carried out at various downstream locations from $x/d = 1$ to $x/d = 30$. Flow statistics such as the mean velocity, Reynolds stresses, turbulent kinetic energy, mixture-fraction mean and variance were calculated from the PIV and PLIF data. The PDF of the mixture fraction at some representative positions in the flow as well as the turbulent dissipation rate were estimated from the experimental data. It was observed that the two confined wakes formed by the two splitter plates had completely decayed by $x/d = 30$.

The PIV and PLIF data were used to validate RANS and transported PDF models. In general, the overall agreement between the CFD models and the experimental data for this moderately complex flow is satisfactory. The mean velocity field was accurately predicted, demonstrating that the two-layer $k-\varepsilon$ model represents the Reynolds stresses successfully, even in near-wall regions. However, this turbulence model predicted a lower spreading rate of the turbulent kinetic energy, which consequently slows down the diffusion of the mixture-fraction mean and variance. The predicted mixture-fraction mean and variance indicate that the scalar fluxes were reasonably approximated by the gradient-diffusion models. The scalar dissipation rate was closed by the “equilibrium” model which functioned better for a flow with weak inhomogeneity. Due to the limited spatial resolution, the PLIF measurement could not resolve the scalar variance completely. Nevertheless, the measurement accuracy improved gradually at farther downstream locations. The one-point PDF of the mixture fraction extracted from the
PLIF data was compared with the PDFs predicted by the IEM model and the EMST model at eight points in the transverse direction for selected downstream locations. The experimentally observed PDF tends to be more uniform than that predicted by the micromixing models, partially due to the limited spatial resolution. At the positions where the mixture-fraction variance peaks in value and points nearby, the measured PDF tends to approximate a unimodal distribution more quickly while the predicted PDF shows model characteristics: the IEM model introduced two peaks bounded on the high mixture-fraction and low mixture-fraction sides, respectively; the EMST model features localness.

Acknowledgments

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Table 5.1  Kolmogorov Length Scale and Spatial Resolution of PIV Measurements.

<table>
<thead>
<tr>
<th>$x/d$</th>
<th>$\eta [\mu m]$</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>104</td>
<td>8.7$\eta$</td>
</tr>
<tr>
<td>4.5</td>
<td>139</td>
<td>6.5$\eta$</td>
</tr>
<tr>
<td>7.5</td>
<td>153</td>
<td>5.9$\eta$</td>
</tr>
<tr>
<td>12</td>
<td>183</td>
<td>4.9$\eta$</td>
</tr>
<tr>
<td>15</td>
<td>222</td>
<td>4.1$\eta$</td>
</tr>
</tbody>
</table>

Table 5.2  Batchelor Length Scale and Spatial Resolution of PLIF Measurements.

<table>
<thead>
<tr>
<th>$x/d$</th>
<th>$\eta_B [\mu m]$</th>
<th>Resolution in x-/y-</th>
<th>Resolution in z-</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.93</td>
<td>19.1$\eta_B$</td>
<td>171$\eta_B$</td>
</tr>
<tr>
<td>4.5</td>
<td>3.93</td>
<td>14.2$\eta_B$</td>
<td>127$\eta_B$</td>
</tr>
<tr>
<td>7.5</td>
<td>4.33</td>
<td>12.9$\eta_B$</td>
<td>115$\eta_B$</td>
</tr>
<tr>
<td>12</td>
<td>5.17</td>
<td>10.8$\eta_B$</td>
<td>97$\eta_B$</td>
</tr>
<tr>
<td>15</td>
<td>6.27</td>
<td>8.9$\eta_B$</td>
<td>80$\eta_B$</td>
</tr>
</tbody>
</table>

Table 5.3  Estimated Variance Unresolved by PLIF at the Peak of the Variance Profile.

<table>
<thead>
<tr>
<th>$x/d$</th>
<th>1</th>
<th>4.5</th>
<th>7.5</th>
<th>12</th>
<th>15</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unresolved(%)</td>
<td>24.44</td>
<td>15.36</td>
<td>13.09</td>
<td>11.43</td>
<td>10.64</td>
<td>8.3</td>
</tr>
</tbody>
</table>
Figure 5.1  Schematic of the flow facility and the optical setup used in the PIV and PLIF experiments.

Figure 5.2  Schematic of the confined rectangular-wake reactor.
Figure 5.3 (a) Mean streamwise velocity, (b) turbulent kinetic energy and (c) dissipation at the entrance plane of the wake. —, inlet boundary conditions for simulations; •, PIV data.

Figure 5.4 An instantaneous velocity field as measured by PIV.

Figure 5.5 An instantaneous concentration field as measured by PLIF.
Figure 5.6  Comparison of the mean streamwise velocity profiles measured by PIV (●) and calculated from RANS code (—) for (a) $x/d = 1$, (b) $x/d = 4.5$, (c) $x/d = 7.5$, (d) $x/d = 12$, (e) $x/d = 15$ and (f) $x/d = 30$. 
Figure 5.7 Normalized Reynolds stresses measured by PIV. ■, $x/d = 0$; □, $x/d = 1.0$; ▲, $x/d = 4.5$; A, $x/d = 7.5$; ▼, $x/d = 12$; B, $x/d = 15$; ×, $x/d = 30$. 
Figure 5.8 Normalized velocity defect measured by PIV (left) and predicted by RANS (right). □, $x/d = 1.0$; ▲, $x/d = 4.5$; A, $x/d = 7.5$; ▼, $x/d = 12$; B, $x/d = 15$. 
Figure 5.9  Comparison of the turbulent kinetic energy profiles measured by PIV (●) and calculated from RANS code (—) for (a) $x/d = 1$, (b) $x/d = 4.5$, (c) $x/d = 7.5$, (d) $x/d = 12$, (e) $x/d = 15$ and (f) $x/d = 30$. 
Figure 5.10  Comparison of dissipation rate profiles as measured by PIV (●) and as calculated from RANS code (—) for (a) $x/d = 1$, (b) $x/d = 4.5$, (c) $x/d = 7.5$, (d) $x/d = 12$, (e) $x/d = 15$ and (f) $x/d = 30$. 
Figure 5.11 Comparison of mixture-fraction mean profiles measured by PLIF (●) and calculated from RANS code (—), IEM model (∆) and EMST model (◦) for (a) $x/d = 1$, (b) $x/d = 4.5$, (c) $x/d = 7.5$, (d) $x/d = 12$, (e) $x/d = 15$ and (f) $x/d = 30$. 
Figure 5.12 Comparison of mixture-fraction variance profiles measured by PLIF (•) and calculated from RANS code (—), IEM model (Δ) and EMST model (◦) for (a) $x/d = 1$, (b) $x/d = 4.5$, (c) $x/d = 7.5$, (d) $x/d = 12$, (e) $x/d = 15$ and (f) $x/d = 30$. 
Figure 5.13  Comparison of one-point composition PDF measured by PLIF and calculated from PDF code for \( x/d = 1 \) at transverse distances from the centerline by (a) \( 3\delta/2 \), (b) \( 5\delta/4 \), (c) \( 9\delta/8 \), (d) \( \delta \), (e) \( 7\delta/8 \), (f) \( 3\delta/4 \), (g) \( \delta/2 \) and (h) 0.
Figure 5.14 Comparison of one-point composition PDF measured by PLIF and calculated from PDF code for $x/d = 4.5$ at transverse distances from the centerline by (a) $3\delta/2$, (b) $5\delta/4$, (c) $9\delta/8$, (d) $\delta$, (e) $7\delta/8$, (f) $3\delta/4$, (g) $\delta/2$ and (h) 0.
Figure 5.15  Comparison of one-point composition PDF measured by PLIF and calculated from PDF code for $x/d = 7.5$ at transverse distances from the centerline by (a) $3\delta/2$, (b) $5\delta/4$, (c) $9\delta/8$, (d) $\delta$, (e) $7\delta/8$, (f) $3\delta/4$, (g) $\delta/2$ and (h) 0.
Figure 5.16  Comparison of one-point composition PDF measured by PLIF and calculated from PDF code for $x/d = 12$ at transverse distances from the centerline by (a) $3\delta/2$, (b) $5\delta/4$, (c) $9\delta/8$, (d) $\delta$, (e) $7\delta/8$, (f) $3\delta/4$, (g) $\delta/2$ and (h) 0.
Figure 5.17 Comparison of one-point composition PDF measured by PLIF and calculated from PDF code for $x/d = 15$ at transverse distances from the centerline by (a) $3\delta/2$, (b) $5\delta/4$, (c) $9\delta/8$, (d) $\delta$, (e) $7\delta/8$, (f) $3\delta/4$, (g) $\delta/2$ and (h) 0.
Figure 5.18 Comparison of one-point composition PDF measured by PLIF and calculated from PDF code for $x/d = 30$ at transverse distances from the centerline by (a) $3\delta/2$, (b) $5\delta/4$, (c) $9\delta/8$, (d) $\delta$, (e) $7\delta/8$, (f) $3\delta/4$, (g) $\delta/2$ and (h) 0.
CHAPTER 6. SCALE UP OF GAS-PHASE CHLORINATION REACTORS USING CFD

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Ying Liu, Venkatramanan Raman, Rodney O. Fox and Albert D. Harvey

Abstract

Gas-phase chlorination of methyl chloride is an important industrial process producing widely applied chlorinated derivatives. Control over reactor stability and product distribution necessitates a thorough study of the strongly coupled turbulent flow and reaction processes in chlorination reactors. In this work, a hybrid finite-volume (FV)/transported probability density function (PDF) method is employed to analyze the performance of a coaxial jet-stirred reactor with three feed-stream configurations when it is scaled up from lab scale to pilot scale, and then to plant scale. The reduced mechanism used here has 21 reactions and 15 species. With premixed inlets, the pilot-scale reactor is prone to extinguish. Strategies based on turbulence-chemistry interaction analysis for ensuing reactor stability are proposed and confirmed by simulations. On the other hand, nonpremixed inlets maintain reaction in the scaled-up reactors, but produce poor product yields.

6.1 Introduction

Computational fluid dynamics (CFD) is a powerful tool for chemical reactor analysis, design and optimization [Fox, R. O. (2003)]. Here it is employed for the scale-up of gas-phase chlorination reactors used for the production of chloroform from methyl chloride. The predicted flow field and product distribution facilitate better understanding of the dynamic behavior of
the plant-scale reactor based on chemistry models developed at the lab scale.

Gas-phase chlorination of methyl chloride is one of the two common methods for the commercial production of chloroform. Chloroform and two other chloride derivatives, methylene dichloride and carbon tetrachloride, are the three main products of this process. They are widely used as industrial solvents, and intermediates in the preparation of refrigerants, dyes and pesticides. In the present study, methyl chloride and methyl dichloride are grouped as the organic reactants and are considered as nonpremixed from the pure chlorine stream. The recirculation of heat released by the highly exothermic reactions heats up the reactants that are typically introduced at a temperature much below the ignition temperature. As the disassociation of chlorine molecules increases the chlorine radical concentration level, the chlorination of methyl chloride proceeds and more heat is fed back to the incoming feed inlets. However, excessive heat tends to result in higher temperatures at which the product decomposes and multi-bonded hydrocarbons form. Since the feed configuration plays a key role in determining the distribution of temperature and products, a complete investigation on the effects of premixed and nonpremixed inlet streams on the performance of the scaled-up reactor is essential for obtaining optimized operating conditions.

Researchers have made a few attempts to model chlorination reactors using simplified kinetics or simple flow models [West, D. H. et al. (1999)]. These studies have concluded that unless more detailed kinetic schemes [Tirtowidjo, M. (1997)] and source term closures are used [Raman, V. et al. (2001, 2003); Shah, J. J. and Fox, R. O. (1999)], CFD does a poor job of predicting finite-rate chemistry effects, minor species formation and reactor extinction. In addition, micromixing effects, which are known to affect reaction rates [Fox, R. O. (2003)], are important to predict the reactor dynamics accurately. Due to its ability to account for turbulence-chemistry interactions, a transported PDF method is employed in this work to treat chemistry and micromixing. In this formulation, the chemical source terms appear in closed form and require no modeling [Fox, R. O. (2003)]. Free of stiffness due to the wide range of time scales of the reactions, a standard FV code computes the velocity and turbulence fields. The hybrid FV-PDF code employed in the work has been validated for a turbulent nonpremixed
flame and generally excellent agreement with experimental data was obtained [Raman, V. et al. (2004)]. This code as well as a reduced 21-step scheme involving 15 species [Shah, J. J. and Fox, R. O. (1999)], that has been demonstrated to capture the essential dynamics of the reactor and agrees closely with results obtained using detailed chemistry, has been used to investigate the behavior of lab-scale chlorination reactors [Raman, V. et al. (2001, 2003)].

In our earlier work, the premixed case was shown to offer the best performance with a high chloroform yield and maximum reactor stability. In the case of nonpremixed inlets, it is safer to use chlorine as the inner stream but the lab-scale reactor operation is unstable and prone to extinction [Raman, V. et al. (2003)].

As in our earlier work [Raman, V. et al. (2001, 2003)], the jet-stirred reactor has two coaxial inlets (see Fig. 6.1). The two streams can be introduced premixed or nonpremixed, leading to three different configurations that are analyzed. The rest of this paper is arranged in the following manner. First, in Sec. 6.2, we briefly describe the mathematical formulation and the numerical scheme. The reactor configuration and simulation conditions are described in Sec. 6.3, followed by a discussion of the dynamics of the scaled-up reactor. Conclusions are drawn about reactor performance in Sec. 6.5.

### 6.2 Description of CFD model

In this work, a structured FV code solves the Favre-averaged Navier-Stokes equations. A short overview of the compressible flow model used in the FV code is given below, followed by a short description of the composition PDF model. More details on both models can be found elsewhere [Fox, R. O. (2003); Raman, V. et al. (2004)].

#### 6.2.1 Compressible flow code

Neglecting body forces and external heat sources, the 3-D equations for continuity, momentum, and energy in a standard generalized frame of reference are of the form

\[
\Gamma \partial_t \hat{P} + \partial_t \hat{Q} + \partial_z \left( \hat{E} - \hat{E}_v \right) + \partial_\eta \left( \hat{F} - \hat{F}_v \right) + \partial_\zeta \left( \hat{G} - \hat{G}_v \right) = 0
\]  

(6.1)
where quantities in the generalized coordinate system are represented with hats. Using standard notation for mean-flow quantities, $\bar{\rho}$, $\bar{p}$, $\bar{T}$, $\bar{h}$ and $\bar{U}$ are the Reynolds-averaged mean density and pressure, and Favre-averaged temperature, enthalpy and Cartesian velocity components, respectively. $\hat{P}$, the primary variable vector, and $\hat{Q}$, the conserved variable vector, are related to the corresponding vectors in the Cartesian frame by $\hat{P} = J^{-1} P$ and $\hat{Q} = J^{-1} Q$, where $P = \left[ \bar{p}, \bar{U}, \bar{V}, \bar{W}, \bar{T} \right]^T$ and $Q = \left[ \bar{\rho}, \bar{\rho} \bar{U}, \bar{\rho} \bar{V}, \bar{\rho} \bar{W}, \bar{\rho} \bar{E} \right]^T$. $J$ represents the Jacobian of the transformed coordinates with respect to a Cartesian frame.

Similarly, the inviscid and viscous flux vectors in different reference frames are related by an expression of the form $\hat{E} = J^{-1} (\kappa_x E + \kappa_y F + \kappa_z G)$. It should be noted that the energy equation, although a part of the original FV formulation, is not solved to obtain the Favre-average temperature, which, instead, is determined by the PDF code [Raman, V. et al. (2004)]. The matrix $\Gamma$ is the preconditioner described elsewhere [Weiss, J. M. and Smith, W. A. (1994)]. $\tau$ and $t$ represent the pseudo-time and physical time, respectively. The turbulent viscosity $\mu_t = C_\mu \bar{k}^2/\varepsilon$ is obtained by solving a two-layer $k - \varepsilon$ model [Chen, H. C. and Patel, V. C. (1988)], and $C_\mu$ is a turbulence model constant equal to 0.09.

The FV code, working as a flow solver, provides a solution to the mean fields ($\bar{p}$, $\bar{U}$, $\bar{V}$, $\bar{W}$) and the turbulence fields ($\bar{k}$ and $\varepsilon$) conditioned on variables $W$ and $\bar{T}$, exclusively determined by the PDF code [Raman, V. et al. (2004)]. Using these flow quantities, the PDF code, which is briefly summarized below, is employed to obtain a new temperature $\bar{T}$ and molecular weight $W$. These variables are fed back to the FV code to update the flow field and turbulence fields. In the FV code, the gas mixture is regarded as an ideal gas, and $\bar{p} = \bar{\rho} R \bar{T} / W$ is used to update the mean density $\bar{\rho}$.

6.2.2 Lagrangian PDF code

Taking the molecular transport coefficients for all species and temperature to be equal and constant, the density-weighted composition PDF transport equation is [Pope, S. B. (1976,
\[ \frac{\partial \tilde{\rho} \tilde{f}_\phi}{\partial t} + \frac{\partial}{\partial x_i} \left( \tilde{\rho} \tilde{U}_i \tilde{f}_\phi \right) + \frac{\partial}{\partial x_i} \left[ \tilde{\rho} (\tilde{u}_i | \psi) \tilde{f}_\phi \right] = \theta \frac{\partial}{\partial x_i} \left[ \tilde{\rho} (\Gamma \nabla^2 \tilde{\phi}_i | \psi) \tilde{f}_\phi \right] - \frac{\partial}{\partial x_i} \left[ \tilde{\rho} \left( \Gamma \nabla^2 \tilde{\phi}_i + S_i (\psi) \right) \tilde{f}_\phi \right], \tag{6.2} \]

where \( \psi \) represents the composition vector. It can be noticed that the chemical source term \( S_i \) is in closed form and requires no modeling. However, the scalar-flux term \( \tilde{\rho} (\tilde{u}_i | \psi) \tilde{f}_\phi \) due to the scalar-conditioned velocity fluctuations (mesomixing) must be closed by a model that is consistent with the Reynolds-stress closure (\( k-\varepsilon \) model). In this work, a gradient-diffusion model is employed [Fox, R. O. (2003)]:

\[ \frac{\rho (\tilde{u}_i | \psi) \tilde{f}_\phi}{Sc_t} \frac{\partial \tilde{f}_\phi}{\partial x_i} = - \mu_t \frac{\partial \tilde{f}_\phi}{\partial x_i}, \tag{6.4} \]

where \( Sc_t \), the turbulent Schmidt number, is assumed to be a constant (0.8). In addition, the micromixing term \( (\tilde{\Gamma} \nabla^2 \tilde{\phi}_i | \psi) \) due to molecular mixing must be represented by a micromixing model. Here we use the interaction-by-exchange-with-the-mean (IEM) model [Villermaux, J. and Devillon, J. C. (1972)]. This model assumes a linear relaxation of the scalars towards their mean values:

\[ (\tilde{\Gamma} \nabla^2 \tilde{\phi}_i | \psi) = \frac{C_{\phi \varepsilon}}{2k} (\tilde{\phi} - \psi), \tag{6.5} \]

where \( C_{\phi} = 2 \) in this study.

For a 3-D time-dependent system involves \( N \)-species, the \( (N + 4) \) variables in Eq. 6.2 makes it intractable to solve using standard discretization methods [Fox, R. O. (2003)]. Pope proposed Lagrangian PDF methods to express the problem in terms of stochastic differential equations for so-called “notional” particles [Pope, S. B. (1976, 1985)]. Denoting the position and composition of a notional particle by \( X^* \) and \( \phi^* \), respectively, transport in physical space and composition space are governed by stochastic differential equations corresponding to Eq. 6.2 [Fox, R. O. (2003)]:

\[ dX^* = \left[ \tilde{u}(X^*, t) + \frac{1}{\tilde{\rho}(X^*, t)} \nabla \tilde{\rho}(X^*, t) \Gamma_{eff}(X^*, t) \right] dt + \sqrt{2 \Gamma_{eff}(X^*, t)} dW(t). \tag{6.6} \]

and

\[ \frac{d\phi^*}{dt} = C_{\phi \varepsilon}(X^*, t) \left( \tilde{\phi}(X^*, t) - \phi^* \right) + S(\phi^*), \tag{6.7} \]
where the mean velocity $\bar{U}(X^*, t)$ and the turbulence fields $\tilde{k}(X^*, t)$ and $\varepsilon(X^*, t)$ are known from the FV solution. The effective diffusivity $\Gamma_{eff}$ is the sum of the molecular and turbulent diffusivities. $dW(t)$ is a multi-variate Wiener process with mean zero $\langle dW_i(t) \rangle = 0$ and covariance structure $\langle dW_i(t)dW_j(s) \rangle = \delta_{ij}\delta(t-s)dt$.

Equations 6.6 and 6.7 are solved using a fractional time-stepping method [Fox, R. O. (2003)]. The transported PDF simulations of the chlorination reactor require at least $10^6$ particles. Solving Eq. 6.7 for such a large number of particles is prohibitive with traditional stiff ODE solvers. As in our earlier works [Raman, V. et al. (2001, 2003, 2004); Shah, J. J. and Fox, R. O. (1999)], a novel algorithm for reaction computation, in situ adaptive tabulation (ISAT) [Pope, S. B (1997)], is used to obtain considerable computational gains. Details on ISAT can be found elsewhere [Fox, R. O. (2003)].

### 6.3 Simulation conditions

In the cases studied here, an axisymmetric grid is used which necessities a particle clustering and breakup algorithm in the PDF code [Fox, R. O. (2003); Haworth, D. C. and El Tahry, S. H. (1991)]. Weights of particles are adjusted to be consistent with the cells in which they reside. In addition, a particle-tracking algorithm [Raman, V. et al. (2004)] which is applicable to nonorthogonal and clustered grids is employed. Readers may refer to our earlier work [Raman, V. et al. (2004)] for more details.

The global time step is controlled by the minimum local micromixing time for a nonreacting flow field. It was noticed that the change in the minimum micromixing time due to chemical reactions was so small that it could be neglected. In our simulations, the time step was set to $2 \times 10^{-3}$ s. Smaller time steps did not yield differences in the solutions.

The configuration of the jet-stirred chlorination reactor is represented in Fig. 6.1. The reactor walls are insulated unless specified otherwise. Three configurations are considered: (i) premixed inlets, (ii) nonpremixed inlets with chlorine in the inner jet, and (iii) nonpremixed inlets with chlorine in the outer jet. The inlet streams with a temperature of 323 K are introduced via two coaxial feed pipes. In the lab-scale reactor with premixed inlets and non-
premixed inlets with chlorine in the inner jet, the diameters of the inner and outer pipes are 0.02 m and 0.04 m, respectively. In the other nonpremixed case, the inner-jet diameter of the lab-scale reactor was increased to 0.034 m and the outer-jet diameter was kept the same. The inlet velocity of the streams in the lab-scale reactor is 3.1 m/s for both the premixed and nonpremixed cases. The Reynolds number based on the inlet-stream properties is $7 \times 10^4$ for the lab-scale reactor.

Inspired by West’s study on a simple perfectly stirred reactor that behaves similar to the real reactors, this work maintains the geometry similarity and residence time similarity. For the pilot-scale reactor, all the dimensions of the lab-scale reactor and the inlet velocity are multiplied by a factor of two. Thus the residence time $^1$ remains unchanged, although the Reynolds number increases by a factor of four to $2.8 \times 10^5$. For the plant-scale reactor, the dimensions of the lab-scale reactor are multiplied by a factor of ten, keeping the residence time unchanged. The corresponding Reynolds number increases by a factor of 100 to $7 \times 10^6$. The scale-up behavior of the reactor is analyzed by comparing the different reactors using the same feed-stream configurations.

The two-dimensional axisymmetric simulation domain is a rectangular area. All the simulations were executed on orthogonal axisymmetric meshes. Grid points are denser near the entrance region and at the interface of the two inlet jets in order to resolve sharp gradients. In the lab-scale reactor, a $53 \times 33$ mesh was used for all the feed configurations except the nonpremixed case with chlorine in outer jet, which adopted a $53 \times 69$ mesh. The grid number in each dimension is multiplied by a factor of two in simulations of the pilot-scale reactor. Initially there are 100 particles in each grid cell. A coarser grid ($200 \times 125$) is used for the plant-scale reactor, and 50 particles are used in order to save computational time.

The simulations were performed on a single processor on a 900-MHz SUNFIRE 6800, and carried out in three stages. First, a nonreacting field was generated by the FV code alone. Then the PDF code was run with infinitely fast micromixing ($\phi^* = \tilde{\phi}$) without update of the flow or turbulence fields. In the final stage, the IEM model was turned on, and the PDF

$^1$Calculation of the residence time is based on the assumption that chemicals in the reactor mix completely therefore the residence time is exclusively controlled by the flow filed.
code ran 1.5 – 2 residence times. The flow and turbulence fields were corrected every ten PDF steps. The FV solver iterates $M$ times before the next ten PDF steps are initialized. $M$ is a case-based number. It was reduced from 2500 to 500 and then to 200 as the reactor was scaled up to pilot scale and plant scale, respectively. More details on the simulation parameters can be found elsewhere [Raman, V. et al. (2004)].

6.4 Scale-up results

6.4.1 Premixed inlets

For this case, both inlet streams contain 25% chlorine, 36% methyl chloride and 39% methyl dichloride (% based on total mass). Sample results are shown in Figs. 6.2 and 6.3. Streamlines (black curves in figures) illustrate changes in the flow structure at each scale. Although the lab-scale reactor shows maximum stability [Raman, V. et al. (2003)] and high product yield (Fig. 6.3a), the pilot-scale reactor is prone to extinguish (Figs. 6.2b and 6.3b). The contracting recirculation area reduces energy feedback, leading to low temperatures at which chlorine disassociation becomes weaker. Since the chlorination process is initialized with chlorine free-radical formation, the primary reaction zone is controlled by the radical distribution. The efficiency of the reactor is determined by the chlorine dissociation to a large degree. As observed in the lab-scale reactor, most chlorine reactions occur in the thin diffusion layer surrounding the chlorine jet in the pilot-scale reactor. However, the amount of the residual free radicals is only one twentieth of that in the lab-scale reactor. More chlorine molecules leave the reactor, leading the outlet level of chlorine to increase to 1.1% which is $10^7$ times higher than that in the lab-scale reactor. All these observations indicate the scarcity of disassociated chlorine molecules causing slower chlorination and less reaction released heat. Therefore a non-reacting cold flow is expected as the eventual equilibrium state in the pilot-scale reactor. In order to keep the pilot-scale reactor lit, a change in operating conditions is required. We have tested two possibilities: an increased inlet chlorine level and heating the reactor walls.

An increase of the inlet chlorine level keeps the pilot-scale reactor lit and improves the
conversion of reactants (Figs. 6.2c and 6.3c). In this case, the inlet streams contain 27% chlorine and 34% methyl chloride, while the fraction of methyl dichloride remains unchanged. Although the maximum temperature of 750 K, which is situated between the inlet and the wall, is less than in the lab-scale reactor by 40 K, the pilot-scale reactor remains lit and gives a chloroform yield of 16% (Fig. 6.3c). The concentration of carbon tetrachloride in the outlet stream increases slightly from 0.045, and minor species formation is not favored. It is found that both chlorine molecules and the free chlorine radicals are consumed completely before the gas flow leaves the reactor. Moreover, methyl chloride consumption increases by 1.5%. This can be well understood if the effect of chemistry on the flow structures is taken into consideration. Due to the lower temperature rise, the tendency that gases are pushed out of the reactor is weaken. This increases the effective residence time of the reactants in the main stream, thereby increasing the extent of reaction and temperature. However, the shorter reattachment length indicates that less fluid is trapped in the recirculation zone. Thus, less reaction-released heat is carried back into the reaction zone, leading to a lower temperature rise. Eventually an equilibrium is reached where chlorine consumption is complete and the enthalpy increase is limited.

If an increase in the chlorine level of the inlet streams is not preferred, supplying heat is a feasible alternative to keep the reactor lit (Figs. 6.2d and 6.3d). The reactor walls, instead of being insulated, are maintained at a constant temperature of 753.15 K. The chloroform yield across the outlet is 14% by mass (Fig. 6.3d), which is equivalent to that in the lab-scale reactor. However the tetrachloride increases by 2%. Most tetrachloride forms at the corner of walls where chlorine free radicals are extremely scarce and the temperature is lower. It is interesting that the chlorine jet becomes sharper and shorter, illustrating a faster chlorine dissociation. This is a result of higher temperature gradients surrounding the jet caused by energy supplied by the reactor walls. The recirculation zone is much bigger than that shown in Fig. 6.2a, resulting in a longer residence time within which more heat is released. The maximum temperature in this reactor is 760 K.

These two strategies are also utilized as the reactor is further scaled up to the plant scale
(Figs. 6.2 and 6.3). In both cases, the computational domain consists of 25,452 control volumes. The total number of particles is more than one million. The turbulence time scale indicates slower mixing in the dead zone and the mixing time is around 1.5 times that in the lab-scale reactor. It can be seen (Figs. 6.2e and 6.2f) that the temperature in the reaction zone and the recirculation zone reaches 900 K. Both cases give a chloroform yield of 18% (Figs. 6.3e and 6.3f), which is the highest among all the studied cases. However, more minor species are generated at the same time. The reactor with isothermal walls tends to form more tetrachloride, which is similar to that seen in the pilot-scale reactor. Reactions become progressively faster as fluid travels across the reaction zone defined as the thin region with large temperature gradients. The plug-flow region following the reaction zone contains a homogeneous product and very little decomposition is observed.

The stability shown by the plant-scale reactor with a higher chlorine level motivates us to investigate how that reactor behaves with the feed configuration studied in the lab-scale reactor (Fig. 6.2g and Fig. 6.3g). Although the recirculation area is smaller than that shown in Fig. 6.2e, the reactor keeps lit and the maximum temperature reaches 900 K. As a result of the low inlet chlorine level, the product yield decreases to 15% (Fig. 6.8). Figures 6.2a, 6.2b and 6.2g indicate an interesting behavior of the reactors with this premixed feed configuration: the rate of mixing between the feed streams and the recirculated hot gases does not increase in proportion to the increase in the volume of incoming gases at the larger scales.

### 6.4.2 Chlorine in the inner jet

In this case, the reactants are nonpremixed and the chlorine stream is fed through the inner jet. The outer jet contains 48% methyl chloride and 52% methyl dichloride. Unlike the premixed case, the behavior of the reactor changes only slightly after scale up to pilot scale (Fig. 6.4b). At all three scales, the reaction zones are located at the end of the jet core. This is quite obvious considering the fact that a high degree of mixing is required to sustain reaction. The reaction zones have a “two-pronged” structure because of the entrainment of the outer cold streams in the recirculation zone. In the pilot-scale reactor, the streams mix faster at
the end of the jet core due to the smaller mixing timescale. This moves the hot zone towards the middle of the entrainment region, leading to stronger heat recirculation and higher outlet temperature (Fig. 6.4b). It should be mentioned that excessive reaction in the jet core tends to cause the reactor to run away. However, movement of the reaction further downstream will cut off enthalpy feedback resulting in reactor extinction. Hence this configuration is inherently unstable Raman, V. et al. (2003)]. This instability is apparent in the plant-scale reactor in which the hot zone keeps changing its location and shape along the stream wise direction. Figure 6.4c illustrates an instantaneous profile of the temperature.

In lab-scale and pilot-scale reactors, the chloroform mass fraction peaks downstream of the peak of the temperature due to the high decomposition rates at high temperatures (Fig. 6.4). The yield of the pilot-scale reactor is 9.5% (Fig. 6.4b). The carbon tetrachloride yield is reduced to 0.2%, which is much lower than that found in the lab-scale reactor. In the sharper reaction zone, species interact faster. The concentration of excess chlorine free radicals is much higher due to the fast dissociation of chlorine at high temperatures. This indicates an extremely low concentration of organic free radicals that can consume chlorine atoms. More organic free radicals are involved in the formation of carbon-carbon bonds. In the plant-scale reactor, the outlet product yield varies between 8-11% as a result of the instability.

6.4.3 Chlorine in the outer jet

In this case, the organics stream is in the inner jet and chlorine in the outer jet. The jet diameters have been changed to ensure that the inlet velocities are the same as the other two cases. In the lab-scale and pilot-scale reactors, the reaction zone is confined between the recirculation region and the outer jet (Fig. 6.5). The chlorine stream tends to enter the recirculation area, creating a “bifurcated” front. In the pilot-scale reactor, the recirculation region shifts to further downstream, leaving in the corner of the walls a zone in which the turbulence time scale is of the same order as the residence time. This explains the movement of the reaction zone in the streamwise direction. The recirculation region moves such a long distance that it disconnects from the hot zone, resulting in decreased temperatures (Fig. 6.5b).
Slower mixing and lower temperatures lead to slower depletion of chlorine. Thus the tendency to quench through carbon-carbon bond formation is inhibited while tertiary chlorination that forms carbon tetrachloride is favored, improving the product yield to 0.07 (Fig. 6.5b) as compared to 0.06 in the lab-scale reactor. Nevertheless, this yield is the lowest among all of the configurations studied for the pilot-scale reactor. The location of the reaction zone causes much of the primary chlorinated derivatives to pass through the reactor without reactions.

Although the reactor for this case remains lit after scale up, the reactor itself is inherently unstable [Raman, V. et al. (2003)]. Hence this reactor is of least industrial interest. For this reason, the behavior of the plant-scale reactor for this case was not investigated.

Centerline profiles of the temperature and chloroform are presented in Figs. 6.6–6.8 for each feed configuration and reactor scale. In general, we find the best product yield is obtained at all scales with premixed feed streams. We are thus motivated to use CFD to investigate possible instabilities in the premixed plant-scale reactor.

6.4.4 Instabilities in the plant-scale reactor

Plant operations are subject to a certain degree of uncertainty in the control of operating parameters. One of the important control parameters for the chlorination reaction is the mass fraction of chlorine in the inlet stream. Since high chlorine mass fraction can lead to secondary reactions and product decomposition, optimization and control of the inlet chlorine level is vital. Here, two different plant conditions that exhibit extinction instabilities are investigated. Details on the feed-stream configurations and other parameters are given in Table 6.1. Note that for these cases the premixed inlet jet is introduced through a coaxial sparger pipe to better represent the actual plant-scale reactor (see Fig. 6.9).

Case A represents a stable configuration with maximum product yield and is the desired set-point for the control system. Case B is an unstable operation in which reactor quenching has been observed. For each of the cases, two simulations were performed - one using the IEM micromixing model and the other assuming complete mixing as is usually done in FV simulations without sub-grid closure.
The results of Case A with and without a micromixing model are shown in Fig. 6.9. It can be seen that the micromixing model has very little effect on the temperature field. The addition of micromixing usually lengthens the reaction zone as seen in the simulations with the pilot-scale reactor. However, quantitatively there is little difference in the final product yield with both simulations predicting 14.3% chloroform mass fraction at the outlet. From the streamlines in Fig. 6.9), it can be seen that, qualitatively, the recirculation zone appears identical and the re-attachment point is located at almost the same axial location. It can be concluded that in this case, the micromixing model has very little effect on reactor performance.

In contrast, Case B corresponding to an unstable reactor configuration yielded very interesting results. The temperature plots in Fig. 6.10 show the results of both FV-PDF and no-closure FV simulations. The operating conditions correspond to a lower inlet chlorine mass-fraction and shorter mean residence time. Though the infinite-rate micromixing case shows reduced temperatures, the reactor stays lit. On the other hand, when finite-rate micromixing is used, the reactor quenches with a blob of unreacted reactants spreading into the reaction zone. The quenching process is initiated by the lowering of the temperature in the dead zone above the sparger. This leads to progressive cooling as observed in the infinite-rate micromixing case. However, slower heat-transfer rates fail to sustain the reaction. The ignition temperature for this mixture is around 650 K. It can be seen that the reaction zone near the sparger exit is significantly cooler than the ignition temperature. In addition, lower temperature gradients lead to weaker recirculation zones that do not penetrate the dead zone. The reduced enthalpy feedback leads finally to global extinction.

To understand the process of extinction, the axial profile of chlorine close to the outlet is studied. The axial plot of chlorine (Fig. 6.11) shows increasing mass fraction in the outlet stream. This indicates that the chlorination reactions are not complete as compared to previous cases where the chlorine consumption was close to 100%. The plot at the longest time corresponds to the instant at which extinction was observed. The reduction in reaction rate leads to residual chlorine in the outlet, indicating that extinction is not local and that the process was initiated long before the unreacted fluid entered the reaction zone. This observa-
tion rules out extinction due to numerical instabilities, which would have caused extinction to occur locally and would have occurred simultaneously with the cold fluid entrainment. The progressive cooling can be attributed only to the weak recirculation and lower heat-transfer rates.

6.5 Conclusions

A hybrid finite-volume/joint composition PDF simulation code with detailed chemistry has been used to simulate scale up of a gas-phase chlorination reactor with different feed-stream configurations. The detailed chemistry enabled the study of the reactor based on free-radical formation and turbulent transport.

The effects of reactor scale at constant residence time on the temperature and chemical conversion in a chlorination reactor were investigated. For the premixed case, it was found that as the size of the reactor increases, the temperature decreases until eventually extinction occurs. The latter is mainly due to the fact that the rate of enthalpy recirculation decreases with scale, resulting in reduced heating of the inlet stream. Although the reactor with premixed feed tends to extinguish after scale up, we show that the plant-scale reactor can be stabilized either by increasing the inlet chlorine level by 2%, or by heating the reactor walls to 753.15 K. In contrast, reactors with nonpremixed inlets are easier to scale up. Neither reactor efficiency nor stability changes significantly with scale. However, nonpremixed reactors yield poor selectivity to the desired product. In all cases, both the flow structure and chemistry are important in predicting the reactor performance.

PDF simulations take up to 99% of the total computational time. For the grid used in the simulations of the plant-scale reactor, the total number of Lagrangian particles employed is more than one million. Higher resolution solutions might give more details about the reactor performance; however, the computational cost is prohibitive on a single CPU. Parallelization of the PDF code will be implemented to overcome this difficulty.
Acknowledgments

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Table 6.1 Feed-Stream Composition and Operating Conditions for the Plant-Scale Reactor.

<table>
<thead>
<tr>
<th>Case</th>
<th>( Y_{\text{Cl}_2} )</th>
<th>( Y_{\text{CH}_3\text{Cl}} )</th>
<th>( Y_{\text{CH}_2\text{Cl}_2} )</th>
<th>Flow Rate (kg/s)</th>
<th>Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.2724</td>
<td>0.3819</td>
<td>0.3457</td>
<td>7.38</td>
<td>2.36</td>
</tr>
<tr>
<td>B</td>
<td>0.2184</td>
<td>0.4025</td>
<td>0.3791</td>
<td>8.84</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Figure 6.1 Schematic representation of jet-stirred reactor (not drawn to scale).
Figure 6.2  Temperature profiles for the premixed cases. a: Lab scale. b: Pilot scale (before extinction). c: Pilot scale, higher inlet chlorine level. d: Pilot scale, isothermal walls. e: Plant scale, higher inlet chlorine level. f: Plant scale, isothermal walls. g: Plant scale, lab-scale inlet chlorine level.
Figure 6.3 Chloroform profiles for the premixed cases. a: Lab scale. b: Pilot scale (before extinction). c: Pilot scale, higher inlet chlorine level. d: Pilot scale, isothermal walls. e: Plant scale, higher inlet chlorine level. f: Plant scale, isothermal walls. g: Plant scale, lab-scale inlet chlorine level.
Figure 6.4  Temperature (left) and chloroform (right) profiles for the non-premixed case with chlorine as the inner jet. a: Lab scale. b: Pilot scale. c: Plant scale.

Figure 6.5  Temperature (left) and chloroform (right) profiles for the non-premixed case with chlorine as the outer jet. a: Lab scale. b: Pilot scale.
Figure 6.6  Centerline profiles of (left) temperature and (right) chloroform in lab-scale reactor. —: premixed. · · ·: nonpremixed, chlorine in inner jet. − − −: nonpremixed, chlorine in outer jet.

Figure 6.7  Centerline profiles of (left) temperature and (right) chloroform in pilot-scale reactor. —: premixed, higher inlet chlorine level. •: premixed, isothermal walls. · · ·: nonpremixed, chlorine in inner jet. − − −: nonpremixed, chlorine in outer jet.
Figure 6.8  Centerline profiles of (left) temperature and (right) chloroform in plant-scale reactor. — : premixed, higher inlet chlorine level. • : premixed, isothermal walls. − − − : premixed, lab-scale inlet chlorine level.

Figure 6.9  Temperature profiles and streamlines of plant-scale reactor for Case A. Left: Infinite-rate micromixing. Right: Finite-rate micromixing.

Figure 6.10 Instantaneous temperature profiles of plant-scale reactor for Case B. Left: Infinite-rate micromixing. Right: Finite-rate micromixing.
Figure 6.11  Centerline profiles of chlorine (ppm) near reactor exit for Case
B. Arrow indicates the direction of increasing time. 

\[ \cdot \cdot \cdot \text{: } 0.01 \text{ s. } -- -- \text{: } 3 \text{ s. } -- \text{ : } 9 \text{ s.} \]
CHAPTER 7. CFD PREDICTIONS FOR CHEMICAL PROCESSING IN A CONFINED IMPINGING-JETS REACTOR

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Abstract

Confined impinging-jets reactors (CIJR) offer many advantages for the chemical processing of rapid processes such as precipitation and the production of organic nanoparticles. Nevertheless, due to the lack of predictive design criteria, the use of such a reactor for a new process currently requires a significant experimental campaign before it can be used commercially. Experimentally derived scale-up rules for CIJRs have recently been reported. Using carefully controlled experiments with a fast parallel-reaction system, these authors have measured the conversion of 2,2-dimethoxypropane (DMP) for a wide range of jet Reynolds numbers. In this work, we demonstrate that the experimental conversion data can be accurately predicted using computational fluid dynamics (CFD) for the range of jet Reynolds number where the flow is turbulent. In addition, we show that CFD provides a wealth of detailed information on the reacting flow inside of the CIJR. Such information provides excellent guidance for improving the performance of the reactor by, for example, changes in the geometry. By clearly illustrating the ability of CFD to reproduce (without adjustable parameters) the experimental data for a CIJR, this study makes a significant step in the direction of “experiment-free” design and scale up of chemical reactors.
7.1 Introduction

A confined impinging-jets reactor (CIJR) consists of two high-velocity, coaxial liquid jets that collide and produce mixing times on the order of milliseconds. As discussed in detail elsewhere [Johnson, B. K. and Prud’homme, R. K. (2003a)], the use of confined impinging jets for chemical processing has been widely studied in the past. In recent years, there has been a renewed interest in these devices due to their ability to achieve very fast mixing relative to other fast processing steps. This fact has proven crucial in a number of high-value applications such as the precipitation of biochemicals [Mahajan, A. J. and Kirwan, D. J. (1993, 1996)], and the precise control of the particle-size distribution in the production of nanoparticles containing organic actives and block copolymer [Johnson, B. K. and Prud’homme, R. K. (2003b,c)].

Although CIJRNs have been successfully used in production-scale processes [Johnson, B. K. and Prud’homme, R. K. (2003a)], scale-up rules have only recently been elucidated based on a comprehensive experimental study. Even so, these scale-up rules require the user to run at least one experiment for any new geometry or operating conditions in order to fix a proportionality constant in the expression for the mixing time. In theory, by employing a computational approach based on computational fluid dynamics (CFD) for turbulent reacting flow [Fox, R. O. (2003)], “experiment-free” design and scale up of CIJRNs should be possible. In practice, experiments would be required only to determine the fundamental rate constants appearing in the chemical kinetics. However, once determined, these constants could be used for arbitrary flow and geometrical conditions. Nevertheless, before such an approach can be used with confidence in industry, it must first be demonstrated that CFD predictions for a carefully designed and executed laboratory experiment are accurate and reliable.

The objective of this work is thus to validate a CFD model for mixing-sensitive reactions using the experimental data reported by Johnson and Prud’homme [Johnson, B. K. and Prud’homme, R. K. (2003a)]. The CFD model is based on solving the composition probability density function (PDF) transport equation [Fox, R. O. (2003)] using the direct-quadrature-method-of-moments (DQ MOM) [Marchisio, D. L. and Fox, R. O. (2005)]. The conditional molecular diffusion term is closed with the interaction-by-exchange-with-the-mean
(IEM) model. [Villermaux, J. and Devillon, J. C. (1972)] Wang and Fox [Wang, L. and Fox, R. O. (2004)] provide a complete description of the resulting DQMOM-IEM model. The geometry of the CIJR used in our CFD simulations is identical to the experiments, and is shown in Fig. 9.1. The diameter of the impinging jets, \(d\), is 0.5 mm. Letting \(D\), \(H\), \(Z\) and \(\delta\) represent the chamber diameter, height, length and the outlet diameter, respectively, their scaled values are \(D/d = 4.76\), \(H = 0.8D\), \(Z = 1.2D\), and \(\delta = 2d\). More details on the CIJR and the experimental setup can be found in the original article [Johnson, B. K. and Prud’homme, R. K. (2003a)].

The remainder of this work is organized as follows. First, we review briefly the parallel-reaction system used in the experiments and show that it can be modeled by two variables: mixture-fraction and a reaction-progress variable. Next, we introduce the CFD model and discuss how it can be employed to study the different scales of mixing present in the CIJR. An overview of the simulation conditions is then followed by a detailed discussion of our results. We close by drawing conclusions from our study that are relevant to the use of CFD for analyzing the CIJR and to chemical reactor scale up in general.

### 7.2 Parallel-reaction system

#### 7.2.1 Reaction kinetics

In the experiments, a pair of second-order parallel reactions is employed to evaluate the extent of mixing [Baldyga, J., et al. (1998)]. The reaction stoichiometry can be expressed as

\[
\begin{align*}
\text{H}^+ (A) + \text{OH}^- (B) & \xrightarrow{k_1} \text{H}_2\text{O} (P_1) \\
\text{H}^+ (A) + \text{CH}_3\text{C(}\text{OCH}_3\text{)}_2\text{CH}_3 (D) + (\text{H}_2\text{O}) & \xrightarrow{k_2} \text{H}^+ (A) + \text{CH}_3\text{COCH}_3 (P_2) + 2\text{CH}_3\text{OH} (P_3)
\end{align*}
\]

with rate constants \(k_1 = 1.4 \times 10^8\) m\(^3\)/mol-s and

\[
k_2 = 7.32 \times 10^7 \exp(-5556/T)10^{(0.05434+7.07 \times 10^{-5}C_s)} \text{ m}^3/\text{mol-s,}
\]

where \(C_s\) is the concentration of sodium chloride in the feed streams. As shown in Eq. 7.1, hereinafter we will refer to the reactants as \(A\), \(B\), and \(D\), and the products as \(P_1\), \(P_2\) and \(P_3\).
Note that the second reaction is catalytic so that $A$ appears as both a reactant and a product with no net consumption. Non-premixed feed conditions are used with $A$ in one stream, and $B$ and $D$ in the other stream. The reactor is operated in continuous mode with mass flow rate $m_1$ for the first stream containing $A$ and $m_2 = m_1$ for the second stream containing $B$ and $D$.

As discussed elsewhere [Johnson, B. K. and Prud’homme, R. K. (2003a)], since the first reaction is very rapid, when excess $B$ is present the second reaction will take place only under conditions where mixing is slow compared to its reaction rate. Thus, the conversion of $D$ is a sensitive measure of the extent of mixing in the CIJR. These authors [Johnson, B. K. and Prud’homme, R. K. (2003a)] have thus varied the reaction rate (by changing the feed concentrations) and the mixing rate (by changing $m_1$) independently, and measured the conversion of $D$. Using CFD to model the reactor, in this work we will vary the same operating parameters and compare the predicted conversion to the experimental data.

### 7.2.2 Model variables

As discussed by Fox [Fox, R. O. (2003)], mixing between two inlet streams can be described by a mixture fraction $\xi$, which is not affected by chemistry. By convention, we will set $\xi = 0$ in the stream containing $A$ and $\xi = 1$ in the other stream. Thus, the value of the average mixture fraction after complete mixing is

$$\bar{\xi} = \frac{m_2}{m_1 + m_2} = 0.5.$$  \hspace{1cm} (7.3)

Any deviations from complete mixing will manifest themselves as values of the mixture fraction different than $\bar{\xi}$. Likewise [Fox, R. O. (2003)], the chemical kinetics in Eq. 7.1 can be described by two reaction-progress variables $Y_1$ and $Y_2$, which are zero in the feed streams but otherwise always positive.

In terms of the mixture fraction and reaction-progress variables, the reactant concentrations are

$$c_A = A_0 \left[ 1 - \xi - (1 - \xi s_1) Y_1 \right],$$  \hspace{1cm} (7.4)

$$c_B = B_0 \left( \xi - \xi s_1 Y_1 \right)$$  \hspace{1cm} (7.5)
and

\[ c_D = D_0 (\xi - \xi_s Y_2), \quad (7.6) \]

where

\[ \xi_{s1} = \frac{A_0}{A_0 + B_0}, \quad (7.7) \]

and

\[ \xi_{s2} = \frac{A_0}{A_0 + D_0}, \quad (7.8) \]

and \( A_0, B_0, \) and \( D_0 \) are the inlet molar concentrations of reactants \( A, B \) and \( D \), respectively. Thus, in the absence of chemical reactions (that is, \( Y_1 = Y_2 = 0 \)), after complete mixing the reaction concentrations will depend only on \( \xi = \bar{\xi} \).

By making the change of variables given in Eqs. 7.4-7.6, the reaction rates for the reaction-progress variables can be expressed as

\[ S_1(\xi, Y_1) = \frac{k_1}{B_0 \xi_{s1}} c_A c_B = B_0 \xi_{s1} k_1 \left( \frac{1 - \xi}{1 - \xi_{s1}} - Y_1 \right) \left( \frac{\xi}{\xi_{s1}} - Y_1 \right), \quad (7.9) \]

and

\[ S_2(\xi, Y_1, Y_2) = \frac{k_2}{D_0 \xi_{s2}} c_A c_D = B_0 \xi_{s1} k_2 \left( \frac{1 - \xi}{1 - \xi_{s1}} - Y_1 \right) \left( \frac{\xi}{\xi_{s2}} - Y_2 \right). \quad (7.10) \]

Note that since the reaction rates must always be non-negative, the chemically accessible values of the reaction-progress variables will depend on the value of the mixture fraction. We will discuss this point further by looking next at limiting cases where the rate constant \( k_1 \) is very large and \( k_2 \) is finite.

### 7.2.3 Limiting cases

Due to the large value of \( k_1 \), the first reaction is essentially instantaneous compared to the characteristic mixing times in the CIJR. This implies that \( Y_1 \) can be written in terms of \( \xi \) by setting the corresponding reaction-rate expression \( (S_1) \) equal to zero:

\[ Y_{1\infty} = \min \left( \frac{\xi}{\xi_{s1}}, \frac{1 - \xi}{1 - \xi_{s1}} \right). \quad (7.11) \]
In order to avoid numerical difficulties associated with treating the first reaction with a finite-rate chemistry solver, we will use this infinite-rate approximation in our CFD simulations of the CIJR.

Note that Eq. 7.11 implies that \( A \) and \( B \) cannot coexist at any point in the flow. Using this infinite-rate approximation, we need only solve transport equations for \( \xi \) and \( Y_2 \), where the source term for \( Y_2 \) is now

\[
S_{2\infty}(\xi, Y_2) = B_0 \xi s_2 k_2 \left( \frac{1 - \xi}{1 - \xi s_1} - Y_{1\infty} \right) \left( \frac{\xi}{\xi s_2} - Y_2 \right).
\] (7.12)

Note that \( S_{2\infty} \) must be non-negative, and thus the expression above only holds for \( \xi \) and \( Y_2 \) values that satisfy this condition. For all other values, \( S_{2\infty} \) is null. Applying Eq. 7.11, we find that when \( S_{2\infty} \) is non-zero, it equals

\[
S_{2\infty}(\xi, Y_2) = A_0 k_2 \left( 1 - \frac{\xi}{\xi s_1} \right) \left( \frac{\xi}{\xi s_2} - Y_2 \right) \text{ if } 0 \leq \xi \leq \xi s_1 \text{ and } 0 \leq Y_2 \leq \xi/\xi s_2.
\] (7.13)

The region in \( \xi-Y_2 \) composition space where this chemical source term is non-zero is shown in Fig. 7.2. Note that the maximum conversion of \( D \) occurs when \( \xi = \xi s_1 \) and corresponds to \( Y_{2\max} = \xi s_1/\xi s_2 \) or (using Eq. 7.6) to \( c_D = 0 \) (that is, complete conversion).

As mentioned earlier, the reactor is operated with excess \( B \) so that \( \xi s_1 = 0.4878 \). Since equal flow rates are used for the inlet streams, the average mixture fraction is just outside the reaction region: \( \xi s_1 < \bar{\xi} = 0.5 \). Thus, if mixing were much faster than the characteristic reaction time of Eq. 7.13 \( ((A_0 k_2)^{-1}) \), the mixture fraction in all fluid particles would be equal to the mean \( (\xi = \bar{\xi}) \) and no reaction would occur so that \( Y_2 = 0 \).

In the opposite limit, the maximum attainable value for \( Y_2 \) when \( \xi s_1 \leq \xi \leq 1 \) is the mixing line [ Fox, R. O. (2003)], defined by

\[
Y_{2\text{mix}}(\xi) = Y_{2\max} \left( \frac{1 - \xi}{1 - \xi s_1} \right) \text{ for } \xi s_1 \leq \xi \leq 1,
\] (7.14)

and shown as a dashed line in Fig. 7.2. Using this expression, we find that the maximum attainable conversion is

\[
X_{\max} = \frac{\xi s_1(1 - \bar{\xi})}{\bar{\xi}(1 - \xi s_1)} \text{ for } \xi s_1 \leq \bar{\xi} \leq 1.
\] (7.15)
In the experiments, the maximum conversion is thus \( X_{\text{max}} = 0.9524 \), and would occur when the second reaction is very fast relative to mixing.

In summary, the accessible \( \xi-Y_2 \) phase space for this chemical system is given by the triangular region in Fig. 7.2. Phase-space trajectories begin at the two feed streams [stream 1: \((0, 0)\) and stream 2: \((1, 0)\)] and end at the perfect-mixing point \((\bar{\xi}, \bar{Y}_2)\). If \( \xi_{s1} < \bar{\xi} \), then the value of \( \bar{Y}_2 \) is determined by the amount of time spent in the region with non-zero source term \( (t_{\text{mix}}) \) and the characteristic time of the second reaction \( (t_r) \). If \( t_r \) is large compared to \( t_{\text{mix}} \), then \( \bar{Y}_2 \) will be near zero. If the inverse is true, then \( \bar{Y}_2 \) will be near \( Y_{2\text{max}} \). The predicted value of \( \bar{Y}_2 \) thus serves as a measure of the average mixing time for the CIJR.

### 7.3 Reactive mixing model

#### 7.3.1 DQMOM-IEM model

In order to model reactive mixing using CFD, a micromixing model is needed to describe the interactions between chemistry and turbulent mixing [Fox, R. O. (2003)]. In this work, we will use the two-environment DQMOM-IEM model [Wang, L. and Fox, R. O. (2004)]. The CFD model solves transport equations for the mixture fraction \( \xi_n \), and reaction-progress variable \( Y_{2n} \) in the \( n \)th environment with \( n = 1, 2 \). Each environment represents one inlet stream. The total number of transport equations needed to treat mixing and chemical reactions for the chemical system under consideration is five. The conserved scalars appearing in the model are \( p_1, p_1\xi_1, p_2\xi_2, p_1Y_{21} \) and \( p_2Y_{22} \), where \( p_n \) is the mass fraction of the \( n \)th environment.

Denoting the mean fluid velocity and mean density as \( \langle U \rangle \) and \( \rho \), respectively, the transport equation for the mass fraction of fluid coming from the first inlet \( (p_1) \) is

\[
\frac{\partial \rho p_1}{\partial t} + \nabla \cdot (\rho \langle U \rangle p_1) = \nabla \cdot (\rho \Gamma_T \nabla p_1),
\]

(7.16)

and the mass fraction of fluid coming from the second inlet is \( p_2 = 1 - p_1 \). In Eq. 7.16, the turbulent diffusivity is defined as

\[
\Gamma_T = \frac{C_\mu k^2}{S_{CT} \varepsilon},
\]

(7.17)
with $C_\mu = 0.09$ and $Sc_T = 0.7$. $k$ and $\varepsilon$ are the turbulent kinetic energy and the turbulent dissipation rate, respectively, and are computed using the $k$-$\varepsilon$ model. More details on turbulence modeling can be found elsewhere [Pope, S. B. (2000)].

The transport equations for the mixture fraction in the two environments are

$$\frac{\partial \rho p_1 \xi_1}{\partial t} + \nabla \cdot (\rho \langle U \rangle p_1 \xi_1) = \nabla \cdot [\rho \Gamma_T \nabla (p_1 \xi_1)]$$

$$+ \rho \gamma p_1 p_2 (\xi_2 - \xi_1) + \frac{\rho \Gamma_T}{\xi_1 - \xi_2} \left( p_1 |\nabla \xi_1|^2 + p_2 |\nabla \xi_2|^2 \right) \quad (7.18)$$

and

$$\frac{\partial \rho p_2 \xi_2}{\partial t} + \nabla \cdot (\rho \langle U \rangle p_2 \xi_2) = \nabla \cdot [\rho \Gamma_T \nabla (p_2 \xi_2)]$$

$$+ \rho \gamma p_1 p_2 (\xi_1 - \xi_2) + \frac{\rho \Gamma_T}{\xi_2 - \xi_1} \left( p_1 |\nabla \xi_1|^2 + p_2 |\nabla \xi_2|^2 \right). \quad (7.19)$$

The final two terms in these equations represent micromixing. If these terms are neglected, then it can easily be shown using Eq. 7.16 that $\xi_1$ and $\xi_2$ will be constant and equal to their inlet values. Thus, the effect of micromixing is to move the mixture fraction in each environment towards the local mean value $\langle \xi \rangle$, or in other words to reduce the mixture-fraction variance $\langle \xi'^2 \rangle$.

The transport equations for the reaction-progress variable in the two environments are

$$\frac{\partial \rho p_1 Y_{21}}{\partial t} + \nabla \cdot (\rho \langle U \rangle p_1 Y_{21}) = \nabla \cdot [\rho \Gamma_T \nabla (p_1 Y_{21})] + \rho p_1 S_{2\infty}(\xi_1, Y_{21})$$

$$+ \rho \gamma p_1 p_2 (Y_{22} - Y_{21}) + \frac{\rho \Gamma_T}{Y_{21} - Y_{22}} \left( p_1 |\nabla Y_{21}|^2 + p_2 |\nabla Y_{22}|^2 \right) \quad (7.20)$$

and

$$\frac{\partial \rho p_2 Y_{22}}{\partial t} + \nabla \cdot (\rho \langle U \rangle p_2 Y_{22}) = \nabla \cdot [\rho \Gamma_T \nabla (p_2 Y_{22})] + \rho p_2 S_{2\infty}(\xi_2, Y_{22})$$

$$+ \rho \gamma p_1 p_2 (Y_{21} - Y_{22}) + \frac{\rho \Gamma_T}{Y_{22} - Y_{21}} \left( p_1 |\nabla Y_{21}|^2 + p_2 |\nabla Y_{22}|^2 \right). \quad (7.21)$$

Except for the chemical source term, these equations have the same form as those used for the mixture fractions. Note that the chemical source term ($S_{2\infty}$) is evaluated using the mixture fraction and reaction-progress variable in the particular environment. The average chemical
source term \( \langle S_2^{\infty}(\xi, Y_2) \rangle \) will thus not be equal to \( S_2^{\infty}(\langle \xi \rangle, \langle Y_2 \rangle) \) unless micromixing occurs much faster than the second reaction.

Once the mixture fraction and the reaction-progress variable in each environment are known, the species concentrations in the \( n \)th environment can be obtained using Eqs. 7.4–7.6:

\[
c_{An} = A_0 \left[ 1 - \xi_n - (1 - \xi_{s1}) Y_{1n} \right],
\]

\[
c_{Bn} = B_0 (\xi_n - \xi_{s1} Y_{1n})
\]

and

\[
c_{Dn} = D_0 (\xi_n - \xi_{s2} Y_{2n}).
\]

The mean concentrations are then defined by

\[
\langle c_A \rangle = p_1 c_{A1} + p_2 c_{A2},
\]

\[
\langle c_B \rangle = p_1 c_{B1} + p_2 c_{B2}
\]

and

\[
\langle c_D \rangle = p_1 c_{D1} + p_2 c_{D2}.
\]

The overall conversion of \( D \), denoted by \( X \), is computed using

\[
X = 1 - \frac{\langle c_D \rangle}{D_0 \xi},
\]

where the “mixing-cup” average of \( \langle c_D \rangle \) at the outlet is defined by [ Bird, R. B. et al. (2002)]

\[
\langle c_D \rangle = \frac{1}{m_3} \int_{\text{outlet}} \rho \langle c_D \rangle \langle U \rangle \cdot \mathbf{n} dS.
\]

\( m_3 = m_1 + m_2 \) is the outlet mass flow rate, and \( \mathbf{n} \) is the outward-directed normal vector on the outlet surface \( S \). Note that \( \langle c_D \rangle \) would be equal to \( \langle c_D \rangle \) if the outlet flow were completely macromixed. Also note that due to the small Reynolds number in the outlet tube, the outlet velocity is far from plug flow. Thus, the mixing-cup average in Eq. 7.29 cannot be replaced with the surface average when computing \( \langle c_D \rangle \).
7.3.2 Scales of mixing

In terms of the model variables, the mixture-fraction mean is defined by

\[ \langle \xi \rangle = p_1 \xi_1 + p_2 \xi_2, \] (7.30)

and the mixture-fraction variance by

\[ \langle \xi'^2 \rangle = p_1 \xi_1^2 + p_2 \xi_2^2 - \langle \xi \rangle^2. \] (7.31)

By summing Eqs. 7.18 and 7.19, the Reynolds-average transport equation for \( \langle \xi \rangle \) is recovered:

\[ \frac{\partial \rho \langle \xi \rangle}{\partial t} + \nabla \cdot (\rho \langle U \rangle \langle \xi \rangle) = \nabla \cdot (\rho \Gamma_T \nabla \langle \xi \rangle). \] (7.32)

Using similar manipulations, [Fox, R. O. (2003)] the Reynolds-average transport equation for \( \langle \xi'^2 \rangle \) can also be recovered:

\[ \frac{\partial \rho \langle \xi'^2 \rangle}{\partial t} + \nabla \cdot (\rho \langle U \rangle \langle \xi'^2 \rangle) = \nabla \cdot (\rho \Gamma_T \nabla \langle \xi'^2 \rangle) + 2 \rho \Gamma_T |\nabla \langle \xi \rangle|^2 - 2 \rho \gamma \langle \xi'^2 \rangle. \] (7.33)

The second term on the right-hand side is a production term due to gradients in the mixture-fraction mean. The final term is a dissipation term due to micromixing.

Using the mixture-fraction mean and variance, we can define two types of segregation. The first type, large-scale segregation (LSS), is defined as deviations of \( \langle \xi \rangle \) from the average \( \bar{\xi} \) and can be measured by a LSS variance:

\[ \langle \xi'^2 \rangle_{LSS} = (\langle \xi \rangle - \bar{\xi})^2. \] (7.34)

Starting from Eq. 7.32, the transport equation for the LSS variance can be found:

\[ \frac{\partial \rho \langle \xi'^2 \rangle_{LSS}}{\partial t} + \nabla \cdot (\rho \langle U \rangle \langle \xi'^2 \rangle_{LSS}) = \nabla \cdot (\rho \Gamma_T \nabla \langle \xi'^2 \rangle_{LSS}) - 2 \rho \Gamma_T |\nabla \langle \xi \rangle|^2. \] (7.35)

The characteristic decay time for LSS variance is thus given by

\[ t_{LSS} = \frac{\langle \xi'^2 \rangle_{LSS}}{2 \Gamma_T |\nabla \langle \xi \rangle|^2}, \] (7.36)

which in the mixing community is commonly called the “blend” or “macromixing” time (albeit defined in this case as a local quantity). Note that the LSS variance has no production term.
in its transport equation. Instead, \( \langle \xi'^2 \rangle_{\text{LSS}} = 0.25 \) is non-zero in the inlet streams, and decays towards zero at the outlet. (Or at least it should if the residence time is long enough to allow for complete mixing).

The loss of LSS variance leads to production in Eq. 7.33 of small-scale segregation (SSS), which is measured by \( \langle \xi'^2 \rangle \). The characteristic decay time for SSS variance is given by

\[
t_{\text{SSS}} = \frac{1}{2\gamma},
\]

and is commonly known in turbulent-mixing theory as the micromixing time [Fox, R. O. (2003)]. In turbulent-transport models, the micromixing parameter \( \gamma \) is modeled by

\[
\gamma = \frac{C_\phi \varepsilon}{2k},
\]

with \( C_\phi \approx 2 \) for high-Reynolds-number flow [Fox, R. O. (2003)]. Note that if \( C_\phi = 0 \), the mixture fractions and reaction-progress variables in the DQ MOM-IEM model will stay at their (constant) inlet values throughout the flow domain, and hence no reactions will occur in this limit. The SSS variance and the conversion of \( D \) are thus controlled directly by the model used for \( \gamma \), and indirectly by \( t_{\text{LSS}} \) (since LSS variance must be eliminated before any reactions can occur).

For a fixed Schmidt number (\( Sc = \nu/\Gamma \) where \( \nu \) is the molecular kinematic viscosity and \( \Gamma \) is the molecular diffusivity), it is well known that \( C_\phi \) is a function of the local turbulent Reynolds number [Corrsin, S. (1964)]. In general, for \( Sc \gg 1 \) (that is, liquids), Eq. 7.38 with \( C_\phi \approx 2 \) overestimates the micromixing rate [Fox, R. O. (2003)]. The local turbulence level can be quantified by a turbulent Reynolds number defined as [Fox, R. O. (2003)]

\[
Re_1 = \frac{k}{(\varepsilon \nu)^{1/2}},
\]

where \( \nu \approx 2.073 \times 10^{-6} \text{ m}^2/\text{s} \) in this work.

The dependence of \( C_\phi \) on \( Re_1 \) can be understood by considering the shape of the scalar energy spectrum \( E_\phi(\kappa) \) as a function of \( Re_1 \) for fixed \( Sc = 1000 \) (the shape is insensitive to \( Sc \) for values much larger than unity). Using a model scalar spectrum [Fox, R. O. (2003)] for \( Re_1 = (1, 10, 100, 1000) \) we find the spectra shown in Figs. 7.3 and 7.4 where we have
implicitly assumed that the turbulence integral scale $L_u$ is independent of $Re_1$ (that is, it is fixed by the geometry of the CIJR). Thus, the dimensionless wavenumber $\kappa = 1$ corresponds to the turbulence integral scale [Fox, R. O. (2003)]. These scalar spectra can be interpreted as follows. For $Re_1 = 1$, the turbulence integral scale and the Kolmogorov scale $\eta$ are equal so that the scalar energy spectrum has no inertial-convective sub-range. Instead, for $1 < \kappa$ it is composed almost entirely of a viscous-convective subrange that scales like $E_\phi \sim \kappa^{-1}$, followed by an exponentially decaying viscous-diffusive sub-range beginning near the Batchelor scale $\lambda_B = Sc^{-1/2}\eta$ (or, in terms of dimensionless wavenumbers, near $\kappa = Sc^{1/2}Re_1^{3/2}$). At $Re_1 = 10$, there is still no well-defined inertial-convective sub-range. However, at $Re_1 = 100$, a short inertial-convective sub-range exists up to approximately $\kappa = Re_1^{3/2}$, which scales like $E_\phi \sim \kappa^{-5/3}$. This is followed by a viscous-convective sub-range where $E_\phi \sim \kappa^{-1}$, and then by the viscous-diffusive sub-range. Finally, at $Re_1 = 1000$ the scalar spectrum is fully developed with clearly visible inertial-convective, viscous-convective, and viscous-diffusive sub-ranges.

Likewise, in the model turbulent energy spectra (Fig. 7.3), the $-5/3$ law can only be seen clearly at high Reynolds numbers.

As explained by Fox [Fox, R. O. (2003)] and originally proposed by Corrsin [Corrsin, S. (1964)], by integrating over the model scalar spectrum we can compute the mechanical-to-scalar time-scale ratio $R$, which is equal to $C_\phi$. Assuming $Sc = 1000$, the dependence of $C_\phi$ on $Re_1$ found in this manner is shown in Fig. 7.5. As expected, the shape of the scalar spectrum has a strong effect on $C_\phi$, especially at low Reynolds numbers. In general, the decay rate of SSS variance is considerably smaller than the rate seen for a fully developed spectrum when $Re_1 < 100$. The dependence of $C_\phi$ on $Re_1$ is approximated in our CFD simulations by the following expression:

$$C_\phi = \sum_{n=0}^{6} a_n (\log_{10} Re_1)^n \quad \text{for } Re_1 \geq 0.2,$$

which is also shown in Fig. 7.5. Here $a_0 = 0.4093$, $a_1 = 0.6015$, $a_2 = 0.5851$, $a_3 = 0.09472$, $a_4 = -0.3903$, $a_5 = 0.1461$, and $a_6 = -0.01604$.

Because the local turbulent Reynolds number in the CIJR is found to be less than 65 for all of the flow conditions used in the experiments, accurate predictions of the chemical conversion
are only possible by including low-Reynolds-number effects in the model for the micromixing rate. Finally, note that this procedure for finding the dependence of $C_\phi$ on $Re_1$ can be used for other Schmidt numbers. For example, we have included in Fig. 7.5 the results for $Sc = 1$, which would be appropriate for modeling gas-phase flows.

Differences in our interpretation of the micromixing time $t_{SSS}$ as compared to “classical” micromixing theory [Baldyga, J. and Bourne, J. R. (1984); Baldyga, J. A. and Bourne, J. R. (1999)] deserve comment. First, in the classical theory it is implicitly assumed that the flow is turbulent enough to allow for a clear separation of scales between the energy-containing and dissipation ranges. As seen in Fig. 7.4, this will only occur if the local turbulence Reynolds number is greater than approximately 100. As mentioned above, even for the highest inlet jet Reynolds numbers investigated, the CIJR has $Re_1$ values that are much lower than 100. Thus, fully developed turbulence theory does not apply for the CIJR. Nevertheless, because of the lack of an inertial-convective subrange at low Reynolds numbers, $t_{SSS}$ does not have pure inertial-range scaling either (that is, $C_\phi$ is not constant). Instead, as the jet Reynolds number is increased, $Re_1$ increases leading to an increase in $C_\phi$ due to changes in the shape of the scalar spectrum. The fact that the experiments exhibit Kolmogorov scaling for the micromixing time [Johnson, B. K. and Prud’homme, R. K. (2003a)] can be attributed to the presence of only the viscous-convective subrange for low $Re_1$. Thus, the question of how the micromixing time depends on the inlet jet Reynolds number is more complicated than the simple scaling theory presented by Johnson and Prud’homme [Johnson, B. K. and Prud’homme, R. K. (2003a)]. We will return to this topic later when discussing the CFD simulation results.

7.4 Simulation conditions

The CFD code Fluent 6.2 was used to solve the turbulence model and scalar transport equations. The computational grid consisted of at least 20880 hexahedral cells, with more cells required for grid-independent solutions at higher Reynolds numbers. The five dependent variables used in the DQMOM-IEM model are

$$X_1 = p_1, X_2 = p_1 \xi_1, X_3 = p_2 \xi_2, X_4 = p_1 Y_{21} \text{ and } X_5 = p_2 Y_{22};$$
where \( p_2 = 1 - X_1 \). These variables were implemented in Fluent 6.2 as user-defined scalars. The inlet conditions in the first inlet stream are \( X_1 = 1 \) and \( X_2 = X_3 = X_4 = X_5 = 0 \), and in the second inlet stream, \( X_1 = X_2 = 0 \), \( X_3 = 1 \), and \( X_4 = X_5 = 0 \). Note that by definition, \( \xi_1 = 0 \) and \( \xi_2 = 1 \) in both inlet streams. Thus, for example, whenever \( p_2 = 0 \) the ratio \( X_3/p_2 = 1 \). The flow rates of the two inlet streams are equal. Therefore, under perfectly mixed conditions, the outlet values for the mass fractions would be \( p_1 = p_2 = 0.5 \). The properties of the flow are assumed to be constant. The density and the viscosity are 962.5 kg/m\(^3\) and 0.001995 kg/m·s, respectively.

The characteristic reaction time is defined as \( t_r = (k_2C_{A0})^{-1} \), where \( C_{A0} \) is the average concentration of \( A \) after mixing as if no reaction had occurred:

\[
C_{A0} = (1 - \xi)A_0 = 0.5A_0. \tag{7.41}
\]

The temperature is assumed to be 298 K and kept constant. Therefore the rate constant (Eq. 7.2) based on the inlet stream containing \( A \) and 90 mol/m\(^3\) sodium chloride is \( k_2 = 0.67313 \) m\(^3\)/mol·s. As in the experiments, \( t_r \) (ms) was chosen to be 317, 181, 61, 28, 16.7, 9.5, 6.5, and 4.8. Therefore, the value of \( C_{A0} \) corresponding to \( t_r = 317 \) ms is 4.686 mol/m\(^3\) and thus \( A_0 = 9.373 \) mol/m\(^3\). The inlet concentration of \( B \) is \( B_0 = 9.842 \) mol/m\(^3\) and \( D_0 = 9.373 \) mol/m\(^3\) to satisfy the molar ratio of reagents (1:1.05:1) adopted in all the experimental runs. The inlet concentrations corresponding to the characteristic reaction times are summarized in Table 7.1.

As done in the experiments, the inlet jet Reynolds number, defined by

\[
Re_j = \frac{d_1 U_1}{\nu_1}, \tag{7.42}
\]

is computed based on the inlet velocity, the diameter of the inlet tube \((d_1 = 0.5 \) mm\) and the properties of the mixed stream as if only the first reaction has occurred. Note that \( Re_j \) represents the integral-scale Reynolds number in the CIJR. Thus, the local turbulence Reynolds number will scale like \([\text{Fox, R. O. (2003)}] Re_1 \sim Re_j^{1/2} \). Hence the micromixing time \( t_{SSS} \) will depend on \( Re_j \) through both the \( Re_1 \)-dependence of \( C_\phi \) and the dependence of \( \gamma \) (Eq. 7.38) on \( k/\varepsilon \sim Re_j^{-1} \). The overall dependence of the micromixing time on \( Re_j \) will thus scale like
\( t_{\text{SSS}} \sim [Re_j C_\phi(Re_j)]^{-1} \), and will vary from \( t_{\text{SSS}} \sim Re_j^{-3/2} \) at low to moderate jet Reynolds numbers to \( t_{\text{SSS}} \sim Re_j^{-1} \) at (very) high jet Reynolds numbers. The jet Reynolds numbers and the corresponding inlet velocities adopted in the simulations are shown in Table 7.2. The standard \( k-\varepsilon \) model in Fluent 6.2 with enhanced wall treatment was employed to compute the turbulent kinetic energy and dissipation. Fluent 6.2 offers another two wall treatment options: the standard wall functions and the non-equilibrium wall functions. However, they were not employed in our simulations since the law of the wall assumption is questionable for the three-dimensional flow in the CIJR. The enhanced wall treatment involves a two-layer \( k-\varepsilon \) model the performance of which is satisfactory for complex flows. More details can be found elsewhere [Chen, H. C. and Patel, V. C. (1988)].

It should be noted that the length-to-diameter ratio, \( L/d \), of the inlet feed tubes in the experiments was designed to be a minimum of eight to ensure that the jets were stable. However, in order to improve the computational efficiency, \( L/d = 1.62 \) in the computations. The inlet boundary conditions for the two jets are assumed to be identical and given by the outflow of a tube with \( L/d = 10 \). Similarly, in the experiments the exit-tube runner was designed to be at least ten times the outlet diameter in order to ensure that the streams were fully mixed prior to sample collection. However, we use \( K/\delta = 1.62 \) in our computations. The simulation results revealed that unless \( t_r \) is small (for example, 4.8 ms) and the jet Reynolds number is not high enough (that is, \( Re_j < 500 \)), the simulated conversion of \( D \) for a domain with \( K/\delta = 10 \) (Domain B) is very close to that for a domain with \( K/\delta = 1.62 \) (Domain A). More details are given in the discussion of the results below. Unless specified otherwise, the computational results are found using Domain A.

Because the density and viscosity are constant (that is, independent of the scalar fields), the turbulent flow field can be obtained first before solving the other scalar transport equations. Thus, for a fixed jet Reynolds number, the CFD solution procedure can be divided into three sequential steps:

1. Solve the turbulence model for \( \langle U \rangle, k \) and \( \varepsilon \).

2. Solve the non-reacting DQMOM-IEM model to find \( p_1, \xi_1 \) and \( \xi_2 \).
3. For each value of $t_r$, solve the reacting DQMOM-IEM model for $Y_{21}$ and $Y_{22}$.

This procedure is facilitated by the ability to solve only selected transport equations in Fluent 6.2 while holding all other variables constant.

### 7.5 Results and discussion

#### 7.5.1 Turbulent-flow fields

Sample distributions of the turbulent kinetic energy and dissipation rate with $Re_j = 400$ are shown in Fig. 7.6. The turbulent kinetic energy has a peak value at the interface of the impinging jets as expected. In general, the zone of intense mixing is limited to a small region of the total volume of the CIJR. At lower values of $Re_j$, fluid from the inlets can easily bypass the mixing zone and large-scale segregation is observed in the reactor and at the reactor outlet. The pressure drop across the CIJR is shown in Table 7.3 as a function of the jet Reynolds number. Note the substantial increase in the pressure drop between $Re_j = 1000$ and 2000. This increase is due to the formation of a turbulent zone at the reactor outlet as discussed below.

Note that $Re_1$ is the ratio of the turbulence integral time scale $\tau_u = k/\varepsilon$ and the Kolmogorov time scale $\tau_\eta = (\nu/\varepsilon)^{1/2}$. Thus, at least conceptually, $Re_1 = 1$ would correspond to a flow with only one time scale (that is, laminar), and $Re_1$ increases proportional to the Taylor-scale Reynolds number [Fox, R. O. (2003)] as the flow becomes more turbulent. Generally speaking, a flow must have $Re_1 \gg 10$ in order to be considered turbulent (that is, amenable to Reynolds-average turbulence models). Moreover, using the model energy spectrum [Pope, S. B. (2000)], it is possible to show [Fox, R. O. (2003)] that $Re_1 > 100$ is required for the existence of an inertial range (that is, high-Reynolds-number flow). In general, care must be taken when using standard turbulence models for flows with $Re_1 < 10$.

$Re_1$ in the CIJR varies with $Re_j$ as shown in Fig. 7.7. When $Re_j = 200$, $Re_1 < 23$ everywhere except in a small central core of the impingement zone, indicating that the predictions of the turbulence model must be treated with caution when $Re_j \leq 200$. When $Re_j = 400$, $Re_1 \leq 26$ in much of the flow, indicating that the flow is moderately turbulent (although no
inertial range exists). When \( Re_j = 1000 \), \( Re_1 \leq 30 \) in much of the flow. Hence, as noted earlier, the flow in a CIJR cannot be considered to be fully developed turbulence in most of the range considered in the experiments. When \( Re_j = 4000 \), a second zone of turbulence with \( Re_1 \leq 64 \) is found at the outlet to the reactor. It is this zone that changes the scaling behavior of the mixing times for \( Re_j > 1000 \) seen below. Due to the high anisotropy of the flows in the CIJR, the turbulent field and the mixing timescales predicted tend to be affected by the turbulence model. As done elsewhere [Li, H. et al. (2005); Feng, H. et al. (2005)], it would be useful to validate the turbulence-model predictions against microscale particle-image velocimetry (micro-PIV) measurements of \( \langle U \rangle \) and \( k \) in the CIJR or conventional PIV measurements in a suitably scaled CIJR.

### 7.5.2 Mixture-fraction fields

Figure 7.8 shows contour plots of the mixture-fraction variance predicted by the DQMOM-IEM model and by the Reynolds-average transport equation at the central plane of the CIJR with \( Re_j = 400 \). The mixture-fraction mean and variance at different \( Z \)-positions are shown in Fig. 7.9. The results given by the DQMOM-IEM model are very close to those given by the Reynolds-average transport equations, indicating that the DQMOM-IEM model predicts the first-order and second-order moments of the mixture fraction consistently. As done elsewhere [Feng, H. et al. (2005)], it would be useful to validate these predictions using planar laser-induced fluorescence (PLIF) measurements in a CIJR.

If the dissipation term, \( \varepsilon_\phi \), is set to zero (this is equivalent to turning off the micromixing terms in the DQMOM-IEM simulations), the mixture-fraction variance is related to the mixture-fraction mean analytically by [Feng, H. et al. (2005)].

\[
\langle \xi'^2 \rangle = \langle \xi \rangle (1 - \langle \xi \rangle).
\]

(7.43)

Figure 7.10 shows that the RANS and DQMOM-IEM simulations agree with Eq. 7.43. We should note, however, that in order to obtain good agreement for the RANS simulation a significantly finer grid is required than for the DQMOM-IEM simulations. This difference is due to the structure of the models (that is, when \( \varepsilon_\phi = 0 \) the mixture-fraction variables \( \xi_n \)
are constant in the DQMOM-IEM model and only the values of $p_n$ change), and in general the solution to the DQMOM-IEM model will be less sensitive to the grid refinement. Thus, when the RANS model is employed, the case with $\varepsilon_\phi$ equal to zero can be used to check for grid independence via Eq. 7.43. Analogous remarks hold for the LES model of the SGS mixture-fraction variance.

The volume-averaged LSS and SSS time scales in the CIJR decrease with increasing $Re_j$ as shown in Fig. 7.11. Consistent with the dependence of the residence time in the CIJR on $Re_j$, $t_{\text{LSS}}$ scales like $Re_j^{-1}$. In contrast, $t_{\text{SSS}}$ falls off at a faster rate, but with a slope that depends on $Re_j$. As anticipated in our discussion of the scaling of $Re_1$ with $Re_j$, the observed slope is due to the fact that $C_\phi$ increases with $Re_1$ (and hence with $Re_j$). It can be seen that in the range of jet Reynolds numbers from 500 to 1000, the micromixing time scales approximately like $Re_j^{-3/2}$ due to the Reynolds-number dependence of $C_\phi$. Nevertheless, at jet Reynolds numbers greater than 1000, $C_\phi$ approaches its high-Reynolds-number limiting value shown in Fig. 7.5, in which case the micromixing time scales like $Re_j^{-1}$. In the literature, this change of slope has been referred to as a transition from “micromixing” to “mesomixing” [Baldyga, J. A. and Bourne, J. R. (1999)]. Here we interpret it instead as a low-Reynolds-number effect where for $Re_j < 1000$ the scalar spectrum has no inertial-convective sub-range. Thus, if the change of shape of the scalar spectrum is appropriately accounted for, we argue that the distinction between “micromixing” and “mesomixing” is unnecessary for this flow. Instead, they can both be related to the scalar dissipation rate (which is the accepted measure of molecular mixing in the turbulent-mixing community [Pope, S. B. (2000); Fox, R. O. (2003)]) using the integral method proposed by Corrsin [Corrsin, S. (1964)].

Finally, note that due to the $Re_1$-dependence of $C_\phi$ there exists a cross-over point in Fig. 7.11 near $Re_j \approx 400$ marking a change from SSS-controlled mixing at low Reynolds numbers to LSS-controlled mixing at high Reynolds numbers. The effect of this cross over is also observable in the DMP conversion results shown below. Based on turbulence theory [Pope, S. B. (2000)], there is no fundamental reason to expect that $t_{\text{SSS}}$ should ever be larger than $t_{\text{LSS}}$. Thus, the existence of a cross-over point can be interpreted as an indication that a
low-Reynolds-number (or Schmidt-number) correction is also needed for the turbulent Schmidt number $\text{Sc}_T$ appearing in Eq. 7.17 (which determines $\Gamma_T$ and hence $t_{LSS}$). From a chemical-reaction-engineering perspective, operating at low jet Reynolds numbers should be avoided due to the relatively poor mixing conditions. Nevertheless, from a CFD-modeling perspective it would most likely be possible to improve the predictions for low jet Reynolds numbers by resorting to large-eddy simulations (LES), which resolve the large-scale eddies in the flow. We thus note in passing that with suitable modifications to the parameters [Fox, R. O. (2003)], the DQMOM-IEM model can be applied to model reactive mixing in the context of LES, and thus could easily be implemented with the LES models available in Fluent 6.2.

### 7.5.3 Concentration fields

Representative distributions of the Reynolds-average species (OH$^-$, H$^+$ and DMP) are shown in Fig. 7.12. When $Re_j = 400$ and $t_r = 61$ ms, H$^+$ is consumed completely and little OH$^-$ is left in the outflow. The concentration of DMP does not change much outside of the reaction zone (defined quantitatively below). For the CIJR experiments, no information about the local concentration distributions is available. Thus, it would be useful to validate these CFD predictions using local planar laser-induced fluorescence (PLIF) measurements of an acid-base reaction with a pH-sensitive dye [Koochesfahami, M. M. and Dimotakis, P. E. (1986)].

### 7.5.4 DMP conversion

The conversion of DMP (Eq. 7.28) is shown in Fig. 7.13 for both the experiments [Johnson, B. K. and Prud’homme, R. K. (2003a)] and the CFD simulations as a function of the jet Reynolds number ($Re_j$) and the characteristic reaction time ($t_r$). When $400 \leq Re_j$ and $t_r \geq 9.5$ ms, the simulation results and the experimental measurements are in close agreement. The conversion decreases when $Re_j$ increases, indicating (as expected) that poor mixing favors the slow reaction. Once $Re_j \geq 2000$, $X$ changes more slowly with $Re_j$ due to the creation of the turbulent zone at the outlet to the CIJR seen in Fig. 7.7.

For $t_r < 9.5$ ms, the experimental curves show higher conversion (that is, poorer mixing)
than the simulations. Because the agreement for larger $t_r$ is good and the species do not affect the flow field, this anomaly cannot be assigned to a change in the micromixing time. In order to test if the CFD code was generating an anomalous upper limit, we set $t_r = 0$ and computed the dashed line at $X = 0.85$ appearing in Fig. 7.13. Although this is slightly lower than the theoretical limit $X_{max}$, it is well above the experimental curve for $t_r = 4.8$ ms. Thus the poor agreement cannot be assigned to the numerics used in the CFD code. In their analysis of the data, Johnson and Prud’homme [ Johnson, B. K. and Prud’homme, R. K. (2003a)] show that for $t_r \leq 6.5$ ms the data do not follow the expected experimental scaling law. We are thus inclined to believe that other factors (such as incomplete reaction in the CIJR as discussed below) are involved that cannot be captured in the CFD model.

When $Re_j = 100$ and $t_r = 317$ ms, the computed conversion is much lower than the experimental value. This is due to the fact that for $Re_j < 200$ the flow has a turbulence Reynolds number that is too low for the turbulence model to work correctly. Indeed, as discussed above, the accuracy of the micromixing parameter $C_\phi$ and the turbulent diffusivity $\Gamma_T$ predicted by the standard $k-\varepsilon$ model at low jet Reynolds numbers are questionable. Nevertheless, the combined $k-\varepsilon$, DQMOM-IEM model works satisfactorily when the flow is more turbulent (that is, $200 \leq Re_j$).

By adding a polymer, the molecular viscosity of the inlet streams was increased in the experiments to 0.0071 kg/m·s. The conversion of DMP as a function of $Re_j$ is shown in Fig. 7.14. Note that most of the experimental data are in the low to very-low range of turbulence Reynolds numbers where (as discussed above) we cannot expect good agreement. On the other hand, for $Re_j \geq 200$ the agreement is satisfactory. We should stress, however, that for these data the Reynolds number is so low that no inertial-convective sub-range exists. For this reason, one cannot except to find for large Schmidt numbers anything but viscous-convective scaling for the micromixing time scale. Moreover, because the range of length scales in the velocity field is very narrow, such low-Reynolds-number flows have more in common with chaotic mixing [ Ottino, J. M. (1989)] than with high-Reynolds-number turbulent mixing. In any case, if such low-Reynolds-number flows in a CIJR were of technological interest, they could be computed
directly using direct-number simulation for the velocity field [Pope, S. B. (2000)] and a sub-grid-scale mixing model (like DQMOM-IEM) for the scalar field.

7.5.5 Effect of outflow boundary location

The outlet conversions found when $Re_j = 400$ and $t_r = 4.8$ ms using Domains A and B are 0.362 and 0.364, respectively. The values for other Reynolds numbers are given in Table 7.4. The differences between values at the same Reynolds number are small and might lead one to assume that the outlet stream is well mixed. However, this is not always the case. The effect of $K/\delta$ on the outflow concentration distributions when $Re_j = 400$ and $t_r = 4.8$ ms is shown in Fig. 7.15. From this figure, it can clearly be seen that the mixture fractions in the two environments are not uniform across the outflow boundary, indicating that the outlet streams are not completely mixed in the CIJR when the Reynolds number and mixing rates are too low. The reactions will thus continue (under poorly mixed conditions!) after the outlet, and the conversion of DMP will change before the collection point used in the experiments (that is, the end of the outlet tube). This may be one reason why the measured conversions are higher than the computed values for $t_r < 9.5$ ms in Fig. 7.13. The effect of $K/\delta$ becomes weaker as $Re_j$ increases due to creation of the turbulent zone at the outlet of the CIJR (Fig. 7.7), or as $t_r$ decreases, under which conditions the reactions have less effect on the conversion. In order to determine when the reaction zone extends into the outlet of the CIJR, we have developed a method to visualize the reaction and segregation zones described next.

7.5.6 Reaction and segregation zones

In the scaling theory developed by Johnson and Prud’homme [Johnson, B. K. and Prud’homme, R. K. (2003a)], the zones in the CIJR where energy is dissipated or “mesomixing” and reactions occur are required to complete the scaling law. As noted by these authors, one of the advantages of CFD is that such zones can easily be visualized and studied, for example, as a function of the jet Reynolds number. Of particular interest are the reaction zone (defined below) and the zones with significant large-scale and small-scale segregation.
From Eq. 7.13, it can be seen that the second reaction only occurs at spatial locations where
\[ 0 \leq \xi_1(x, t) \leq \xi_{s1} \quad \text{or} \quad 0 \leq \xi_2(x, t) \leq \xi_{s1}. \]

We will refer to such regions in the CIJR as the reaction zone (RZ). Note that this definition of the reaction zone includes regions where the second reaction is very slow (that is, \( \xi \approx \xi_{s1} \)), and hence essentially negligible. In order to have a more precise definition of the reaction zone, we can define a local mixing time by
\[ t_{\text{mix}} = t_{\text{LSS}} + t_{\text{SSS}}, \quad (7.44) \]
and a local Damköhler number using Eq. 7.13:
\[ Da_{\text{loc}}(\xi) = t_{\text{mix}} A_0 k_2 \left( 1 - \frac{\xi}{\xi_{s1}} \right) \quad \text{for} \quad 0 \leq \xi \leq \xi_{s1} \quad (7.45) \]
and zero otherwise. Note from Fig. 7.11 that the volume-averaged local mixing time decreases from approximately 10 ms at \( Re_j = 100 \) to approximately 0.3 ms at \( Re_j = 2000 \).

The local Damköhler number found from Eq. 7.45 is shown for \( Re_j = 400 \) and 1000 with \( t_r = 4.8 \) ms in Fig. 7.16. Because \( \xi_1 \leq \xi_2 \), only the Damköhler number in environment 1 in shown. From this figure we can observe that \( Da_{\text{loc}} \leq 1 \), indicating that the mixing is relatively good at these Reynolds numbers. Moreover, as expected, the Damköhler number decreases with increasing Reynolds number. We can also observed that the bulk of the conversion occurs on the side of the CIJR where the acid enters the reactor, and that this zone extends along the entire height of the CIJR. Thus, relative to the reaction time scales, macromixing is not particularly good in this reactor, and bulk-scale segregation cannot be neglected when modeling the CIJR.

In the reaction zone, the reactions are controlled by large-scale segregation (LSS) alone if
\[ \langle \xi^2 \rangle_{\text{LSS}} \geq \sigma^2 \quad \text{and} \quad \langle \xi^2 \rangle < \sigma^2, \]
where we define the cut-off standard deviation \( \sigma \) to be the distance in mixture-fraction space (see Fig. 7.2) from the end of reactions (\( \xi_{s1} \)) to complete mixing (\( \bar{\xi} \)):
\[ \sigma = \bar{\xi} - \xi_{s1} = 0.0122. \]
Note that the exact choice of $\sigma$ is not crucial: it just serves as a cut-off point for defining regions in the flow field. An alternative representation of the LSS and SSS zones could be found by using contour plots like the ones shown in Fig. 7.8.

In the reaction zone, the reactions are controlled by small-scale segregation (SSS) alone if

$$\langle \xi'^2 \rangle_{\text{LSS}} < \sigma^2 \quad \text{and} \quad \langle \xi'^2 \rangle \geq \sigma^2,$$

or by both LSS and SSS if

$$\langle \xi'^2 \rangle_{\text{LSS}} \geq \sigma^2 \quad \text{and} \quad \langle \xi'^2 \rangle \geq \sigma^2.$$

The distributions of the various reaction and mixing zones for $Re_j = 400$ and $Re_j = 1000$ are shown in Fig. 7.17.

From this figure, we can observe that the volume of the reaction zone decreases slightly when $Re_j$ increases, indicating that the overall mixing process is faster. Nevertheless, the reaction zone extends into the outlet tube since macromixing is not complete (see Fig. 7.12). On the axis of the inlet jets, the reactions are controlled by both LSS and SSS. In contrast, the region where the reactions are controlled only by SSS has the form of a distorted torus around this axis. Note that the SSS-controlled region shrinks with increasing $Re_j$ due to the increase in $C_\phi$. Also note that there is no region where reactions are controlled by LSS alone.

From the reaction zone in Fig. 7.17 and from Fig. 7.15, we can observe that complete mixing at all scales is not achieved in the CIJR (that is, $\xi_1$ is not larger than $\xi_{s1}$ at all points on the outlet surface). We can therefore conclude that although the CIJR enables intense micromixing, the flow does not macromix completely during its residence time in the reactor. In order to avoid that the reaction zone extends beyond the CIJR, it would suffice to separate more $\bar{\xi}$ from $\xi_{s1}$. If equal flow rates are used (thereby keeping the flow field unchanged and $\bar{\xi}$ constant), this can be done by making $\xi_{s1}$ smaller (for example by increasing $B_0$ or decreasing $A_0$). From the plots of $\xi_1$ in Fig. 7.15 we can observe that lowering $\xi_{s1}$ to 0.470 would be sufficient to avoid reactions in the outflow for $Re_j \geq 400$. Another alternative would be to make the outlet tube diameter smaller in order to decrease LSS at the outflow. This method has been investigated experimentally [Johnson, B. K. and Prud’homme, R. K. (2003a)].
disadvantage of employing this method would be an increase in the pressure drop across the CIJR.

7.6 Conclusions

The major conclusion that can be drawn from this work is that a CFD model based on fundamental turbulent-transport theory can accurately predict the experimental conversion data [Johnson, B. K. and Prud’homme, R. K. (2003a)] in the range of jet Reynolds numbers corresponding to turbulent flow. We have also demonstrated that the method [Corrsin, S. (1964)] for determining the micromixing time as a function of turbulent Reynolds number and Schmidt number can be combined with the model scalar spectrum [Fox, R. O. (2003)] to accurately account for the Reynolds- and Schmidt-number effects present at low jet Reynolds numbers. Thus, when combined with accurate chemical-rate expressions, the CFD model used in this work should be adequate for design and scale up of CIJR s for other processes.

The secondary conclusions pertain to the particular CIJR used in the CFD simulations. These conclusions are as follows.

1. Although the mixing times are short, the turbulent flow in the CIJR is not fully developed for the jet Reynolds numbers used in the experiments. It is thus crucial to account for Reynolds- and Schmidt-number effects on the micromixing time scale.

2. Low-Reynolds-number effects are responsible for the experimentally observed Kolmogorov scaling of the micromixing time. At higher jet Reynolds numbers, inertial-range scaling is observed in accordance with turbulent-mixing theory.

3. Despite rapid mixing, the outlet stream is not completely mixed. Thus, because the reactant concentrations (that is, $\xi_{s1}$) were chosen such that conversion continues to increase nearly up to the point of complete mixing, the reaction zone extends into the outlet tube. As pointed out in the discussion, this can be avoided in future experimental studies by lowering $\xi_{s1}$. 
Finally, because the experimental data were limited to overall conversion, it was not possible to validate the local turbulence and concentration fields predicted by the CFD model. We would thus recommend that future experimental studies of the CIJR include PIV and PLIF measurements of the local velocity and scalar fields. As shown elsewhere [Feng, H. et al. (2005)] for a confined planar-jet reactor, these data would be extremely valuable for validating the turbulence and scalar-mixing models used in the CFD simulations.

Acknowledgments

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Table 7.1  Average Inlet Concentrations for Various Values of the Characteristic Reaction Time.

<table>
<thead>
<tr>
<th>$t_r$(ms)</th>
<th>317</th>
<th>181</th>
<th>61</th>
<th>28</th>
<th>16.7</th>
<th>9.5</th>
<th>6.5</th>
<th>4.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0/2$ (mol/m³)</td>
<td>4.69</td>
<td>8.21</td>
<td>24.36</td>
<td>53.06</td>
<td>88.96</td>
<td>156.39</td>
<td>228.56</td>
<td>309.50</td>
</tr>
<tr>
<td>$B_0/2$ (mol/m³)</td>
<td>4.92</td>
<td>8.62</td>
<td>25.57</td>
<td>55.71</td>
<td>93.41</td>
<td>164.21</td>
<td>239.99</td>
<td>324.98</td>
</tr>
<tr>
<td>$D_0/2$ (mol/m³)</td>
<td>4.69</td>
<td>8.21</td>
<td>24.36</td>
<td>53.06</td>
<td>88.96</td>
<td>156.39</td>
<td>228.56</td>
<td>309.50</td>
</tr>
</tbody>
</table>

Table 7.2  Inlet Jet Velocity for Various Jet Reynolds Numbers.

<table>
<thead>
<tr>
<th>$Re_j$</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
<th>4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_1$ (m/s)</td>
<td>0.415</td>
<td>0.83</td>
<td>1.66</td>
<td>2.10</td>
<td>2.49</td>
<td>3.32</td>
<td>4.15</td>
<td>8.30</td>
<td>12.45</td>
<td>16.6</td>
</tr>
</tbody>
</table>

Table 7.3  Pressure Drop Across CIJR for Various Jet Reynolds Numbers.

<table>
<thead>
<tr>
<th>$Re_j$</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>500</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta p$ (psia)</td>
<td>214.1</td>
<td>565.2</td>
<td>1528</td>
<td>2186</td>
<td>2843</td>
</tr>
<tr>
<td>$Re_j$</td>
<td>800</td>
<td>1000</td>
<td>2000</td>
<td>3000</td>
<td>4000</td>
</tr>
<tr>
<td>$\Delta p$ (psia)</td>
<td>4552</td>
<td>6680</td>
<td>23720</td>
<td>38910</td>
<td>45460</td>
</tr>
</tbody>
</table>
Table 7.4 Effect of Outflow Boundary Location on Conversion for $t_r = 4.8$ ms.

<table>
<thead>
<tr>
<th>$Re_j$</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>800</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X$ (Domain A)</td>
<td>0.588</td>
<td>0.505</td>
<td>0.362</td>
<td>0.320</td>
<td>0.286</td>
<td>0.230</td>
<td>0.185</td>
</tr>
<tr>
<td>$X$ (Domain B)</td>
<td>0.592</td>
<td>0.505</td>
<td>0.364</td>
<td>0.322</td>
<td>0.286</td>
<td>0.233</td>
<td>0.188</td>
</tr>
</tbody>
</table>
Figure 7.1  Schematic of the confined impinging-jets reactor (CIJR).
Figure 7.2 Region in $\xi$–$Y_2$ phase space with non-zero chemical source term and the mixing line.

Figure 7.3 Dependence of model turbulent energy spectrum on the turbulent Reynolds number.
Figure 7.4 Dependence of scalar energy spectrum on the turbulent Reynolds number for $Sc = 1000$.

Figure 7.5 Dependence of $C_\phi$ on the turbulent Reynolds number for $Sc = 1$ (typical gases) and $Sc = 1000$ (typical liquids).
Figure 7.6  Turbulence fields for $Re_j = 400$. 

![Turbulence fields for $Re_j = 400$.](image-url)
Figure 7.7  Turbulent Reynolds number in the CLJR for different values of $Re_j$. Top left: 200. Top right: 400. Bottom left: 1000. Bottom right: 4000.
Figure 7.8  Contours of mixture-fraction variance $\langle \xi'^2 \rangle$ on the central plane for $Re_j = 400$ predicted by (left) the DQMOM-IEM model and (right) the Reynolds-average transport equation.

Figure 7.9  Profiles on the central plane of mixture-fraction mean (left) and variance (right) for $Re_j = 400$ predicted by the DQMOM-IEM model and the Reynolds-average transport equations at different $Z$-positions. (See Fig. 7.8 for location of $Z$.)
Figure 7.10  Profiles on the central plane of mixture-fraction variance for $Re_j = 400$ predicted by the DQMOM-IEM model and the Reynolds-average transport equations with no dissipation at different $Z$-positions. (See Fig. 7.8 for location of $Z$.)

Figure 7.11  Dependence of volume-averaged time scales on $Re_j$. 
Figure 7.12 Reynolds-average species distributions for $Re_j = 400$ and $t_r = 61$ ms.

Figure 7.13 Conversion of DMP versus $Re_j$ in the CIJR. Open symbols: experiments. Closed symbols: simulations.
Figure 7.14  Effect of increased molecular viscosity on DMP conversion for $t_r = 29.7$ ms.

Figure 7.15  Distribution of the mixture fraction, reaction-progress variable and DMP on the outflow surface for $Re_j = 400$ and $t_r = 4.8$ ms. Top row: Domain A ($K/\delta = 1.62$). Bottom row: Domain B ($K/\delta = 10$).
Figure 7.16  Profiles of the local Damköhler number in environment 1 for \( t_r = 4.8 \) ms. Left: \( Re_j = 400 \). Right: \( Re_j = 1000 \).

Figure 7.17  Distribution of the reaction (RZ) and segregation (LSS, SSS) zones for (left) \( Re_j = 400 \) and (right) \( Re_j = 1000 \).
CHAPTER 8. A CFD MODEL FOR FINE-PARTICLE PRODUCTION BY REACTIVE PRECIPITATION

A paper in preparation
Ying Liu, Rodney O. Fox

Abstract

The multi-environment direct quadrature method of moments (DQMOM) – interaction by exchange with the mean (IEM) model is applied to the population balance equation (PBE) governing the univariate and bivariate number density function (NDF) of fine particles produced in a turbulent reacting flow. The time/space evolution of NDF is approximated using both the quadrature method of moments (QMOM) and the direct quadrature method of moments (DQMOM). By using the resulting QPDI and DPDI models, reactive precipitation of BaSO$_4$ in a plug flow reactor (PFR) with non-premixed inlet streams is simulated, and the univariate NDF moments predicted by the QPDI and DPDI models are shown to be identical.

A strong dependence of the particle number density and diameter on the local species composition is observed by varying the inlet species concentrations. The processes of nucleation, growth, aggregation and breakage under the effects of mixing are also investigated.

8.1 Introduction

In many industrial processes, fine particles are the desired product (e.g. nanoparticle formation in flames or colloidal particles), but in others they may be an undesired by-product (e.g. soot formation in flames). Due to their small size (i.e. less than 10 microns in diameter), fine particles can often be treated as a pseudo species [Piton, D. et al. (2000); Johannessen,
T. et al. (2000); Johannessen, T. et al. (2001); Fox, R. O. (2006a) that follow the local fluid velocity. Thus, in principle, any computational fluid dynamics (CFD) model for turbulent reacting flows [Fox, R. O. (2003)] could be used to describe their formation. However, the physical and chemical processes that lead to transformations in the properties of fine particles are rather complicated and lead to new challenges that are not present in most reacting flow simulations in which fine-particle formation is of no interest. For example, in reactive precipitation the local superstaturation is controlled by mixing, and thus it is necessary to describe accurately the mixing at all scale in order to predict the properties of the particles [Liu, Y. and Fox, R. O. (2006); Fox, R. O. (2006a)].

In order to describe a population of fine particles with different sizes, we introduce the number density function (NDF) $n(L)$ representing the number density of particles with diameter in the interval $(L, L + dL)$. For each value of $L$, $n(L)$ depends on the spatial location and time. Thus, it is a pseudo chemical species, but in fact the transport problem involves an infinite number of such species parameterized by $L$. Note that this will also be true if a different variable (such as volume $v$ or surface area $s$) were used to described the fine particles. From the standpoint of CFD, we are therefore dealing with a turbulent reacting flow with an infinite number of reacting scalars. Note that in most practical applications such as nanoparticle production in flames, the “normal” reacting scalars associated with the chemistry and energy balance (denoted by $\phi$) must be solved in addition to $n(L)$. In fact, these scalars and $n(L)$ are strongly coupled, and one must consider how mixing affects the spatial distribution of all scalars (i.e. $n(L)$ and $\phi$). Moreover, the situation becomes even more complicated when a bivariate NDF such as $n(v, s)$ is considered.

equation of the NDF for homogeneous problems. However, when applied to inhomogeneous problems, only moment methods are currently tractable [Fox, R. O. (2006a)]. The most well-known difficulty of moment methods is the closure problem since the formulation of moments results in an excess of unknowns with respect to equations. It is thus necessary to have recourse to closure approximations.

A powerful approach for closing the moment equations is the quadrature method of moments (QMOM)[McGraw, R. (1997)], which expresses the NDF moments in terms of a finite set of $M$ weights $w_m$ and $M$ abscissas $L_m$:

$$m_k = \sum_{m=1}^{M} w_m L_m^k.$$  \hspace{1cm} (8.1)

In practice, excellent predictions are often possible with small values of $M$ (2–5). Thus, the infinite set of scalars $n(L)$ is replaced by a total of $2M$ scalars (i.e. a set of $2M$ NDF moments). In practice, QMOM is feasible numerically due to the existence of the product-difference (PD) algorithm [McGraw, R. (1997)] that solves Eq. (8.1) for $w_m$ and $L_m$ given the set of $2M$ moments $\mathcal{M} = (m_0, m_1, \ldots, m_{2M-1})$. In other words, if $\mathcal{M}$ is known by solving the transport equations for the NDF moments, then one can rapidly compute the corresponding weights and abscissas. The latter are used to close the source term $S_k(\phi, L)$ due to the physical processes such as reaction, nucleation, growth, aggregation and breakage.

Quadrature methods can be straightforwardly extended to a system with more than one internal coordinate, such as volume and the surface area of the particles. For a bivariate system, the moments are related to the weights and abscissas by

$$m_{kl} = \sum_{m=1}^{M} w_m v_m^k s_m^l,$$  \hspace{1cm} (8.2)

where $k$ is the order of the volume moment and $l$ the order of the surface moment. However, numerical challenges [Wright, D. L. et al. (2001); Rosner, D. E. and Pykkonen, J. J. (2002)] involved in inverting Eq. (8.2) limit the application of QMOM in bivariate problems although it has been reported bivariate QMOM is able to yield accurate results for simultaneous coagulation and sintering in a homogeneous system [Wright, D. L. et al. (2001)].
Marchisio, D. L. and Fox, R. O. (2005) developed the direct quadrature method of moments (DQMOM) approach to derive the transport equations for the weights and abscissas directly (i.e. instead of solving the transport equations for the NDF moments). DQMOM can be easily applied to spatially inhomogeneous transport equations [Marchisio, D. L. and Fox, R. O. (2005); Fan, R. et al. (2004)] and it keeps all of the moments realizable as long as the weights remain non-negative in the numerical algorithm [Fox, R. O. (2006a)]. However, the problem of treating fine-particle formation in turbulent reacting flow using a CFD model (e.g. Reynolds-average Navier-Stokes (RANS) or large-eddy simulation (LES)) still remains to be investigated. In our previous work [Liu, Y. and Fox, R. O. (2006)], we have introduced a CFD model based on probability density function (PDF) methods [Fox, R. O. (2003)] that can predict accurately the yield of mixing-sensitive reactions. This model uses DQMOM to represent the one-point scalar PDF generated by turbulent mixing, and closes the micromixing term with the interaction-by-exchange-with-the-mean (IEM) model. The CFD model is thus referred to as the DQMOM-IEM model [Fox, R. O. (2003); Wang, L. and Fox, R. O. (2004); Liu, Y. and Fox, R. O. (2006)].

The goal of the present work is to demonstrate how QMOM and DQMOM can be used to solve the population balance equation (PBE) coupled with the DQMOM-IEM model [Liu, Y. and Fox, R. O. (2006)] to describe simultaneous turbulent mixing and reactive precipitation. In order to avoid confusion, we will refer to the QMOM-PBE and DQMOM-PBE methods for solving the PBE, and the DQMOM-IEM model for reactive mixing. The combined models are then denoted by (QMOM-PBE)-(DQMOM-IEM) and (DQMOM-PBE)-(DQMOM-IEM), respectively, or more simply by the QPDI and DPDI models. As discussed elsewhere [Fox, R. O. (2006a)], the QPDI model is a straightforward extension of previous work. On the other hand, the consistent implementation of the DPDI model is more involved [Fox, R. O. (2006a)] because the weights and abscissas are nonlinear functions of the moments. In this work, the CFD model equations are derived in detail and the predictions from the QPDI and DPDI models for the univariate moments of the fine particles formed by mixing, reaction, nucleation, growth, aggregation and breakage are compared. We also investigate the effects of reacting
scalars (i.e. supersturation) on the spatial distribution of the NDF moments. Finally, we show how the DPDI model can be used for a bivariate case for which the QPDI model is no longer tractable.

8.2 Population balances in turbulent reacting flow

We begin with a general overview of how population balances for fine particles evolve in a turbulent reacting flow. Note that we will assume that because the particles are very small, they follow the instantaneous flow just like molecular species (i.e., they have vanishing Stokes number). If the complete set of scalars describing the chemistry and the fine particles ($\phi$ and $M$) is considered, the modeling problem is conceptually the same as treating any turbulent reacting flow with complex chemistry [Fox, R. O. (2003)]. Thus, the treatment of turbulent reacting flows can be done by combining the DQMOM-IEM model with the transport equations for the NDF moments using QMOM-PBE to find the weights and abscissas. Alternatively, we can combine the DQMOM-IEM model with the transport equations for the weights and abscissas directly (i.e. DQMOM-PBE). In either representation, the $\alpha$th environment (or fluid element) in the DQMOM-IEM model [Liu, Y. and Fox, R. O. (2006)] contains a set of NDF moments $m_{k\alpha}$ or, equivalently, a set of weights and abscissas ($w_{ma}, L_{ma}$).

The key conceptual idea when thinking about the CFD model for fine-particle formation in a turbulent flow is that each environment (or fluid element) has its own NDF, and thus its own set of NDF moments (and weights and abscissas). Note that this is entirely consistent with the usual one-point statistical description of turbulent reacting flows [Fox, R. O. (2003)]. Thus, for example, in a RANS model we will have a Reynolds-average NDF denoted by $\langle n(L) \rangle$ and Reynolds-average NDF moments denoted by $\langle m_k \rangle$. In the context of multi-environment models, the latter are computed in the usual manner:

$$\langle m_k \rangle = \sum_{\alpha=1}^{N_e} p_\alpha m_{k\alpha},$$

(8.3)

where $p_\alpha$ is the mass fraction of the $\alpha$th environment, and $N_e$ is the number of environments. Note that this also implies that the NDF moments (like any other one-point scalar field) will
have Reynolds-average moments of arbitrary order. For example, the second-order moment of \( m_k \) is

\[
\langle m_k^2 \rangle = \sum_{\alpha=1}^{N_c} p_\alpha m_{k\alpha}^2.
\]

(8.4)

The existence of both the NDF and the one-point PDF of the NDF can be a source for confusion (especially when stochastic solution methods are used to find approximate solutions for the NDF). The reader should keep in mind that the NDF is not a probabilistic quantity, but instead arises due to the infinite possible number of particle sizes present in the system. In contrast, the one-point PDF arises from the statistical modeling approach used to describe turbulent mixing.

Here we denote the mass fraction, chemical composition, and the NDF of the \( \alpha \)th environment by \( p_\alpha, \phi_\alpha, \) and \( n_\alpha, \) respectively. For simplicity we consider only one scalar \( \phi, \) but it is straightforward to extend the description to multiple scalars [Fox, R. O. (2003)]. Likewise, the Reynolds-average velocity, the turbulent kinetic energy, the dissipation rate, and the turbulent diffusivity are denoted by \( \langle U \rangle, k, \varepsilon \) and \( \Gamma_T, \) respectively. The basic idea of the DQMOM-IEM model [Fox, R. O. (2003); Wang, L. and Fox, R. O. (2004)] is to represent the joint PDF (where the sample-space variables are \( \psi \) for the chemical composition and \( n \) for the NDF) as

\[
f (\psi, n; \mathbf{x}, t) = \sum_{\alpha=1}^{N_c} p_\alpha (\mathbf{x}, t) \delta [\psi - \phi_\alpha (\mathbf{x}, t)] \delta [n - n_\alpha (\mathbf{x}, t)],
\]

(8.5)

and derive the transport equations for \( p_\alpha, p_\alpha \phi_\alpha, \) and \( p_\alpha n_\alpha \) by inserting the presumed PDF into the Eulerian transport equation for \( f \) closed by the IEM model [Fox, R. O. (2003)]:

\[
\frac{\partial f}{\partial t} + \nabla \cdot (\langle U \rangle f) = \nabla \cdot (\Gamma_T f) - \frac{\partial}{\partial \psi} \left[ f \left( C_\phi \frac{\varepsilon}{k} (\langle \phi \rangle - \psi) + S_\phi (\psi, n) \right) \right] - \frac{\partial}{\partial n} \left[ f \left( C_n \frac{\varepsilon}{k} (\langle n \rangle - n) + S_n (\psi, n) \right) \right].
\]

(8.6)

In this expression, \( S_\phi \) is the source term for the chemical composition and \( S_n \) is the source term for the NDF (i.e. nucleation, growth, aggregation, etc.). The mechanical-to-scalar-time-scale ratio, \( C_\phi, \) adopts it typical value of two in this work. Following this procedure, the model
The DQMOM-IEM model for a reactive scalar is given by Eqs. (8.7) and (8.8). The term $b^*_\alpha$ is a correction term that forces the moments of $\phi$ to be exact [Wang, L. and Fox, R. O. (2004)]. For example, for $N_e = 2$ these terms are defined by

$$b^*_1 = -b^*_2 = \frac{\Gamma_T}{(\phi_1 - \phi_2)} \left( p_1 |\nabla \phi_1|^2 + p_2 |\nabla \phi_2|^2 \right)$$

(8.10)

Likewise, in Eq. (8.9) $c^*_\alpha$ is a correction term that is proportional to $\Gamma_T$ and depends on the spatial gradients of $n_\alpha$ [Fox, R. O. (2006a)].

Equation (8.9) is the starting point to derive the QPDI and the DPDI model equations. Note that Eq. (8.9) represents a set of $N_e$ coupled PBE for the set of NDF $n_\alpha, \alpha = 1, \ldots, N_e$. Thus, in order to have a tractable CFD model we must reduce the number of scalars needed to represent $n_\alpha$ as much as possible without losing accuracy. In this work, we will use quadrature methods for this purpose.

8.2.1 The QPDI model

Univariate NDF

As an example, a univariate case with NDF $n_\alpha(L)$ will be discussed first. Applying the moment transformation defined by

$$m_{k\alpha} = \int_0^\infty L^k n_\alpha(L) \, dL$$

(8.11)

to Eq. (8.9) leads to

$$\frac{\partial p_\alpha m_{k\alpha}}{\partial t} + \nabla \cdot (\langle U \rangle p_\alpha m_{k\alpha}) = \nabla \cdot (\Gamma_T p_\alpha m_{k\alpha}) + p_\alpha M_{k\alpha} + p_\alpha S_{k\alpha} + c^*_{k\alpha}.$$
where \( M_{k\alpha} \) denotes the closed term for micromixing:

\[
M_{k\alpha} = C_\phi \frac{\varepsilon}{k} \langle m_k \rangle - m_{k\alpha}.
\] (8.13)

In Eq. (8.12) \( S_{k\alpha} \) represents the source term for the moments, and \( c^*_{k\alpha} \) is the correction term for the moments (see Eq. 8.10). The latter depends on the spatial gradients of the moments \( m_{k\alpha} \) in the same way as for any scalar [Liu, Y. and Fox, R. O. (2006); Fox, R. O. (2006a)]. In general, the source term is nonlinear and must be closed using the quadrature approximation in terms of the weights and abscissas. The latter are found from the moments using the PD algorithm. Equation (8.12) is different from the microscopic transport equation for the NDF moment [Fox, R. O. (2006a)] mainly in that it accounts for the sub-grid mixing by introducing more than one environment, making the computational studies of the effects of mixing on the particle size distribution in a turbulent flow possible.

In summary, Eqs. (8.7), (8.8), and (8.12) are the QPDI model equations. The \( 2(M+1) \times N_e \) dependent variables solved in this model are

\[
\mathcal{M} = \left[ \mathcal{M}_1 \cdots \mathcal{M}_{N_e} \right] = \begin{bmatrix} p_1 & p_1\phi_1 & p_1m_{01} & p_1m_{11} & \cdots & p_1m_{M-1} \\ p_2 & p_2\phi_2 & p_2m_{02} & p_2m_{12} & \cdots & p_2m_{M-1} \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ p_{N_e} & p_{N_e}\phi_{N_e} & p_{N_e}m_{0N_e} & p_{N_e}m_{1N_e} & \cdots & p_{N_e}m_{M-1N_e} \end{bmatrix}^T, \quad (8.14)
\]

and the primary variables are

\[
\mathcal{P} = \left[ \mathcal{P}_1 \cdots \mathcal{P}_{N_e} \right] = \begin{bmatrix} p_1 & \phi_1 & m_{01} & m_{11} & \cdots & m_{M-1} \\ p_2 & \phi_2 & m_{02} & m_{12} & \cdots & m_{M-1} \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ p_{N_e} & \phi_{N_e} & m_{0N_e} & m_{1N_e} & \cdots & m_{M-1N_e} \end{bmatrix}^T. \quad (8.15)
\]

For each value of \( \alpha \), given the \( 2M \) moments \( m_{k\alpha} \), the \( M \) weights \( w_{ma} \) and \( M \) abscissas \( L_{ma} \) can be computed with the PD algorithm.
Bivariate NDF

For a bivariate problem with NDF $n_{\alpha}(v, s)$, the moment transformation is defined by

$$m_{k\ell\alpha} = \int_0^\infty v^k s^\ell n_{\alpha}(v, s) \, dv \, ds. \quad (8.16)$$

Applying Eq. (8.16) to Eq. (8.9) gives the bivariate QPDI model equation for $p_{\alpha}m_{k\ell\alpha}$ [Fox, R. O. (2006a)]:

$$\frac{\partial p_{\alpha}m_{k\ell\alpha}}{\partial t} + \nabla \cdot \langle U \rangle p_{\alpha}m_{k\ell\alpha} = \nabla \cdot (\Gamma p_{\alpha}m_{k\ell\alpha}) + p_{\alpha}M_{k\ell\alpha} + p_{\alpha}S_{k\ell\alpha} + c^*_{k\ell\alpha}, \quad (8.17)$$

where $M_{k\ell\alpha}$ denotes the closed micromixing term for $m_{k\ell\alpha}$:

$$M_{k\ell\alpha} = C_{\phi} \varepsilon_k \langle m_{k\ell} \rangle - m_{k\ell\alpha}, \quad (8.18)$$

with

$$\langle m_{k\ell} \rangle = \sum_{\alpha=1}^{N_\alpha} p_{\alpha}m_{k\ell\alpha}. \quad (8.19)$$

The rest of the terms in Eq. (8.17) have definitions analogous to the univariate case. The moments can be expressed in terms of weights $w_{ma}$ and abscissas $(v_{ma}, s_{ma})$ as

$$m_{k\ell\alpha} = \sum_{m=1}^{M} w_{ma} v_{ma}^k s_{ma}^\ell. \quad (8.20)$$

Note that the weights and abscissas are needed to close the source term $S_{k\ell\alpha}$. Theoretically, the $M$ weights and $2M$ abscissas can be found from $3M$ linearly independent moments. However, the PD algorithm is not able to solve for the weights and abscissas given moments that involve more than one variable. Thus, in order to have a tractable CFD model, it is preferable to solve for the weights and abscissas directly using DQMOM.

8.2.2 The DPDI model

Univariate NDF

Instead of solving the moments in each environment, the DPDI approach solves for the weights and abscissas directly. For a univariate case, the weights and abscissas in the $\alpha$th
environment are related to \( n_{\alpha} \) by
\[
n_{\alpha} (L; \mathbf{x}, t) = \sum_{m=1}^{M} w_{ma} \delta [L - L_{ma} (\mathbf{x}, t)].
\]
(8.21)

Note that this expression yields the moments
\[
m_{ka} = \sum_{m=1}^{M} w_{ma} L_{ma}^k.
\]
(8.22)

We will thus derive the transport equations for the weights and abscissas using Eq. (8.22) to make a change of variable in Eq. (8.12).

Inserting Eq. (8.22) into Eq. (8.12) gives the transport equations for \( p_{\alpha} w_{ma} \) and \( p_{\alpha} w_{ma} L_{ma} \) [Fox, R. O. (2006a)]:
\[
\frac{\partial p_{\alpha} w_{ma}}{\partial t} + \nabla \cdot ([\mathbf{U}] p_{\alpha} w_{ma}) = \nabla \cdot [\Gamma_T \nabla (p_{\alpha} w_{ma})] + A_{ma},
\]
(8.23)
\[
\frac{\partial p_{\alpha} w_{ma} L_{ma}}{\partial t} + \nabla \cdot ([\mathbf{U}] p_{\alpha} w_{ma} L_{ma}) = \nabla \cdot [\Gamma_T \nabla (p_{\alpha} w_{ma} L_{ma})] + B_{ma}.
\]
(8.24)

In these equations, \( A_{ma} \) and \( B_{ma} \) are the combined terms for micromixing and the NDF moment source terms. These terms can be found for each environment \( (\alpha = 1, \ldots, N_e) \) by solving the linear system defined by [Fox, R. O. (2006a)]
\[
(1 - k) \sum_{m=1}^{M} L_{ma}^k A_{ma} + k \sum_{m=1}^{M} L_{ma}^{k-1} B_{ma} = c_{ka}^* + p_{\alpha} M_{ka} + p_{\alpha} S_{ka}
\]
\[
+ k (k-1) \sum_{m=1}^{M} p_{\alpha} w_{ma} L_{ma}^{k-2} \Gamma_T |\nabla L_{ma}|^2
\]
(8.25)

for \( k = 0, 1, \ldots, 2M - 1 \); where the terms \( c_{ka}^* \), \( M_{ka} \) and \( S_{ka} \) are identical to those in Eq. (8.12).

Equations (8.7), (8.8), (8.23) and (8.24) are the univariate DPDI model equations. The dependent and primary variables in these equations are
\[
\mathbf{M}^* = \begin{bmatrix} \mathbf{M}_1^* & \cdots & \mathbf{M}_{N_e}^* \end{bmatrix}^T
\]
\[
= \begin{bmatrix} p_1 & p_1 \varphi_1 & p_1 w_{11} & \cdots & p_1 w_{1M_1} & p_1 w_{11} L_{11} & \cdots & p_1 w_{1M_1} L_{M_1} \\
p_2 & p_2 \varphi_2 & p_2 w_{12} & \cdots & p_2 w_{1M_2} & p_2 w_{12} L_{12} & \cdots & p_2 w_{1M_2} L_{M_2} \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\
p_{N_e} & p_{N_e} \varphi_{N_e} & p_{N_e} w_{MN_e} & \cdots & p_{N_e} w_{MN_e} & p_{N_e} w_{MN_e} L_{MN_e} & \cdots & p_{N_e} w_{MN_e} L_{MN_e} \end{bmatrix}
\]
(8.26)
and
\[ P^* = \begin{bmatrix} P_1^* & \cdots & P_{N_e}^* \end{bmatrix} = \begin{bmatrix} p_1 & \phi_1 & w_{11} & \cdots & w_{M1} & L_{11} & \cdots & L_{M1} \\ p_2 & \phi_2 & w_{12} & \cdots & w_{M2} & L_{12} & \cdots & L_{M2} \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ p_{N_e} & \phi_{N_e} & w_{1N_e} & \cdots & w_{MN_e} & L_{1N_e} & \cdots & L_{MN_e} \end{bmatrix}^T , \tag{8.27} \]

respectively.

**Bivariate NDF**

For a bivariate case, the dependence of \( n_\alpha(v, s) \) on \( w_{ma}, v_{ma}, \) and \( s_{ma} \) can be represented by
\[ n_\alpha(v, s; x, t) = \sum_{m=1}^{M} w_{ma} \delta [v - v_{ma}(x, t)] \delta [s - s_{ma}(x, t)] , \tag{8.28} \]
which leads to the moments given in Eq. (8.20). Using the latter to make a change of variables in Eq. (8.17) leads to the bivariate DPDI model:
\[
\begin{align*}
\frac{\partial p_\alpha w_{ma}}{\partial t} & + \nabla \cdot (\langle U \rangle p_\alpha w_{ma}) = \nabla \cdot [\Gamma_T \nabla (p_\alpha w_{ma})] + A_{ma}, \\
\frac{\partial p_\alpha w_{ma} v_{ma}}{\partial t} & + \nabla \cdot (\langle U \rangle p_\alpha w_{ma} v_{ma}) = \nabla \cdot [\Gamma_T \nabla (p_\alpha w_{ma} v_{ma})] + B_{ma}, \\
\frac{\partial p_\alpha w_{ma} s_{ma}}{\partial t} & + \nabla \cdot (\langle U \rangle p_\alpha w_{ma} s_{ma}) = \nabla \cdot [\Gamma_T \nabla (p_\alpha w_{ma} s_{ma})] + C_{ma},
\end{align*}
\tag{8.29-31}
\]
in which the terms \( A_{ma}, B_{ma}, \) and \( C_{ma} \) are determined for each \( \alpha = 1, \ldots, N_e \) from the following linear system [Fox, R. O. (2006a)]:
\[
(1 - k - l) \sum_{m=1}^{M} v_{ma}^k s_{ma}^l A_{ma} + k \sum_{m=1}^{M} v_{ma}^{k-1} s_{ma}^l B_{ma} + l \sum_{m=1}^{M} v_{ma}^k s_{ma}^{l-1} C_{ma}
\]
\[
= c_{a1}^k + p_a M_{a1} + p_a S_{a1} + k (k - 1) \sum_{m=1}^{M} p_a w_{ma} v_{ma}^k s_{ma}^{l-1} \Gamma_T \nabla v_{ma}^2 \\
+ kl \sum_{m=1}^{M} p_a w_{ma} v_{ma}^{k-1} s_{ma}^l \Gamma_T \nabla v_{ma} \nabla s_{ma} \\
+ l (l - 1) \sum_{m=1}^{M} p_a w_{ma} v_{ma}^k s_{ma}^{l-2} \Gamma_T \nabla s_{ma}^2 . \tag{8.32}
\]
The terms $c_{kla}^*$, $M_{kla}$, and $S_{kla}$ are identical to those in Eq. (8.17). In order to solve Eq. (8.32) for the unknowns $A_{m\alpha}$, $B_{m\alpha}$, and $C_{m\alpha}$, it is necessary to choose $3M$ distinct sets of indices $(k, l)$. We will discuss how this is done in a bivariate example below.

The DPDI model avoids the need to invert the moments (Eq. 8.20) to find the weights and abscissas during the course of the CFD simulation and is more powerful for solving the bivariate case. It is noted that the DPDI model is derived from Eq. (8.6) by applying the DQMOM approach twice. The derivation of the QPID model, on the other hand, involves the DQMOM-IEM approach for turbulent mixing, followed by the QMOM-PBE moment method for the NDF. Theoretically, these two models should yield identical results for the NDF moments $\langle m_k \rangle$ ($\langle m_{kl} \rangle$) since they both originate from Eq. (8.6). We will verify this equivalence for a univariate test case described in the next section.

**8.3 Univariate Test Case**

The univariate test case is taken from Wang, L. and Fox, R. O. (2003), and corresponds to precipitation of barium sulfate in a turbulent flow with non-premixed inlet conditions. All of the kinetic parameters are taken from the literature (as indicated below). We are interested in predicting the moments of the NDF $n(L)$ using the two CFD models presented above. For the DQMOM-IEM model, we will use $N_e = 2$ environments. The liquid-phase reaction can be described by the mixture fraction $\xi$ and a reaction-progress variable $Y$ [Wang, L. and Fox, R. O. (2003)].

**8.3.1 DQMOM-IEM model**

The multi-environment DQMOM-IEM model equations for the mixture fraction and the reaction-progress variable are ($\alpha = 1, 2$)

$$
\frac{\partial p_{\alpha \xi}^*}{\partial t} + \nabla \cdot (\langle U \rangle p_{\alpha \xi}^*) = \nabla \cdot [\Gamma_T \nabla (p_{\alpha \xi})] + p_{\alpha \xi}^* \frac{C_s}{k} (\langle \xi \rangle - \xi_{\alpha^*}) + b_{\xi_{\alpha^*}}^* \tag{8.33}
$$
and

$$\frac{\partial p_{\alpha} Y_{\alpha}}{\partial t} + \nabla \cdot (\langle U \rangle p_{\alpha} Y_{\alpha}) = \nabla \cdot \left[ \Gamma_T \nabla (p_{\alpha} Y_{\alpha}) \right] + p_{\alpha} C_{\phi} \frac{\varepsilon}{k} (\langle Y \rangle - Y_{\alpha})$$

$$+ p_{\alpha} S_{Y\alpha} + b_{\phi\alpha}^*, \quad (8.34)$$

respectively. The term $b_{\phi\alpha}^*$ for $\phi = \xi,Y$ can be found from

$$b_{\phi1}^* + b_{\phi2}^* = 0$$

$$\phi_1 b_{\phi1}^* + \phi_1 b_{\phi1}^* = \sum_{\alpha=1}^{2} p_{\alpha} \Gamma_T |\nabla \phi_{\alpha}|^2. \quad (8.35)$$

The mean concentrations in Eqs. (8.33) and (8.34) are defined by $\langle \phi \rangle = p_1 \phi_1 + p_2 \phi_2$ with $p_1 + p_2 = 1$. The chemical source term $S_Y$ depends on the particle nucleation and growth rates as discussed below.

### Chemical kinetics

The chemical species considered in this study are barium chloride (BaCl$_2$) and sodium sulfate (NaSO$_4$) dissolved in water. After mixing, they react to form barium sulfate (BaSO$_4$), the fine particles of which precipitate due to its extremely low solubility. This precipitation reaction can be expressed as

$$\text{Ba}^{2+} (A) + \text{SO}_4^- (B) \xrightarrow{k} \text{BaSO}_4 (P). \quad (8.36)$$

As shown in Eq. (8.36), hereinafter, we will refer to the reactants as $A$ and $B$, and the product as $P$. We assume that the reactor is operated in continuous mode with the first inlet stream containing $A$ and the second inlet stream containing $B$. As discussed in Fox, R. O. (2003), mixing between two inlet streams can be described by a mixture fraction $\xi$ that is independent of chemistry. Likewise, the chemical kinetics in Eq. (8.36) can be described by a reaction-progress variable $Y$. In terms of the mixture fraction and reaction-progress variable, the reactant concentrations are

$$c_A = c_{A0} (\xi - \xi_s Y), \quad (8.37)$$

$$c_B = c_{B0}[1 - \xi - (1 - \xi_s) Y], \quad (8.38)$$
where
\[ \xi_s = \frac{c_{B0}}{c_{A0} + c_{B0}}, \]  
(8.39)
and \( c_{A0} \) and \( c_{B0} \) are the inlet molar concentrations of reactants \( A \) and \( B \), respectively. Therefore, the chemical species vector for this problem is \( \phi = (\xi, Y) \).

For this irreversible reaction, the rate at which the reactants are consumed is mainly determined by the growth rate, \( G \), of the particles formed. However, there is also loss of reactants due to the nucleation of finite-size \( (d_p) \) particles, where \( d_p \) is the maximum diameter of the nuclei \( (d_p = 10^{-10} \text{ m in our simulations}) \). Applying the conservation of mass to the reactants gives the source term for the reaction-progress variable:
\[ S_Y = \frac{\pi \rho d_p^3}{3M\xi_s c_{A0}} J(c_A, c_B) + \frac{\rho k_v}{M\xi_s c_{A0}} 3G(c_A, c_B)m_2, \]  
(8.40)
where \( k_v \), \( M \), and \( m_2 \) represent the particle shape factor, molecular weight of \( P \), and the second-order moment of \( n(L) \), respectively. The first term on the right-hand side of Eq. (8.40) is due to particle nucleation and the second to surface growth.

**Moments of NDF**

The moments of the NDF \( m_{k\alpha} \) are found from Eq. (8.12) for the QMOM-PBE method. Likewise, the weights and abscissas are found from Eqs. (8.23) and (8.24) for the DQMOM-PBE method. The correction terms \( c_{k\alpha}^* \) for \( k = 0, \ldots, 2M - 1 \) are found from
\[ c_{k1}^* + c_{k2}^* = 0 \]
\[ m_{k1}c_{k1}^* + m_{k2}c_{k2}^* = \sum_{\alpha=1}^{2} p_\alpha \Gamma_T |\nabla m_{k\alpha}|^2. \]  
(8.41)
Note that the correction terms are well defined as long as \( m_{k1} \neq m_{k2} \). The purpose of the correction terms is to ensure that the Reynolds-average quantity \( \langle m_k^2 \rangle \) evolves correctly. In other words, \( c_{k\alpha}^* \) produces variance due to mean gradients of \( m_k \) and turbulent diffusion. If we set \( c_{k\alpha}^* = 0 \), the variance of \( m_k \) will be underpredicted. Physically, this means that the NDF in the environments \( (n_\alpha(L)) \) will approach the Reynolds-average NDF \( \langle n(L) \rangle \) too quickly. Nevertheless, because most of the fluctuations in the NDF are due to the non-premixed inlet
conditions (as opposed to mean scalar gradients generated by the flow), setting \( c_{ka}^* = 0 \) should not have a significant effect on the NDF moments for the cases considered in this work.

### 8.3.2 Source term for the moments

The NDF may change due to nucleation, growth, aggregation and breakage. Denoting the rates of nucleation, growth, aggregation and breakage as \( J, G, A \) and \( B \), respectively, the source term for \( n_\alpha(L) \) can be expressed as

\[
S_{n_\alpha} = J_\alpha - \frac{\partial}{\partial L} [G_\alpha n_\alpha] + A_\alpha + B_\alpha. \tag{8.42}
\]

In most practical applications, the dependence of \( J \) and \( G \) on \( L \) is weak and can be neglected. Applying the transformation of moments (Eq. 8.11) to Eq. (8.42) gives the source term for the \( k \)th moment of \( n_\alpha \):

\[
S_{k_\alpha} = \frac{d^k_p}{k+1} J(c_{A\alpha}, c_{B\alpha}) + k \sum_{m=1}^{M} w_{ma} L_{ma}^{k-1} G(c_{A\alpha}, c_{B\alpha}) + \sum_{m=1}^{M} w_{ma} a(L_{ma}) \left[ b^{(k)}(L_{ma}) - L_{ma}^k \right] + \frac{1}{2} \sum_{m=1}^{M} \sum_{p=1}^{M} w_{ma} w_{pa} \left[ (L_{ma}^3 + L_{pa}^3)^{k/3} - L_{ma}^k - L_{pa}^k \right] \beta(L_{ma}, L_{pa}). \tag{8.43}
\]

In this equation, \( a \) and \( b^{(k)} \) are the breakage kernel and the daughter-size distribution, respectively, and \( \beta \) is the aggregation kernel. It is assumed that nucleation produces a uniform distribution of nuclei in the size range \( 0 \leq L \leq d_p \). The kinetic expressions used in the univariate simulations are described below.

#### Nucleation kinetics

The process of nucleation is initialized by the existence of supersaturation, \( \Delta c \). According to Baldyga, J., et al. (1995), the nucleation kinetics are

\[
J(c_{A}, c_{B}) = \begin{cases} 
2.83 \times 10^{10} (\Delta c)^{1.775} \left[ 1/(m^3 s) \right] & \text{if } \Delta c \leq 10 \text{ mol/m}^3 \\
2.53 \times 10^{-3} (\Delta c)^{1.5} \left[ 1/(m^3 s) \right] & \text{if } \Delta c > 10 \text{ mol/m}^3
\end{cases} \tag{8.44}
\]
where $\Delta c$ is defined by

$$\Delta c = \sqrt{c_A c_B} - \sqrt{k_s}. \quad (8.45)$$

Here, $k_s = 1.14 \times 10^{-4}$ mol$^2$/m$^6$ is the solubility product of barium sulfate at room temperature. From Eq. (8.44), it can be concluded that $J$ is a highly non-linear function of $c_A$ and $c_B$ ($\xi$ and $Y$), and thus depends strongly on the local mixing conditions.

**Growth kinetics**

Unlike the nucleation rate $J$, which is a highly non-linear function of local species concentration in most practical applications, the growth kinetics are often limited by mass-transfer to the particle surface. In this work, $G$ is described by a two-step diffusion-adsorption model [Baldyga, J., et al. (1995)]:

$$G(c_A, c_B) = k_r (\Delta c_s)^2 = k_d (c_A - c_{As}) = k_d (c_B - c_{Bs}), \quad (8.46)$$

where $\Delta c_s = \sqrt{c_{As} c_{Bs}} - \sqrt{k_s}$, $k_r = 5.8 \times 10^{-8}$ (m/s)(m$^6$/mol$^2$) [Nielsen, A. E. (1984)], and $k_d$ is the mass-transfer coefficient. $k_d$ is usually size-dependent but remains nearly constant for particles smaller than 10 µm according to Nagata, S. (1975). In this work, $k_d = 10^{-7}$ (m/s) (m$^3$/mol). $c_{is}$ is the concentration of species $i$ near the surface of the crystal at the limit of the adsorption layer. The growth rate is obtained by solving

$$f (G) = G - k_r \left( \sqrt{\left(\frac{c_B - G}{k_d}\right)\left(\frac{c_A - G}{k_d}\right)} - \sqrt{k_s} \right)^2 = 0 \quad (8.47)$$

to find $G$ given $c_A$ and $c_B$.

**Breakage kinetics**

The power-law distribution is one of the breakage rate kernels that has found application to a wide variety of fragmentation phenomena:

$$a(L) = bL^{c_L}. \quad (8.48)$$
The values of breakage exponents are commonly taken as $c_L = 2$ and $c_s = 1$ if $L$ has a unit of m. $b$, the breakage rate coefficient, has the following empirical form for shear-induced fragmentation [Pandya, J. D. and Spielman, L. A. (1982)]

$$b = b' \gamma^y,$$  \hspace{1cm} (8.49)

where the empirical constants $b' = 32$ and $y = 1.85$ if the unit of $\gamma$ is s$^{-1}$. By assuming symmetric binary fragmentation:

$$b \left( \frac{L}{\lambda} \right) = \begin{cases} 
2 & \text{if } L = 2^{-1/3} \lambda \\
0 & \text{otherwise} 
\end{cases}.$$  \hspace{1cm} (8.50)

$b^{(k)}$ can be expressed as

$$b^{(k)}(L) = 2^{(3-k)/3} L^k.$$  \hspace{1cm} (8.51)

**Aggregation kinetics**

Aggregation occurs when two or more particles collide and adhere. For Brownian aggregation of spherical particles, $\beta$ can be written as

$$\beta_1(L_1, L_2) = K \left( L_1 + L_2 \right) \left( L_1^{-1} + L_2^{-1} \right),$$  \hspace{1cm} (8.52)

where $K = 2.74 \times 10^{-18}$ m$^3$s$^{-1}$ in this work. For shear-induced aggregation of spherical particles, $\beta$ can be approximated [Saffman, P. G. and Turner, J. S. (1956)] by

$$\beta_2(L_1, L_2) = 1.294 \gamma \alpha \left( L_1 + L_2 \right)^3,$$  \hspace{1cm} (8.53)

where $\gamma$, the local shear rate, is 750 s$^{-1}$ in order to be consistent with the flow field in the confined impinging-jet reactor (CIJR) studied in our previous work [Liu, Y. and Fox, R. O. (2006)], and $\alpha = 1$ is an efficiency factor. In order to account for the orthokinetic and perikinetic aggregation simultaneously, Eqs. (8.52) and (8.53) are summed together to give the overall aggregation rate: $\beta = \beta_1 + \beta_2$. 
8.4 Bivariate Test Case

For the bivariate test case taken from Fox, R. O. (2006b), we consider volume \( v \) and surface area \( s \) as internal coordinates, and the bivariate NDF \( n(v,s) \). For physical processes, we will consider a mixing-sensitive chemical reaction, particle nucleation, aggregation, and particle sintering (i.e. loss of surface area at constant volume).

8.4.1 DQMOM-IEM model

The multi-environment DQMOM-IEM model equations for the mixture fraction and the reaction-progress variable are the same as in the previous example. However, in this example the chemical source term \( S_Y \) depends only on particle nucleation:

\[
S_Y = \frac{\rho v_p}{M \xi s_{CB0}} J(c_A, c_B). \tag{8.54}
\]

Physically, \( J \) will depend on the rate of mixing relative to the rate of nucleation. If mixing is fast, \( c_A \) and \( c_B \) will be independent of the spatial location. Otherwise, \( J \) will be different in different fluid elements, causing the particle number density to be spatially inhomogeneous.

The weights \( w_m \) and abscissas \( (v_{ma}, s_{ma}) \) needed to describe the bivariate NDF \( n(v,s) \) are found using the DPDI model (Eqs. 8.29–8.31). The correction term \( c_{kl}^* \) is computed for each moment \( (k,l) \) from

\[
c_{kl1}^* + c_{kl2}^* = 0
\]

\[
m_{kl1}c_{kl1}^* + m_{kl2}c_{kl2}^* = \sum_{\alpha=1}^p p_\alpha \Gamma_T |\nabla m_{kl\alpha}|^2.
\]

As discussed previously, the correction terms are well defined as long as \( c_{kl1}^* \neq c_{kl2}^* \).

Following Fox, R. O. (2006b), we will use the following set of \( 3M \) moments:

\[
(k,l) \in (0,0), (1/3,0), \ldots, ((2M-1)/3,0), (0,1/3), \ldots, (0,M/3).
\]

Note that for this moment set, the \( k \)th and \( l \)th moment “directions” are uncoupled in the sense that we are using only “pure” moments in \( k \) and “pure” moments in \( l \) (i.e. no cross moments). With this choice of moments, the source terms in Eqs. (8.29)–(8.31) are found by solving two
linear systems. First, for each $\alpha = 1, 2$,

$$(1 - k) \sum_{m=1}^{M} v_m^k A_{ma} + k \sum_{m=1}^{M} v_m^{k-1} B_{ma}$$

$$= c_{k0a}^* + p_\alpha M_{k0a} + p_\alpha S_{k0a} + k (k - 1) \sum_{m=1}^{M} p_{\alpha} w_{ma} v_m^{k-2} \Gamma_T |\nabla v_{ma}|^2 \quad (8.57)$$

is solved for $A_{ma}$ and $B_{ma}$ using $k = 0, 1/3, \ldots, (2M - 1)/3$. Then

$$l \sum_{m=1}^{M} s_{ma}^{l-1} C_{ma} = (l - 1) \sum_{m=1}^{M} s_{ma}^l A_{ma}$$

$$+ c_{0la}^* + p_\alpha M_{0la} + p_\alpha S_{0la} + l (l - 1) \sum_{m=1}^{M} p_{\alpha} w_{ma} s_{ma}^{l-2} \Gamma_T |\nabla s_{ma}|^2 \quad (8.58)$$

is solved for $C_{ma}$ using $l = 1/3, \ldots, M/3$. The micromixing term $M_{kla}$ is given by Eq. (8.18).

### 8.4.2 Source term for the moments

The NDF may change due to nucleation, sintering, and aggregation. Thus the source term for $m_{kla}$ is

$$S_{kla} = v_p^k s_p^l J(c_{Aa}, c_{Ba}) + l \sum_{m=1}^{M} w_{ma} v_m^k s_{ma}^{l-1} R_s(v_{ma}, s_{ma})$$

$$+ \frac{1}{2} \sum_{m=1}^{M} \sum_{p=1}^{M} w_{ma} w_{pa} \left[(v_{ma} + v_{pa})^k (s_{ma} + s_{pa})^l - v_m^k s_{ma}^l - v_p^k s_{pa}^l\right]$$

$$\times \beta(v_{ma}, v_{pa}, s_{ma}, s_{pa}), \quad (8.59)$$

where $R_s$ is the sintering rate. In this expression, it is assumed that nucleation produces a nuclei of size $v_p$ and surface area $s_p = \pi (6v_p/\pi)^{2/3}$. In our simulations, we set $v_p = 10^{-30}$ m$^3$, corresponding to nanoparticles with a diameter of approximately 10 nm. The kinetic expressions used in the bivariate simulations are described below.

**Nucleation kinetics**

For nucleation kinetics ($J$), we will again use Eq. (8.44) with $k_s = 1.14 \times 10^{-4}$ mol$^2$/m$^6$. 
Sintering kinetics

Sintering is the process whereby particles decrease their surface area at constant volume due to restructuring. Here we use the linear sintering model of Koch and Friedlander (1990):

\[ R_a(v, s) = \frac{1}{t_f} [s_{\text{min}}(v) - s] \]

where \( s_{\text{min}}(v) = \pi(6v/\pi)^{2/3} \) is the surface area of a sphere with volume \( v \), and \( t_f \) is the characteristic sintering time.

Aggregation kinetics

For Brownian aggregation, \( \beta \) can be written as

\[ \beta_1(v_1, v_2, s_1, s_2) = K \left( v_1^{1/D_f1} + v_2^{1/D_f2} \right) \left( v_1^{-1/D_f1} + v_2^{-1/D_f2} \right), \]

where \( D_{f1} = D_f(v_1, s_1) \) and \( D_{f2} = D_f(v_2, s_2) \) are the fractal dimensions of the particles before collision, and \( K = 2.74 \times 10^{-18} \text{ m}^3\text{s}^{-1} \). For shear-induced aggregation, \( \beta \) can be approximated [Saffman, P. G. and Turner, J. S. (1956)] by

\[ \beta_2(v_1, v_2, s_1, s_2) = 1.294 \gamma \alpha \left[ (v_1/v_p)^{1/D_f1} + (v_2/v_p)^{1/D_f2} \right]^3, \]

where \( \gamma = 750 \text{ s}^{-1} \) and \( \alpha = 1 \). The overall aggregation rate is found as \( \beta = \beta_1 + \beta_2 \).

The fractal dimension of an aggregated particle will depend on the values of \( v \) and \( s \), where \( s_{\text{min}}(v) \leq s \leq s_{\text{max}}(v) \) and \( s_{\text{max}}(v) = vs_{\text{min}}(v_p)/v_p \) is the maximum surface area based on the nuclei volume. In the limit of \( s = s_{\text{min}}(v) \) (spherical particles) \( D_f = 3 \), while in the limit \( s = s_{\text{max}}(v) \) (fractal aggregates) \( D_f \approx 1.8 \). We will thus approximate \( D_f \) by the following linear relationship:

\[ D_f(v, s) = 3 - 1.2 \left( \frac{s - s_{\text{min}}(v)}{s_{\text{max}}(v) - s_{\text{min}}(v)} \right). \]

Note that when \( v = v_p \) (i.e. nuclei), we will use \( D_f = 3 \).

8.5 Simulation conditions

As an example, we consider the application of the CFD models with \( M = 3 \) quadrature nodes to the poorly micromixed plug-flow reactor (PFR) (see Fig. 8.1) used in our previous
work [Wang, L. and Fox, R. O. (2003)]. This reactor satisfies the following assumptions:
(i) the turbulence field is homogeneous and stationary with $k/\varepsilon = 0.001 \text{s}$ [Liu, Y. and Fox, R. O. (2006)]; (ii) the mean velocity is constant in the $x$-direction and $\langle U_y \rangle = \langle U_z \rangle = 0$; (iii) the turbulent diffusion term in the $y$-direction is dominant; (iv) the model variables depend on the residence time $t$ and the cross-stream ($y$) length only. Letting $t^* = t\varepsilon/k$ and $\eta = \varepsilon y/k^{1.5}$, the dimensionless CFD model equations are in the form

$$\frac{\partial \mathcal{V}}{\partial t^*} = 0.1286 \frac{\partial \mathcal{V}}{\partial \eta} + \frac{k}{\varepsilon} \mathcal{S},$$

(8.64)

where $\mathcal{V}$ is the set of scalar quantities that define the CFD model, $\mathcal{S}$ is the set of source terms for the scalars, and $0 \leq \eta \leq 2$. The model is solved with periodic boundary conditions: $\mathcal{V}(t^*, 0) = \mathcal{V}(t^*, 2)$. The two inlet streams are non-premixed: one stream contains only environment 1 in which $\xi = 0$ and $Y = 0$; the other contains only environment 2 in which $\xi = 1$ and $Y = 0$. The initial distribution of $p_1$ and $p_2$ across the domain is shown in Fig. 8.2. The inlet conditions for the moments (weights and abscissas) are described below.

By adopting a time-splitting scheme [Press, W. H., et al. (1992)], Eq. (8.64) is decomposed into a partial differential equation (PDE), the right-hand side of which is nothing but the diffusion term:

$$\frac{\partial \mathcal{V}}{\partial t^*} = 0.1286 \frac{\partial \mathcal{V}}{\partial \eta};$$

(8.65)

and an ordinary differential equation (ODE) that involves the combined source term due to mixing, chemistry, nucleation, growth, aggregation and breakage:

$$\frac{\partial \mathcal{V}}{\partial t^*} = \frac{k}{\varepsilon} \mathcal{S}.$$  

(8.66)

Equation 8.65 is solved by the Crank-Nicolson method [Crank, J. and Nicolson, P. (1947)]. The grid consists of 101 points that are uniformly distributed along the $\eta$-direction. The maximum time step that satisfies the CFL number (0.16) is $5 \times 10^{-4}$; thus, $\Delta t^* = 4 \times 10^{-4}$ was chosen as the time step for advancing Eq. (8.65). Due to the stiffness of Eq. (8.66), a stiff ODE solver is needed to advance the scalars over the same time step $\Delta t^*$. Here Eq. (8.66) is solved using dlsoda.f.
One of the major challenges of the DQMOM is that the matrix defined by the linear equation system in Eq. (8.25) can be nearly singular [Fox, R. O. (2006b)], and the system cannot be solved accurately even with the singular value decomposition (SVD) [Press, W. H., et al. (1992)]. An efficient solution of this difficulty is to rescale the abscissas by dividing by $L_{\text{max}}$, where $L_{\text{max}}$ is the largest abscissa [Fox, R. O. (2006b)]. (Note that $L_{\text{max}}$ depends on $t^*$ and $\alpha$.) In addition, greater precision for the solution can be obtained after applying the technique of iterative improvement described in Press, W. H., et al. (1992).

**Univariate test case**

The initial values of the weights and abscissas are the same in both environments, and are set equal to $w_1 = 0.1127$, $w_2 = 0.5$, $w_3 = 0.8873$, $L_1 = 2.778d_p$, $L_2 = 4.444d_p$, and $L_3 = 2.778d_p$. It should be noted that the initial weights and abscissas do effect the values of the source terms for small times. However, the source terms quickly adjust the weights and abscissas so that the predicted moments are independent of their initial values. In fact, the initial values are close to zero compared with the equilibrium values, indicating that they can be used to approximate a system that initially has no particles.

**Bivariate test case**

The initial values of the weights and abscissas are the same in both environments, and are set equal to $w_1 = 1$, $w_2 = 0$, $w_3 = 0$, $v_1 = v_p$, $v_2 = 2v_p$, $v_3 = 3v_p$, $s_1 = s_{\text{max}}(v_1)$, $s_2 = s_{\text{max}}(v_2)$, and $s_3 = s_{\text{max}}(v_3)$.

### 8.6 Results and discussion

#### 8.6.1 Univariate test case

The QPDI and DPDI models were implemented to simulate reactive precipitation in a plug-flow reactor with the particle diameter as the internal coordinate. As a first step, we compare the results from the two models to show that they are identical (as expected). We
then investigate the effects of the model parameters on the predicted results using the DPDI model.

**Equivalence of QPDI and DPDI**

In Fig. 8.3 three NDF moments in the two environments are compared for the two methods with $c_{A0} = 200 \text{ mol/m}^3$ and $c_{B0} = 100 \text{ mol/m}^3$. NDF moments predicted by DPDI and QPDI are in close agreement. The zero-order NDF moment $(m_0)$ increases quickly for $t^* \leq 1$, indicating that a large number of particles are being produced by nucleation which occurs right after the non-premixed inlet streams begin to mix at a rate of $1000 \text{ s}^{-1}$. After $t^* = 2$, $m_0$ begins to decrease quickly as a result of the aggregation favored by the large number density. It is noted that for $1 < t^* \leq 2$ in environment 1 increases at $0 \leq \eta \leq 1.15$ but decreases at $1.15 < \eta \leq 2$ and behaves reversely in environment 2. This is not a surprise if we recall that micromixing causes the NDF moments in the environments to approach the Reynolds-average NDF moments at large times. The behavior of micromixing is also shown by the time evolution of $m_1$, which begins to decrease after $t^* = 2$ in environment 1 but keeps increasing until $t^* = 3$ in environment 2. $m_2$ increases monotonically though the number density $(m_0)$ decreases after $t^* = 2$, indicating that the abscissas increase continuously due to growth and aggregation. Due to diffusion along the $\eta$-direction, the spatial distributions of the NDF moments become uniform at long times.

Being confident with the accuracy of the DPDI method, we will now focus our discussion on the CFD model predictions.

**Evolution of probability and chemical species vector**

The time evolution of $p$, $\xi$ and $Y$ in each environment is shown in Fig. 8.2. The spatial distribution of those variables becomes uniform gradually due to diffusion and approaches to their Reynolds-average values, 0.5 for $p$ and $\xi$, for example, due to micromixing. $Y$ in environment 1 is larger than in environment 2, indicating that the species concentrations in environment 1 are more likely affected by the reaction than in environment 2.
Effect of species concentrations

The effect of chemistry on the evolution of the NDF moments was examined by varying the inlet species concentrations from $c_{A0} = 100 \text{ mol/m}^3$ and $c_{B0} = 50 \text{ mol/m}^3$ (low species concentration) to $c_{A0} = 200 \text{ mol/m}^3$ and $c_{B0} = 100 \text{ mol/m}^3$ (high species concentration). The resulting particle diameter $d_{10} = m_1/m_0$, the particles number density $m_0$, and the Reynolds-average values $\langle d_{10} \rangle$ and $\langle m_0 \rangle$, are presented in Figs. 8.4 and 8.5, respectively.

In general, high species concentrations enable larger supersaturation, and thus produce higher rates of nucleation and growth. Equations (8.44) and (8.47) show that the nucleation rate is an exponential function of the supersaturation while the growth rate only varies with the supersaturation linearly. Thus, nucleation is more favored by the high species concentrations and a higher particle number density is expected. With low species concentrations, $\langle m_0 \rangle$ is $1 \times 10^{18} \text{ m}^{-3}$, which is about 99% less than that given by high species concentrations (compare Figs. 8.4 and 8.5). For the low concentrations (Fig. 8.4), $m_0$ increases at an accelerated speed, indicating that nucleation remains significant at $t^* = 4$. It could be concluded that a large amount of reactants still exist in the flow and thus the growth rate is expected to be high, causing the particles to become larger. Here, the effect of breakage on the particle size is neglected since the particles are smaller than 4 nm. For the high concentrations (Fig. 8.5), $m_0$ in each environment increases quickly before $t^* = 1$ and decreases after $t^* = 2$ but the particles keep growing larger. This tendency indicates that in the initial stages, nucleation produces a large number of particles. While the reactants are being consumed gradually, nucleation slows down and the aggregation among such a large number of particles becomes dominant. Thus, it is aggregation rather than growth that makes the particles larger. In fact, aggregation is prevalent in a system with a high supersaturation.

For both cases, it can be noticed that the NDF moments in the two environments appear to be different after the reactive precipitation begins and before the streams are completely mixed. It is the distribution of the reactants that determines the NDF. Therefore, for any applications such as soot production [Zucca, A. et al (2006)] that involve a strong coupling between the chemistry and the evolution of the NDF, the effects of micromixing on the fine-
particle formation should be taken into consideration. For example, soot will be formed at
locations in composition space that are fuel rich and will be oxidized in locations with excess
oxygen. It can be anticipated that the successful description of fine-particle formation in
such strongly coupled problems will require a detailed CFD model that explicitly accounts for
subgrid-scale fluctuations and the correlations between $Y$ and the NDF.

**Rates of nucleation, aggregation and breakage**

Mixing effects the evolution of the NDF moments directly through the rates of nucleation,
growth, aggregation and breakage (the zeroth-order moments are independent of growth),
which are shown in Fig. 8.6. As expected, the spatial distribution of each of these rates in
one environment is quite different from its counterpart in the other environment before mixing
is complete. For $t^* \geq 2$, the nucleation rate in environment 2 (Fig. 8.6) are much higher
than in environment 1 due to the higher supersaturation in environment 2. As a consequence,
environment 1 contains more larger particles while environment 2 contains more number of
particles. This is confirmed by the results in Fig. 8.5. At $t^* = 4$, the nucleation rate is close to
zero, indicating that most of the reactants have been consumed by that time. The aggregation
rates in the two environments are negative since the effect of aggregation is to reduce the
particle number density. It is noticed that a fast aggregation always happens with a fast
nucleation, demonstrating that aggregation if favored by a larger number density. Breakage is
minor compared with nucleation and aggregation due to the smaller particle size. However, it
increases with the particle size and is likely to be important at long times.

**Rate of micromixing**

The time evolution of the mixing rate of the NDF moments in environment 1 for high species
concentrations is illustrated in Fig. 8.7. Initially, the NDF moments in the two environments
are identical. So all the rates of mixing are zero. Once mixing between the two inlet streams
occurs, the difference between the local species composition in the two environments force
$m_{k1}$ to be distinct from $m_{k2}$, leading to micromixing. Eventually, the micromixing rates
of the moments approach zero, meaning that the NDFs in the two environments are close to the Reynolds-average value. It is noted that the magnitude of the micromixing terms is comparable to its corresponding moments. Thus, for reactive precipitation micromixing should be considered in order to obtain accurate computational results.

For $\eta \leq 1$, $M_0$ is always positive. This is not a surprise since Fig. 8.5 shows that more particles exist in environment 2 at those spatial locations. However, $M_{11}$ and $M_{21}$ are negative almost everywhere during the time interval since the particle diameter in environment 2 is smaller than in environment 2 (Fig. 8.5).

### 8.6.2 Bivariate test case

The CFD predictions for the bivariate test case is being under examination.

### 8.7 Conclusions

In this work, the univariate as well as bivariate QPDI and DPDI model equations are derived starting from the PDF transport equation of the NDF closed by the IEM model. The turbulent reactive precipitation of fine particles of BaSO$_4$ in a PFR model with two non-premixed inlet streams was simulated using these models. As far as we know, this represents the first attempt to account for the effects of mixing on population balance using DQMOM or QMOM.

It has been shown that the DPDI model gives results equivalent to the QPDI model for a univariate case in which the particle diameter is the internal coordinate. In addition, we have demonstrated that the evolution of the NDF moments strongly depend on the local species concentrations that are significantly controlled by mixing in many applications. Hence, a larger particle number density can be expected at locations where the local species concentrations are high, while the particle size tends to be smaller. The time evolution of the rates of mixing, nucleation, growth, aggregation and breakage have been examined. It has been found that mixing cannot be safely neglected if an accurate NDF is desired for reactive precipitation.
Acknowledgments

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Figure 8.1 Sketch of the poorly micromixed plug flow reactor model.
Figure 8.2 Time evolution of the spatial distribution of $p$, $\xi$, and $Y$ with $c_{A0} = 200$ mol/m$^3$ and $c_{B0} = 100$ mol/m$^3$. Left: Environment 1. Right: Environment 2. —: $t^* = 0$. ——: $t^* = 1$. ···: $t^* = 2$. ––: $t^* = 3$. ···: $t^* = 4$. 
Figure 8.3 Time evolution of the spatial distribution of the moments $m_k$ ($k = 0, 1, 2$) predicted by DPDI (lines) and QPDI (symbols) with $c_A = 200$ mol/m$^3$ and $c_B = 100$ mol/m$^3$. Left: Environment 1. Right: Environment 2. —, □: $t^* = 0$. ——, △: $t^* = 1$. ••••, ▽: $t^* = 2$. —, ◦: $t^* = 3$. ••, ◆: $t^* = 4$. 
Figure 8.4 Time evolution of the particle diameter and number density with $c_{A0} = 100$ mol/m$^3$ and $c_{B0} = 50$ mol/m$^3$. Top: Environment 1. Middle: Environment 2. Bottom: Reynolds-average. 

$\cdots$: $t^* = 0$. $\cdots$: $t^* = 1$. $\cdots$: $t^* = 2$. $\cdots$: $t^* = 3$. $\cdots$: $t^* = 4$. 
Figure 8.5 Time evolution of the particle diameter and number density with $c_{A0} = 200 \text{ mol/m}^3$ and $c_{B0} = 100 \text{ mol/m}^3$. Top: Environment 1. Middle: Environment 2. Bottom: Reynolds-average.

$- - : t^* = 0$. $- - - : t^* = 1$. $\ldots : t^* = 2$. $- - : t^* = 3$. $- - - : t^* = 4$. 
Figure 8.6  Time evolution of the rate of nucleation (first row), growth (second row), aggregation (third row) and breakage (fourth row) for the zeroth-order moment with $c_{A0} = 200 \text{ mol/m}^3$ and $c_{B0} = 100 \text{ mol/m}^3$. Left: Environment 1. Right: Environment 2. —: $t^* = 0$. — —: $t^* = 1$. •••: $t^* = 2$. --: $t^* = 3$. ···: $t^* = 4$. 
Figure 8.7  Time evolution of the micromixing rate of the moments $m_k$ ($k = 0, 1, 2$) in environment 1 with $c_{A0} = 200 \text{ mol/m}^3$ and $c_{B0} = 100 \text{ mol/m}^3$. $- - -$: $t^* = 0$. $- - - -$: $t^* = 1$. $\cdots$: $t^* = 2$. $- - - -$: $t^* = 3$. $- \cdots -$: $t^* = 4$. 
CHAPTER 9. TURBULENCE IN A MICROSCALE PLANAR
CONFINED IMPINGING-JETS REACTOR

A paper in preparation
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Abstract

Confined impinging-jets reactors (CIJR) offer many advantages for the chemical processing of rapid processes, such as precipitation and the production of organic nanoparticles. It has been demonstrated that the computational fluid dynamics (CFD) is a promising tool for “experiment-free” design and scale-up of such reactors. However, the validation of the CFD model for the microscale turbulence necessities experimental data the availability of which is so far very limited. In this work, the micro-resolution particle-image velocimetry (micro-PIV) techniques were employed to measure the velocity field for different Reynolds numbers in a planar CIJR. The performance of a CFD model, the two-layer $k-\varepsilon$ model, was evaluated by comparing the predicted flow field with the experimental data. To our knowledge, this study represents the first attempt to directly measure the velocity and turbulence fields in a microreactor and to use the results to validate a CFD model for microscale turbulent flows.

9.1 Introduction

The confined impinging-jets reactor (CIJR) is of great industrial interest due to its ability to generate fast mixing the timescale of which is on the order of millisecond [Johnson, B. K. and Prud’homme, R. K. (2003a,b); Mahajan, A. J. and Kirwan, D. J. (1993, 1996)]. As discussed in detail elsewhere [Liu, Y. and Fox, R. O. (2006)], a computational fluid dynamics (CFD)
approach that involves a two-layer $k - \varepsilon$ model [Chen, H. C. and Patel, V. C. (1988)] and a direct-quadrature-method-of-moments (DQMOM) - interaction-with-the-mean (IEM) model [Liu, Y. and Fox, R. O. (2006); Fox, R. O. (2003)] have successfully reproduced (without adjustable parameters) the experimental data for a microscale CIJR with a fourth Bourne reaction system. Since the experimental data were limited to overall conversion, the local turbulence and concentration fields predicted by those models were unable to be validated. As far as we know, no attempt has been made to validate CFD models against experimental data for turbulence in such a microscale reactor.

It has been proved that the two-layer $k - \varepsilon$ model is able to satisfactorily predict the complex flow fields in a confined planar-jet reactor [Feng, H. et al. (2005)] and a confined planar-wake reactor [Liu, Y. et al. (2006)]. The flow statistics such as the mean velocity, turbulent kinetic energy and dissipation rate predicted by the CFD model agrees well with the experimental data measured by the particle-image velocimetry (PIV) techniques. However, the performance of this model for the CIJR with microscale dimensions in which the wall effects and the complexity of the flow are significant is still open to question.

The objectives of this work are to measure the velocity and turbulence fields using the micro-PIV techniques and validate the CFD model against the experimental data. The theory and image analysis techniques of PIV originated with Adrian [Adrian, R. J. (1988), Adrian, R. J. (1991)] and the design rules for optimizing the performance of the PIV system were firstly formulated by Keane and Adrian [Keane, R. D. and Adrian, R. J. (1992)]. Micro-PIV ($\mu$PIV) is a modification of PIV in order to determine the flow field at the micrometer scale. The first application of micro-PIV with fluorescent seed particles was demonstrated by Santiago et al. [Santiago, J. G. et al. (1998)]. As being summarized elsewhere [Wereley, S. T. et al. (2002)], micro-PIV differs from its macroscopic counterpart by three major factors. First, the flow-tracing particles are small compared to the wavelength of the illuminating light but must also be large enough to be recorded. The fluorescent particles have made micro-PIV studies in liquid flows [Santiago, J. G. et al. (1998), Meinhart, C. D. et al. (1999b)] successful and are therefore adopted in this study. Second, Brownian motion of the seeding particles may
decrease the accuracy of the PIV measurements, especially for slow flows, by preventing the particles from following the flow. Nevertheless, such an error can be substantially reduced by increasing the particle density and the number of realizations. The most significant difference is flow illumination. In PIV, measurements are taken on a plane illuminated by a thin laser sheet. In micro-PIV, the entire volume of the flow that can be covered by the microscope objective is illuminated, making the depth of focus, or more appropriately, the depth of correlation, an important issue affecting the accuracy of the measurement of the local flow field.

Micro-PIV has been increasingly employed to measure the flow in many microfluidic devices. Wereley [ Wereley, S. T. et al. (2002)] investigated supersonic gas flows in a micronozzle with $Re = 22$, demonstrating that micro-PIV allows measurements at length scales on the order of 1µm. This study was extended to gas-phase flows further by Meinhart, C. D. et al. [ Meinhart, C. D. et al. (1999a)]. Laminar to turbulent flow transition in microtubes has recently been studied by Sharp and Adrian [ Sharp, K. V. and Adrian, R. J. (2004)]. Li, H. et al. [ Li, H. et al. (2005)] performed the turbulent and transitional velocity measurements in a rectangular microchannel, reporting a transition to turbulence at a Reynolds number lower than that predicted by classical theory. Brown et al. conducted micro-PIV velocity measurement of the flows in a straight channel and a ribbed channel. It has been found that the precision with which the geometrical parameters can be determined affects the accuracy of the experimental data more than the spatial resolution does. However, no attempt has been made to measure the velocity and turbulence fields and validate the CFD model against experimental data for a microscale complex device like the CJFR studied here.

The geometry used in our experiments and simulations is shown in Fig. 9.1. The depth of the reactor is designed to be 1 mm. The width of the impinging jets, $w$ is 0.5 mm. Letting $W, H, Z$ and $\delta$ represent the chamber width, height, length, and the outlet width, respectively, their scaled values are $W/w = 4.76$, $H = 0.8W$, $Z = 1.2W$, and $\delta = 2w$. In order to obtain stable inlet and outlet flows, the length-to-width ratio of the inlet and outlet tubes are $L_1/w = 20$, and $L_2/\delta = 20$, respectively. This geometry differs from the one used in our previous study [ Liu, Y. and Fox, R. O. (2006)] in its planarity. The revision was made
on purpose so that the accuracy of the PIV measurements are not affected by refraction. However, the significance of the wall effects or the complexity of the flow is not fundamentally altered. Thus, the observations of the performance of the CFD model for this planar geometry should be able to be extended to the original design. It is apparent that an inlet tube with a 0.5×0.5 mm² cross section is the best approximation to a round inlet tube. However, with such a small cross-section area, the interface of the connecting tubing and inlet channel has to withstand such a high pressure that the tubing ends to disconnect itself from the device. Moreover, turbulence is more difficulty to be achieved in such a microchannel.

The remainder of this work is organized as follows: First, we introduce the experimental apparatus and methodology. The spatial resolution of the measurements and seed concentration are discussed. Secondly, we review the techniques used to fabricate the microchannel and show their advantages and limitations. Then the simulation conditions are described in brief. A detailed discussion of our results is presented before the conclusions are drawn from our study.

### 9.2 Experimental Apparatus and Methodology

The experimental setup is schematically shown in Fig. 9.2. It consists of a flow delivery system and a micro-PIV system. The fluid, which is nano-pure water with a certain amount of fluorescent particles dissolved, is driven by two microgear pumps (Console digital dispensing drive, Cole-Parmer Instrument Co.) at a rate mainly controlled by the pump heads (0.092 ml/rev suction shoe gear pump heads, Cole-Parmer Instrument Co.) together with the pressure in the impinging area. The reservoir supplies the inflows and collects the outflow. In this way, the particle solution circulates in the flow facility until all the desired PIV images are taken and the amount of fluorescent particles required by each run is quite limited. The nanopure water rather than deionized water was used in this study since its extremely low conductivity (18 mΩ-cm) helps reduce the agglomeration of the seed particles made of polystyrene. About 50 ml of fluid is hold in the reservoir, allowing for longer run times before any viscous heating was discernable. After each experimental run, the particle solution was replaced with
nanopure water and the outflow was collected by a container for 5 minutes. The exact volumetric flow rate was therefore derived from the volume of nanopure water. It should be noted that the physical properties such as density and viscosity of the working fluid are closed to those of nanopure water since the density of the fluorescent particles $\rho_p = 1.005 \text{g/cm}^3$ and the working fluid only contains a small amount of the particles. The microchannel was connected to the flow delivery system via flexible tubing (C-flex tubing, Cole-Parmer Instrument Co.).

The micro-PIV system was used to measure the instantaneous velocity field in the observed flow. All the measurements are two-dimensional. The microchannel is placed on the stage of an inverted biological microscope (Nikon model T-300 Inverted Microscope). By moving the microscope stage along the x- and y-directions horizontally, the observed area can be changed without moving the lasers or the camera. The microscope stage can also be lowered or raised along the z-direction, enabling the focus of the microscope objective. The 532 nm laser beam from a New Wave Research Gemini Nd: YAG PIV laser is expanded before being directed towards the microchannel by a dichronic mirror and passes through the objective. The fluorescent seed particles (Duke Scientific) are excited by the laser beam entering the microchannel from its bottom wall and emit a fluorescence the peak emission wavelength of which is 612 nm. The beamsplitter reflects the 542 nm laser beam and exclusively allows the fluorescence to pass through. In this way, only the light emitted from the particles reaches the CCD camera (12-bit LaVision Flowmaster 3S CCD). The laser and camera were connected to a host computer that controls the timing of laser illumination and image acquisition. Two images were captured per realization at a frame rate of 8 images/s. The corresponding vector field was computed using a cross-correlation techniques [Westerweel, J. (1993); Kompenhans, J. et al. (1998)]. The timing between laser pulses was chosen so that the particles travel across 1/4 of an interrogation window between exposures.

The concentration of the seed particles solution was computed by using the equation

$$C = \frac{N}{A (2Z_{corr})}, \quad (9.1)$$

where $C$ is the number density of the fluorescent particles in the working fluid. $N$ denotes the number of particles in each interrogation volume and is chosen to be 8 in this work [Olsen,
M. G. and Adrian, R. J. (2000). $A$ and $Z_{\text{corr}}$ represent the area of the interrogation window and the depth of correlation, respectively. Given the numerical aperture (NA) and the magnification of an objective ($M$), the wavelength ($\lambda$) of fluorescence emitted by the particles the diameter of which is $d_p$ ($d_p = 2 \mu m$ in this study), the depth of correlation can be estimated by [Olsen, M. G. and Adrian, R. J. (2000)]

$$Z_{\text{corr}} = \left[ \frac{1 - \sqrt{\varepsilon}}{\sqrt{\varepsilon}} \left( f^2 d_p^2 + \frac{5.95 (M + 1)^2 \lambda^2 f^4}{M^2} \right) \right]^{1/2}, \quad (9.2)$$

where $f$ is the focal number of the lens and can be related to NA by [Meinhart, C. D. et al. (2000)]

$$f = \frac{1}{2NA}. \quad (9.3)$$

A sufficient seed particle density is expected in order to obtain an accurate instantaneous velocity vector field. However, achieving a high seed particle density in micro-PIV experiments is more difficult than it is in PIV measurements [Wereley, S. T. et al. (2002), Feng, H. et al. (2005); Liu, Y. et al. (2006)] and usually need sacrifice the spatial resolution [Wereley, S. T. et al. (2002), Li, H. et al. (2005)]. In this study, two objectives, a 4X 0.13NA and a 10X 0.3NA, were used, yielding a depth of correlation of 86 $\mu m$ and 23.8 $\mu m$, respectively. For the 4X objective, the final interrogation windows measure 32×32 pixels, corresponding to a spatial resolution of 115 $\mu m$ in the $x$– and $y$– directions. The adjacent interrogation windows overlap by 50%. For the 10X objective, although the final interrogation windows measure 32×32 pixels too, the spatial resolution increases to 42 $\mu m$. The adjacent interrogation windows were set not to overlap. It should be noted that overlap between the adjacent interrogation windows does not help improve the spatial resolution, but may help reduce some random errors.

The experiments were performed for inlet jet Reynolds numbers ranging from 90 to 1085. The inlet jet Reynolds number, defined by

$$Re_j = \frac{du}{\nu}, \quad (9.4)$$

is computed, based on the inlet bulk velocity, $u$, the hydraulic diameter of the inlet channel, $d$, and the kinematic viscosity of the pure water, $\nu$. For each jet Reynolds number, 500 to
1500, depending on the turbulent intensity of the inlet flows, realizations were taken and then analysis by Davis 6.0 (LaVision). The seed particles are expected to be fine so that they can completely follow the local flow stream. The definition of a “fine” particle can be made more quantitative by introducing the particle Stokes number $St$ that characterize the ratio of particle response time to the flow time scale:

$$St = \frac{\gamma \rho_p d_p^2}{12 \rho_f \nu_f},$$

(9.5)

In the equation above, $\gamma$ is a characteristic strain rate for the flow and can be approximated by $2u/W$. $\rho_f$ and $\nu_f$ are the fluid density and viscosity, respectively. For $Re = 1085$, $St = 2.9 \times 10^{-4}$, indicating that inertia of a particle does not affect the experimental data [Samimy, M. and Lele, S. K. (1991)].

9.3 Microchannel Fabrication

In the design and fabrication of the microchannel, the following requirements were set up and satisfied to the greatest extent:

- The material used to build the microchannel (at least that for the bottom wall) should be transparent and smooth in order to allow the light in and out;

- One of the ultimate objectives of this study is to validate a CFD model against the experimental data. Thus the exact dimensions of the microchannel are highly desired. Only those techniques that are able to ensure precise dimensions were acceptable;

- If the microchannel consists of more than one piece, the adhesion of the pieces should not introduce any uncertainty to the dimensions of the channel. Moreover, the adhesion must be strong so that the microchannel is able to withstand high working pressure as the flow rate increases;

- The alignment of the two inlet channel is quite important to ensure the impingement of the inlet jets;
The buildup of contaminants in the microchannel is almost inevitable. Therefore the microchannel is expected to be "disposable" and affordable.

Over the past two decades, the micro-electro-mechanical systems (MEMS) have developed rapidly and found wide applications in fabricating microfluidic devices. The micromachining processes can selectively etch away parts of the silicon wafer or add new structural layers to form the mechanical and electromechanical devices, the width and length of which can be controlled precisely while the depth (or the height) might vary with the operating conditions but can be measured by a millimeter ruler under a microscope. Given a mold master, the microchannel can be made using polydimethylsiloxane (PDMS) replica molding [Li, H. et al. (2005); Son, S. Y. et al. (2002); McDonald, J. C. et al. (2000)]. That is, casting the mixture of PDMS prepolymer and curing agent onto mold master, peeling the PDMS piece off the mold after it hardens, bonding the PDMS piece to a glass slide with the aid of oxygen plasma that activates the surfaces of the materials. More details can be found elsewhere [Li, H. et al. (2005); Son, S. Y. et al. (2002); McDonald, J. C. et al. (2000)]. In order to make the mold master, the negative photoresist (SU-8, 2100, MicroChem Corp.) was used to construct a high relief for the channel on a silicon wafer (100 mm diameter, Montco Silicon Technologies, Inc.). Unfortunately, the height of the resulting mold is much less than 1 mm since the upper limit of the height that can be given by MEMS is about 300-400 µm. Occasionally a height of 800 µm could be obtained but the quality of the mold was not satisfactory. Meanwhile, we found that the PDMS piece deforms under high working pressure, resulting in the change of the dimensions of the microchannel. We were therefore motivated to propose a new way for the fabrication.

In this study, the device consists of a piece of stainless steel cut through by the electronic discharging machine (EDM) and two glass slides as the top and bottom walls, respectively. An opening was drilled at the location of the end of the inlet/outlet channel on the top glass slide, allowing the flow to enter or leave the device. The stainless steel and the glass slide were bonded by a double-sided silicon transfer adhesive film (Dielectric Polymers) the thickness of which is 0.025 mm. The thickness of the stainless steel is 0.87 mm. Thus the depth of the
resulted device was known as 0.92 mm. The fabrication cost is acceptable.

9.4 Simulation Conditions

The behavior of the planar CIJR was simulated using the CFD code Fluent 6.2 with a steady-state solver. The computational grid consisted of at least 20880 hexahedral cells, with more cells required for grid-independent solutions at higher Reynolds numbers. The two-layer $k - \varepsilon$ model, which is the standard $k - \varepsilon$ model plus the enhanced wall treatment in Fluent 6.2, was employed to compute the turbulent kinetic energy and dissipation. The inlet boundary conditions for the turbulent kinetic energy $k$ and the dissipation $\varepsilon$ were set up through a turbulent intensity, 10%, and an integral length scale of turbulence, 0.5 mm, in this study. In cases where the flow is apparently laminar, no viscous model was employed in the simulations.

9.5 Results and Discussion

The flow field was measured by using a 4X objective for Reynolds numbers ranging from 90 to 1085 and a 10X objective for Reynolds numbers ranging from 211 to 901. All the measurements were performed by focusing the objective on the plane centered in the spanwise direction after the flow had reached the stable state. The inlet flows were balanced with caution by adjusting the needle valves.

9.5.1 Experimentally measured velocity fields

The 4X objective covers an area of $4.6 \times 3.68 \text{ mm}^2$. Figures 9.3 and 9.4 show the instantaneous and ensemble-averaged velocity fields for $Re_j = 90$, and 1085, respectively. In both cases, recirculation areas exist on the shoulders of the impinging jets and near left and right walls of the reactor. This is not a surprise if we recall that the mass flow rate and the velocity of the inlet streams are identical. The $x$-momentum diminishes quickly to zero or even changes its direction once the inlet jets collide while the $y$-momentum remains, leading the fluid to go up and down. The flow going up forms the vortexes on the shoulder of the impinging jets while the vortexes near the walls are initiated by the flow going down. In the ensemble-averaged
velocity field, the vortexes in each pair are symmetric with respect to the $y$-axis if the inlet flows are well balanced (see Figs 9.3 and 9.4). At $Re_j = 90$, the instantaneous velocity field is very similar to the ensemble-averaged one (Fig. 9.3), illustrating that the velocity fluctuations are low in the laminar flow. On the other hand, the instantaneous velocity field for $Re_j = 1085$ (Fig. 9.4) indicates strong turbulence in the flow: the vortexes keep changing their locations and are in irregular shapes. As shown by Figs 9.3 and 9.4, fluid does not reach the very top of the reactor since no valid vector (vectors in Fig 9.3 near the very top were in fact introduced by noise) was found at that area.

The area observed by the 10X objective is as small as $1.72 \times 1.37 \text{ mm}^2$. With this objective, the two inlet streams can not be examined at the same time but the resolution of the measurements improves. The images were taken for different portions of the reactor including A: the left inlet near the entrance to the chamber; B: the right inlet near the entrance to the chamber; C: the areas right above the impinging jets and D: the areas right below the impinging jets (see Fig. 9.5). Figure 9.6 shows the ensemble-averaged velocity fields at those locations for $Re_j = 211, 601$ and $901$, respectively. The inlet flows for $Re_j = 211$ and $601$ are laminar while for $Re_j = 901$, the inlet flow is more turbulent. More discussion can be found in Sec. 9.5.2. Figures in the middle and right columns of Fig 9.6 clearly demonstrate how the velocity was redirected by the impingement of the jets. They even show that the flow at somewhere between the upward and downward flows is stationary for each Reynolds number. The vortexes above the shoulders of the jets for $Re_j = 901$ are not axisymmetric, whether in position or in shape, even the number of images taken were increased to 1500. Similar observations can be found for the flow below the jets. Some sample instantaneous velocity fields are displayed in Fig 9.7. For $Re_j = 901$, the inlet jets significantly flap in reverse direction, though the settled mass flow rate remained constant through the entire run. We contribute this observation mainly to the fluctuation in the inlet flow rate, which is $4.7\%$ of the settled flow rate. It was also noticed that at high Reynolds numbers, the eddies that were able to be dissolved by the PIV measurements were smaller. This can be explained by how the integral lengthscale $L$ is related
to the Kolmogorov scale $L_{\eta}$:

$$\frac{L}{L_{\eta}} = \frac{k^{3/2}}{(\frac{\varepsilon}{\nu})^{1/4}} = Re^{3/4} \quad (9.6)$$

where, $Re$, the turbulent Reynolds number, can be defined as

$$Re \equiv \frac{k^2}{\varepsilon \nu} \quad (9.7)$$

With $Re$ increases, $\varepsilon$ becomes larger and the Kolmogorov scale at the impinging area decreases. Consequently, more smaller eddies appear and then can be captured by the PIV measurements with a certain spatial resolution.

**9.5.2 CFD predictions for mean velocity and turbulent kinetic energy**

The planar CIJR was simulated by using Fluent 6.2 and the predictions are compared with the experimental data in Figs. 9.8 and 9.9.

Figure 9.8 shows that the two-layer $k - \varepsilon$ model satisfactorily captured all the essential behavior of the mean velocity and the turbulent kinetic energy. However, the predicted turbulent kinetic energy is much higher than the measured value. This is not surprising if we recall that the PIV measures a velocity field averaged over the volume of the interrogation windows. The computational results demonstrate that the turbulent kinetic energy peaks its magnitude at the center of the impinging area on the central plane and decays very quickly along the $+z$ and $-z$ directions. The depth of correlation given by the 4X objective is 115 $\mu$m, making the interrogation volume as big as $86 \times 86 \times (2 \times 115) \mu$m$^3$. The turbulent kinetic energy averaged over such a volume is expected to be much lower than that in the central plane. In order to improve the accuracy of the measurements, the 10X objective was used to zoom in the areas interested.

For $Re_j = 211$ and 601, the inlet stream was simulated by assuming a laminar flow. The agreement of the computation with the PIV data confirms the validity of this assumption (Fig. 9.9). For $Re_j = 901$, the shape of the inlet velocity profiles measured by PIV (Fig. 9.9) indicated that the flow is more turbulent than laminar. Therefore the turbulence model was involved in the simulations. It was illustrated by Fig. 9.9 that the velocity profile was suc-
cessfully predicted by this model. Every solid line represents an inlet velocity profile at a certain streamwise location. Unfortunately, the PIV data for the turbulent kinetic energy is much higher than computations for $Re = 601$ and $Re = 901$. And an explanation for this discrepancy is being pursued.

**Conclusions**

In this study, micro-PIV was employed to investigate a planar CIJR with the inlet jet Reynolds numbers ranging from 90 to 1085. Measurements were carried out using a 4X objective and a 10X objective. Flow statistics such as the mean velocity and turbulent kinetic energy were calculated from the PIV data which were then used to validate a turbulence model. In general, the overall agreement between the CFD predictions and the experimental data for mean velocity is satisfactory. However, calculated turbulent kinetic energy differs from the PIV data quantitatively. Based on the experimental observations currently available, we tend to contribute this discrepancy to the instability of the inlet streams which is being under further investigation.

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Figure 9.1 Planar confined impinging-jets reactor (not scaled).
Figure 9.2 Schematic of the experimental setup.
Figure 9.3  The instantaneous (left) and ensemble-averaged (right) velocity fields for $Re_j = 90$. 
Figure 9.4  The instantaneous (left) and ensemble-averaged (right) velocity fields for $Re_j = 1085$. 
Figure 9.5  The locations where the micro-PIV measurements were performed with a 10X objective.
Figure 9.6  The ensemble-averaged velocity fields at locations A (left), C (middle) and D (right) for $Re_j = 211$ (top), 601 (middle), and 901 (bottom).
Figure 9.7  The example instantaneous velocity fields at locations C (top) and D (bottom) for $Re_j = 211$ (left), 601 (middle), and 901 (right).
Figure 9.8  Comparison of PIV measurements (left) with CFD predictions (right) for $Re_j = 1085$. Top: velocity field; bottom: distribution of the turbulent kinetic energy.

Figure 9.9  The inlet velocity profiles predicted by CFD (symbols) and measured by PIV (lines) for $Re_j = 211$ (left), 601 (middle) and 901 (right). Red lines: left inlet stream; green lines: right inlet stream.
CHAPTER 10. CONCLUSIONS

In this report, scalar mixing in single-phase turbulent flows were investigated using CFD models. The RANS models for turbulent transport and the scalar mixing are implemented in a FV RANS/transported PDF code which was employed to simulate a confined planar-jet reactor and a confined planar wake. The RANS code works as a flow solver that provides the transported PDF code with the solution to the flow quantities. The transported PDF code treats the micromixing and the chemical source term by solving the stochastic differential equations of the Lagrangian particles. The Reynolds stresses are closed by a two-layer $k-\varepsilon$ model. The scalar flux and the scalar variance flux are modeled by a gradient-diffusion model. The equilibrium model is used to close the scalar dissipation and the IEM model or the EMST model represents the micromixing. The performance of the models mentioned above were evaluated by comparing the CFD predicted flow and scalar statistics such as the mean flow velocity, turbulent kinetic energy and dissipation rate, mixture-fraction mean and variance, one-point mixture-fraction PDF with the PIV/PLIF data. Generally speaking, the agreement between computations and experiments at different downstream locations is satisfactory, indicating that the models mentioned above close the unknowns reasonably.

The FV RANS/transported PDF code was also used simulate the performance of a gas-phase thermo chlorination reactor when it is scaled up from the lab scale to the pilot scale then to the plant scale. The reduced mechanism consists of 21 reactions and 15 species. The effects of the reactor scale on the temperature and product yield is investigated for three different inlet configurations. It is noticed that the reactor with the premixed inlet streams tends to extinguish when scaled up and can be stabilized either by increasing the inlet chlorine level or by heating up the reactor walls. This phenomena agrees with the on-site observations for the
commercial reactor with the premixed reactants.

A CIJR with a mixing-sensitive reaction system was modeled by a two-environment presumed PDF method that involves the DQMOM-IEM model. The model equations are solved as user-defined functions by FLUENT. The conversion of DMP, which indicates the extent of mixing, is accurately predicted by the computations. The computations also show that the turbulence in the CIJR is not fully developed at the inlet Reynolds numbers for which the simulations were executed. Despite rapid mixing, the outlet stream is not completely mixed and the reactions continue along the outlet tube. Strategies for optimizing the mixing in the CIJR were proposed based on the CFD analysis.

The multi-environment DQMOM-IEM model was extended to systems forming fine particles that follow the local turbulent reactive stream. That is, the DQMOM-IEM model was used to solve the Reynolds-average population balance equations. The particles are formed by nucleation and change their size due to mixing, growth, aggregation and breakage. For a univariate system, the NDF moments predicted by DQMOM-IEM model and the QMOM-IEM model agree well as expected since the equations of the QMOM-IEM model can be exactly recovered from the equations of the DQMOM-IEM model. The variables given by the QMOM-IEM model are the moments from which the weights and abscissas can be derived. On the other hand, the variables solved by the DQMOM-IEM model are the weights and abscissas that can be used to approximate the moments. The accuracy of QMOM has been reported for many cases. Therefore, the agreement between the predictions of DQMOM-IEM model and QMOM-IEM model convinces the accuracy of the DQMOM-IEM-PBE method.

In the computational study of the CIJR, it was not possible to validate the local turbulence and concentration fields predicted by the CFD models. We were thus motivated to execute experimental studies of the CIJR include PIV measurements of the local velocity using the micro-PIV/LIF techniques. A variety of techniques were used to fabricate the microfluidic channel and compared with each other. Our initial experimental results have shown that the micro-PIV techniques are able to measure the inlet velocity accurately. For the mixer, the measured distributions of the velocity and turbulent kinetic energy are consistent with the
CFD predictions, though discrepancy does exist due to the experimental error and instability of the inlet streams.
BIBLIOGRAPHY


