Mixing in a Multi-Inlet Vortex Mixer (MIVM) for Flash NanoPrecipitation

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Abstract

Rapid precipitation of both organic and inorganic compounds at high supersaturation requires homogenous mixing to control the particle size distribution. We present the design and characterization of a new Multi-Inlet Vortex Mixer (MIVM). The four-stream MIVM allows control of both the supersaturation and the final solvent quality by varying stream velocities. The design also enables the separation of reactive components prior to mixing. Finally, the design enables mixing of streams of unequal volumetric flows, which is not possible with alternate confined impinging jet (CIJ) mixing geometries. We characterize the mixing performance of the MIVM using competitive fast reactions (the so called “Bourne reactions”). Adequate micromixing is obtained with a suitably defined Reynolds number when $\text{Re} > 1600$. The experimental results are compared to CFD simulations of the fluid mechanics and parallel reactions in the MIVM. Excellent correspondence is found between the simulation and the experimental results with no adjustable parameters. The CFD simulations provide a powerful tool for the optimization of these complex mixing geometries.

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Introduction

The production of uniform-sized nanoparticles of hydrophobic organic compounds by an economical, scalable process is a considerable challenge. It is motivated by the use and potential use of nanoparticles in drug delivery, especially poorly water soluble drugs\textsuperscript{1-4}, cosmetics\textsuperscript{5-7}, dyes\textsuperscript{3,8}, medical imaging and diagnostic\textsuperscript{9,10}, and pesticides\textsuperscript{11}. One of the advanced processes to produce nanoparticles is “Flash NanoPrecipitation”\textsuperscript{12}, which requires fast mixing of two or more streams to create supersaturation. A dissolved solute and stabilizing amphiphilic polymer are rapidly mixed with an anti-solvent to create high supersaturation over a time scale shorter than the characteristic nucleation and growth time scales for the nanoparticles. This rapid growth from a uniform concentration field and uniform “poisoning” of the nanoparticle surfaces by adsorbed amphiphilic polymer uniformly stops the growth to produce narrow particle size distributions. The process can also provide the capability to coat particles and create composite multi-functional particles.

An understanding of rapid precipitations requires an understanding of the role of macro-, meso- and micromixing on the development of supersaturation. Various mixing devices have been proposed and characterized, including semibatch stirred-tank precipitators\textsuperscript{13} and impinging-jet precipitators\textsuperscript{14}. In a previous study, Johnson and Prud’huihomme determined the dependence of mixing time on Reynolds number and geometry in a Confined Impinging Jet (CIJ) mixer using the conversion of competitive
reactions (the so called “Bourne reactions”) \(^{15}\). Mixing in the CIJ can be as fast as milliseconds, but the CIJ mixer is limited by the requirement of equal momenta of the solvent and anti-solvent streams. The final concentration of the effluent is the average of the two stream concentrations which may compromise particle stability.

To overcome the limitation of the CIJ mixer, but to retain its ability to provide rapid micromixing, scalability, and ease of operation, we developed a Multi-Inlet Vortex Mixer (MIVM) (Fig. 1). The concept of the MIVM is that the momentum from each stream contributes independently to drive micromixing in the cell. Therefore, it is possible to have one or more streams at high volumetric flow rate and another stream at a lower flow rate and still get good micromixing. The design question is -- how efficiently will the mixer operate at different flow velocities and stream ratios? How does it compare to the CIJ where two opposing streams impinge and all the momentum is dissipated in the central region of the cavity? If the MIVM provides rapid micromixing then it has the operational advantages that the final fluid phase is predominantly anti-solvent. This increases the stability of the nanoparticles by depressing the rate of Ostwald ripening \(^{16-19}\). In addition, being able to separate inlet streams enables the introduction of reactive compounds in different streams so that reactive precipitations can be accomplished.

In this paper, we establish the functionality of the mixing time of this MIVM with Reynolds number, inlet velocity, physical properties of the streams and the geometry of the mixer. The characteristic mixing time of the MIVM is measured by the competitive Bourne reactions.\(^{15,20-23}\) The characteristic mixing time of the MIVM can be in the range of milliseconds at Re > 1600. A CFD model that was previously used to model the CIJ
mixer was used to model the MIVM mixer.\textsuperscript{24} The CFD results provide additional insights as to the mixing mechanisms in the MIVM mixer.

**Reaction kinetics**

Baldyga, Bourne, and Walker\textsuperscript{20, 22} developed a competitive reaction scheme that is fast enough to probe the mixing performance of mixing in the MIVM. This “fourth Bourne reaction” has stable reactants and products, and is easily quantified by gas chromatography (GC). Conceptually, the scheme works in this way. The reagents for the competitive reactions are segregated in two (or more) flow streams. If the micromixing is faster than the reaction kinetics of the slow reaction then the conversion of the limiting reagent in the slow reaction will correspond to the ratio of the two reaction rate constants; that is, the conversion can be calculated from the conversion from a homogeneous initial state. However, if the reacting streams are not well mixed, then diffusion limitations will decrease the conversion of the limiting reagent.\textsuperscript{15}

The fast reaction of the competitive reactions is the neutralization of sodium hydroxide with a second-order rate constant $k_1 = 1.4 \times 10^8 \text{ m}^3/\text{mol} \cdot \text{s}$,

$$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}.$$ 

The slow reaction is the acid catalyzed hydrolysis of 2,2-dimethoxypropane (DMP) to form one mole of acetone and two moles of methanol,

$$\text{CH}_3\text{C(OCH}_3\text{)}_2\text{CH}_3 + \text{H}^+ (+\text{H}_2\text{O}) \rightarrow \text{CH}_3\text{COCH}_3 + 2\text{CH}_3\text{OH} + \text{H}^+. $$ 

The rate constant of this reaction is $k_2 = 0.63\text{ m}^3/\text{mol} \cdot \text{s}$.
Since the rate constant of the fast reaction is more than $10^8$ times the rate constant of the slow reaction, the reaction time can be expressed as a pseudo first-order time constant of the slow reaction:

$$
\tau_{\text{run}} = \frac{1}{k_2 C_{\text{DMP0}}}, \quad (1)
$$

where $C_{\text{DMP0}}$ is the DMP concentration after mixing but before the reaction. The mixing effectiveness is measured by the fraction of DMP reacted,

$$
X = 1 - \frac{N_{\text{DMP}}}{N_{\text{DMP0}}}, \quad (2)
$$

where $N_{\text{DMP}}$ and $N_{\text{DMP0}}$ are the molar flow rate of DMP after and before the reaction, respectively. For the experiments, Eqn. 2 was cast in the form,

$$
X = \frac{C_{\text{MeOH, outlet}}}{2C_{\text{DMP, inlet}}} \left( 1 + \frac{1}{F} \right), \quad (3)
$$

where $F$ is the flow ratio of the DMP and NaOH streams/HCl streams. $C_{\text{MeOH, outlet}}$ is the methanol concentration at the outlet of the MIVM, which can be accurately measured by GC, and $C_{\text{DMP, inlet}}$ is the DMP concentration before mixing at the inlet of the MIVM. The constant “2” in front of $C_{\text{DMP, inlet}}$ comes from the fact that every mole of DMP that reacts will generate two moles of methanol.

Conceptually, mixing can be described by a mixture fraction $\xi$, which is independent of chemistry. By convention, we will set $\xi = 0$ in the streams containing acid, and $\xi = 1$ in the streams containing base and DMP. The value of the average mixture fraction at the outlet is,
\[ \xi = \frac{m_2}{m_1 + m_2}, \]  

(4)

where \( m_2 \) is the summation of the mass flow rate of the streams containing DMP, and \( m_1 \) is the summation of the mass flow rate of other streams. The fraction of DMP converted can be evaluated numerically from,

\[ X = 1 - \frac{\langle C_{\text{DMP, outlet}} \rangle}{\xi C_{\text{DMP, inlet}}}, \]  

(5)

where,

\[ \langle C_{\text{DMP, outlet}} \rangle = \frac{1}{m_1 + m_2} \int \rho c_{\text{DMP}} U \cdot \vec{m} dS \]  

(6)

is the “mixing-cup” average at the outlet. Note if DMP were completely mixed at the outlet (which is usually not the case) then \( \langle C_{\text{DMP, outlet}} \rangle \) would be equal to the outlet concentration of DMP.

**Experimental Section**

**Experiment apparatus**

Digitally controlled syringe pumps (Harvard Apparatus, PHD 2000 programmable, Holliston, MA) were used to provide constant and accurate flow rates for the inlet streams of the MIVM. Gas chromatography (GC) HP 5890A (Hewlett Packard, Wilmington, DE) with an autosampler (6890 series injector, Agilent Technologies, Palo Alto, CA) was used to analyze the amount methanol generated compared with ethanol.

**Samples preparation**
Samples were prepared using MilliQ water. The molar ratio of HCl and NaOH is 1:1.05 to ensure that all the acid is consumed. The molar ratio of DMP and NaOH is 1:1 in solution. In every acid or base and DMP solution, 25 vol% of ethanol and 90 mmol/L NaCl were added to DI water. The ethanol serves as an internal GC standard, and the salt suppresses ionic interactions in the reaction. DMP 99+ and 1.000 molar standard NaOH and HCl were purchased from Aldrich.

**Arrangement of Inlet Streams**

**Case I:**

The arrangement of the inlet streams is symmetric as shown in Figure 1. The streams have equal velocities. Two opposing streams are acid with initial concentration 33.0 mole/m$^3$, and the other two opposing streams are base and DMP streams with base concentration 34.65 mole/m$^3$ and DMP concentration 33.0 mole/m$^3$. The ratio of acid to base to DMP is 1:1.05:1. After homogenous mixing without reaction, the DMP concentration would be 16.5 mole/m$^3$, which gives a characteristic reaction time is 96.2 ms.

**Case II:**

The arrangement of the inlet streams is shown in Figure 2. Three streams are acid streams with the same velocity. The last stream is the base and DMP stream with velocity three times that of the acid streams. The acid concentration in each of the acid streams is 33.0 mole/m$^3$. Base concentration is 34.65 mole/m$^3$, and DMP is 33.0 mole/m$^3$. The stoichiometry of the acid, base and DMP is 1:1.05:1. The reaction time is 96.2 ms (from Eqn. 1).
Case III:

The arrangement of the inlet streams is shown in Figure 3. All the streams have the same velocity. Three of them are acid streams with concentration 22.0 mole/m$^3$. The fourth stream is base and DMP stream with base concentration 69.3 mole/m$^3$ and the DMP concentration is 66.0 mole/m$^3$. The ratio of acid, base and DMP, after homogenous mixing before any reaction occurs, is 1:1.05:1, therefore the reaction time is 96.2 ms.

The definition of the Reynolds number (Re) is

$$Re = \sum_{i=1,N} \frac{V_i}{\nu_i} D,$$  \hspace{1cm} (7)

where $V_i$ is the velocity of nth inlet stream, $D$ is the chamber diameter ($D=0.2333$ inch as in Figure 1), $\nu_i$ is the kinematic viscosity of the nth inlet stream, and $N$ is the number of inlet streams.

Numerical Simulation

**CFD model**

In this work, we used the two-environment DQMOM-IEM model implemented by Liu and Fox. The transport equations for the mixture fraction $\xi_n$, and slow reaction progress variable $Y_n$ in the nth (n=1 or 2) environments are solved. The conserved scalars are $p_1$, $p_1\xi_1$, $p_2\xi_2$, $p_1Y_1$, $p_2Y_2$, and $p_2 = 1 - p_1$. $p_1$ and $p_2$ are the mass fraction of fluid coming from the acid streams and the streams containing base and DMP, respectively. Without showing the detailed derivation, the model equations are,

$$\frac{\partial (\rho p_1)}{\partial t} + \nabla \cdot \rho \langle \mathbf{U} \rangle p_1 = \nabla \cdot (\rho \Gamma_p \nabla p_1)$$  \hspace{1cm} (8)
\[
\frac{\partial (\rho p_t \xi)}{\partial t} + \nabla \cdot (\rho \langle \vec{U} \rangle p_t \xi) = \nabla \cdot \left[ \rho \Gamma_T \nabla (p_t \xi) \right] + \rho \gamma p_t p_s (\xi_2 - \xi_1) + \frac{\rho \Gamma_T}{\xi_2 - \xi_1} \left( p_t \left| \nabla \xi_1 \right|^2 + p_s \left| \nabla \xi_2 \right|^2 \right) \quad (9)
\]

\[
\frac{\partial (\rho p_s \xi_2)}{\partial t} + \nabla \cdot (\rho \langle \vec{U} \rangle p_s \xi_2) = \nabla \cdot \left[ \rho \Gamma_T \nabla (p_s \xi_2) \right] + \rho \gamma p_t p_s (\xi_1 - \xi_2) + \frac{\rho \Gamma_T}{\xi_2 - \xi_1} \left( p_t \left| \nabla \xi_1 \right|^2 + p_s \left| \nabla \xi_2 \right|^2 \right) \quad (10)
\]

\[
\frac{\partial (\rho p_t Y_1)}{\partial t} + \nabla \cdot (\rho \langle \vec{U} \rangle p_t Y_1) = \nabla \cdot \left[ \rho \Gamma_T \nabla (p_t Y_1) \right] + \rho \gamma p_t p_2 (Y_2 - Y_1) + \frac{\rho \Gamma_T}{Y_1 - Y_2} \left( p_t \left| \nabla Y_1 \right|^2 + p_2 \left| \nabla Y_2 \right|^2 \right) + \rho p_1 S_\infty (\xi, Y_1) \quad (11)
\]

\[
\frac{\partial (\rho p_s Y_2)}{\partial t} + \nabla \cdot (\rho \langle \vec{U} \rangle p_s Y_2) = \nabla \cdot \left[ \rho \Gamma_T \nabla (p_s Y_2) \right] + \rho \gamma p_t p_2 (Y_1 - Y_2) + \frac{\rho \Gamma_T}{Y_2 - Y_1} \left( p_t \left| \nabla Y_1 \right|^2 + p_2 \left| \nabla Y_2 \right|^2 \right) + \rho p_2 S_\infty (\xi_2, Y_2) \quad (12)
\]

where \( \Gamma_T \) is the turbulent diffusivity, which is defined as

\[
\Gamma_T = \frac{C_\mu}{Sc_T} \frac{k^2}{\varepsilon} \quad (13)
\]

with \( C_\mu = 0.09 \) and \( Sc_T = 0.7 \). These equations are coupled to a CFD turbulence model that computes \( \langle \vec{u} \rangle, k \) and \( \varepsilon \).

The local turbulence level can be described by introducing a turbulent Reynolds number, \( Re_1 \) defined as

\[
Re_1 = \frac{k}{(\varepsilon \nu)^{1/3}} \quad (14)
\]

The micromixing parameter \( \gamma \) is modeled by

\[
\gamma = \frac{C_\phi \varepsilon}{2k} \quad (15)
\]
with $C_{\phi} \approx 2$ for high-Reynolds-number flow. It has been demonstrated by Liu and Fox that at finite turbulent Reynolds numbers $C_{\phi} = 2$ overestimates the micromixing rate. They propose the expression,\textsuperscript{26}

$$C_{\phi} = \sum_{n=0}^{6} a_n \left( \frac{1}{\lg Re_1} \right)^n \quad \text{for } Re_1 \geq 0.2$$

(16)

to account for finite Reynolds-number effects when the Schmitt number is large. Here,

$$a_0 = 0.4093, \quad a_1 = 0.6015, \quad a_2 = 0.5815, \quad a_3 = 0.09472, \quad a_4 = -0.3903, \quad a_5 = 0.1461 \quad \text{and} \quad a_6 = -0.01604.$$\textsuperscript{26}

More detailed derivation can be found from Fox’s articles as well as others\textsuperscript{24-26}.

With the assumption that the fast reaction was instantaneous, which implies that acid and base cannot coexist at any point, the chemical reaction progress variable for the slow reaction, $Y$, is determined by $\xi$ through the chemical source term, $S_\infty$, which is

$$S_\infty (\xi, Y_2) = A_0 k_2 \left( 1 - \frac{\xi}{\xi_{s1}} \right) \left( \frac{\xi}{\xi_{s2}} - Y_2 \right) \quad \text{if } 0 \leq \xi \leq \xi_{s1} \quad \text{and} \quad 0 \leq Y \leq \frac{\xi}{\xi_{s2}},$$

(17)

where,

$$\xi_{s1} = \frac{A_0}{A_0 + B_0}$$

(18)

and

$$\xi_{s2} = \frac{A_0}{A_0 + D_0}.$$\textsuperscript{18}

(19)

$A_0$, $B_0$ and $D_0$ are the inlet molar concentrations of the acid, base and DMP.
**Simulation conditions**

FLUENT 6.2.12 was used to solve the Reynolds-averaged Navier-Stokes (RANS) equations closed by a turbulence model and the transport equations of scalars. The CFD model and numerical simulation method setup are listed in Table I.

The simulation geometry was separated into three parts: the inlets, main mixing cavity and the outlet. The inlet ports have L/D₁=10, where D₁ is the longer side of the section (D₁=0.0571 inch). The inlet profiles of the velocity components, turbulent kinetic energy and turbulent dissipation rate were given by the values for an infinitely long channel at the same flow rate. The main mixing chamber has 165200 hexahedral cells for grid-independent solutions. The grid of the main mixing cavity is shown in Figure 4.

The density and viscosity of all the streams are 964 kg/m³ and 0.002 kg/m-s, respectively.

Six user defined scalars are implemented in FLUENT 6.2.12,

\[
    \begin{align*}
        X_0 &= p_1 \\
        X_1 &= p_1 \xi_1 \\
        X_2 &= p_2 \xi_2 \\
        X_3 &= p_1 Y_1 \\
        X_4 &= p_2 Y_2 \\
        X_5 &= 1 - p_1
    \end{align*}
\]  \hspace{1cm} (20)

The inlet conditions in the acid stream are X₀=1, and X₁=X₂=X₃=X₄=X₅=0. The inlet conditions in the base streams are X₀=X₁= X₃=X₄=0, and X₂=X₅=1. Note that the variable X₅ is redundant (X₅=1−X₀), but is solved to check the consistency of the numerics.
Results and discussion

Case I:

The experimental and numerical simulation data for the DMP conversion versus Reynolds number are reported in Fig. 5.

The simulation results and the experimental measurements are in close agreement in the range $800 \leq \text{Re} \leq 5000$. At higher Re, experimental measurements reach a lower limit, since DMP can be hydrolyzed in water solution even without the presence of acid.

The numerical simulation shows that when Re $> 1600$, essentially all of the mixing is completed in the main mixing chamber, all the acid is consumed at the outlet of the main mixing cavity, and DMP conversion ceases to increase. But with lower Re, reaction continues in the outlet tube. Computational studies were conducted using an extended outlet tube. Each time a tube with a length ten times of the outlet diameter was added at the end and the solution was recomputed. This procedure was continued until the DMP conversion was complete (i.e., acid was completely consumed).

The mixing details of the points at Re=4227 (inlet velocity=0.37 m/s), Re=2285 (inlet velocity=0.2 m/s) and Re=1371 (inlet velocity=0.12 m/s) are shown in Fig. 6. The highest turbulent kinetic energy is near the outlet of the chamber for each case. But for low Re, the very center of the chamber has a low kinetic energy. With increasing Re, the zone of highest kinetic energy moves into the center of the chamber. This observation is in contrast to our previous results for the CIJ mixer in which the kinetic energy dissipation is maximum in the center of the mixing cavity$^{24}$. As a result considerable mixing occurs in the exit region of the MIVM.
From Figs. 7 and 8, it can be seen that with higher Re, the mixing volume increases; compositional uniformity is achieved faster; and acid is consumed more quickly.

Case II:

The experimental and numerical simulation data of DMP conversion versus Reynolds number are reported in Fig. 9. Once more we observe both experimentally and numerically that at higher Re, the mixing was improved, and the turning point appears near Re=1600.

Case III:

The experimental and numerical simulation data of the DMP conversion versus Reynolds number are reported in Fig. 10. A comparison of case I and case III shows that at low Re the symmetric arrangement of the inlet streams results in somewhat better mixing; that is the conversion of DMP is always lower for the symmetric arrangement. Concentrating the reagents in a single stream (case III) results in somewhat worse mixing. The 3-dimensional depiction of the acid concentration in Figs. 11 and 12 shed light on the origin of the effect. In case I, Fig. 11a, the two acid streams swirl down the exit tube as thin filaments. For case III, Fig. 11b, with the single concentrated acid stream the length scale of acid segregation is obviously larger, and therefore mixing poorer. At the lower Reynolds number (Fig. 12) the effect is even more pronounced.

Mixing Scales

At high Re, there is generally a separation of mixing scales. The large-scale motions are mainly influenced by the geometry of the reactor, and the small-scale motions are determined by energy dissipation rate and viscosity.
For the case of two types of inlet streams, the mixture-fraction mean, \( \langle \xi \rangle \), can be written as

\[
\langle \xi \rangle = p_1 \xi_1 + p_2 \xi_2 ,
\]  
(21)

Likewise, the mixture-fraction variance, \( \langle \xi'^2 \rangle \), can be written as

\[
\langle \xi'^2 \rangle = p_1 \xi_1^2 + p_2 \xi_2^2 - \langle \xi \rangle^2 ,
\]  
(22)

Large-scale segregation (LSS) in the reactor can be described by introducing a LSS variance,

\[
\langle \xi'^2 \rangle_{\text{LSS}} = \left( \langle \xi \rangle - \bar{\xi} \right)^2 .
\]  
(23)

where \( \bar{\xi} \) is the average mixture fraction after complete mixing, which is equal to 0.5 in our cases.

The LSS zone can be determined using \( \langle \xi'^2 \rangle_{\text{LSS}} > \sigma^2 \) and \( \langle \xi'^2 \rangle < \sigma^2 \), where \( \sigma \) is the cut-off standard deviation. The reactions are controlled by SSS alone if \( \langle \xi'^2 \rangle_{\text{LSS}} < \sigma^2 \) and \( \langle \xi'^2 \rangle \geq \sigma^2 \). And in the condition that \( \langle \xi'^2 \rangle_{\text{LSS}} \geq \sigma^2 \) and \( \langle \xi'^2 \rangle \geq \sigma^2 \), the reactions are controlled by both LSS and SSS.

From the transport equations of \( \langle \xi'^2 \rangle_{\text{LSS}} \) reported by Ying Liu \( ^{25} \), the characteristic decay time for \( \langle \xi'^2 \rangle_{\text{LSS}} \) is given by,

\[
t_{\text{LSS}} = \frac{\langle \xi'^2 \rangle_{\text{LSS}}}{2 \Gamma_t \left| \nabla \langle \xi \rangle \right|}.
\]  
(24)
The characteristic decay time for SSS variance, also known as the micromixing time in turbulent-mixing theory, is given by,

\[ t_{SSS} = \frac{1}{2\gamma}. \]  \hspace{1cm} (25)

Then, the characteristic mixing time is obtained by

\[ t_{mix} = t_{LSS} + t_{SSS}. \]  \hspace{1cm} (26)

Considering case I (the case with one opposing pair of inlets containing acid and the other containing base and DMP), extracting data at different heights of the reactor can provide more detailed information about the change of \( \langle \xi^{12} \rangle_{LSS} \) and \( \langle \xi^{12} \rangle \). The heights are chosen to emphasize the changes in mixing variables. In the reactor chamber, \( \langle \xi \rangle \) is not equal to \( \bar{\xi} \), indicating the presence of LSS. As seen in Figure 13, \( \langle \xi^{12} \rangle_{LSS} \) decays quickly after inlet streams enter the reactor. At \( Z = 0 \), where \( \bar{Z} = Z/H \) and H is the half thickness of the reactor chamber, \( \langle \xi^{12} \rangle_{LSS} \) remains 0, indicating that mixing is mainly affected by SSS in this zone. On the other hand, \( \langle \xi^{12} \rangle_{LSS} \) has slight variations at \( \bar{Z} = -0.8 \) and \( \bar{Z} = 0.8 \), indicating mixing is affected by LSS in these regions.

Considering the change of \( \langle \xi^{12} \rangle \) at \( \bar{Z} = 0 \) in Figure 14, the SSS mixture-fraction variance is slightly lower at the edge area for the lower Re than higher Re; on the other hand, it changes faster and is higher near the reactor center (\( \bar{Z} = 0 \)) for lower Re. The same characteristics are also shown at \( \bar{Z} = -0.8 \), \( \langle \xi^{12} \rangle \) is much larger for lower Re than higher Re. These differences arise when Re is small -- the flow motions are more
laminar-like and thus $C_\phi$ is smaller. The flow streams are mostly dominated by the geometry of the reactor as they enter and swirl from periphery to the center, where the velocity is the highest and therefore the change of mixture-fraction is greatest. Compared to a low Re case, better mixing takes place at higher Re. Since the flow motions tend to be more turbulent, the variation of mixture-fraction is not as great.

**Segregation Zones**

In case I, both LSS + SSS and SSS overlap with the reaction zone at the center planes as shown in Figure 15, where the cut-off standard deviation was defined as the distance in mixture-fraction space from the end of the reactions ($\xi_{s1}$) to complete mixing ($\bar{\xi}$); i.e.,

$$\sigma = \bar{\xi} - \xi_{s1} = 0.0122.$$  

While in case I the reaction zone overlaps with both SSS and LSS+SSS zones, in case III, $\left<\xi^{12}\right>_\text{LSS}$ decays much more slowly and only an LSS+SSS zone can be identified as shown in Figure 16. These results show that in case III, mixing and reaction are influenced mainly by the geometry of the MIV reactor, resulting in relatively poorer mixing performance.

**Reaction time**

The reaction time is expressed as the pseudo first-order time constant of the slow reaction, as in Eqn. 1. Therefore, the reaction time is dependent on the initial DMP concentration.

The experimental and numerical simulation results with reaction time 48.1ms and 96.2ms are shown in Figure 17 for case I.
At high Re, for both reaction times, the conversion of DMP reaches the same limit, which is set by the sensitivity of the competitive reactions. That is the mixing time is faster than the reaction time and the compositions appear essentially homogeneous. For both reaction times the agreement between the simulations and experimental data is good.

Four inlet streams vs. two inlet streams

The comparison of the MIVM with four inlet streams and two inlet streams by numerical simulation is shown in Figure 18.

The results show that at the same total volume flow rate, the MIVM with four inlet streams has better mixing than the MIVM with the same geometry but two inlet streams. The mixing difference can be attributed to the initially larger segregation length scales with only two inlets. However, the differences in performance are not substantial.

Conclusion

The flexibility and capability of the MIVM for fast micromixing has been demonstrated. The concept behind that MIVM is that each stream contributes independently to the micromixing in the chamber. Both competitive reactions and CFD simulations show that the mixer operates in essentially this way. Changes in the flow rate of individual streams, or concentration of reactants in one stream rather than distribution between two streams makes a relatively minor change in the performance of the MIVM. Another way of saying this is that the choice of definition of the Reynolds number as a linear combination of the stream velocities (Eqn. 7) seems to represent the mixing performance of the MIVM over a relatively wide range of inlet conditions. Operation of the MIVM at Reynolds number above 1600 ensures homogeneous mixing for reactions with time constants
longer than 50 ms. This insensitivity of the MIVM to inlet stream configuration makes it a flexible and useful mixing device.

There are observable, second-order, differences between operations with different inlet configurations. Four equal velocity streams with the reactants distributed symmetrically between the four streams (case I) is more efficient than either unequal stream velocities (case II) or equal stream velocities but unequal reactant distributions (case III). Also, four symmetric streams is more efficient than two symmetric streams at the same Reynolds number. The CFD simulations show that with two inlet streams the length scales of segregation are larger, which results in somewhat inferior mixing.

The ability of the CFD to quantitatively predict mixing and fast competitive reactions is quite striking. It demonstrates that the CFD simulations can be used to design and optimize the design of mixing geometries with a high level of confidence.

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Reference:


Figure 1. Arrangement of the inlet streams for Case 1. All streams have the same volumetric flow rates. Two acid streams (A) come in opposite the two base streams (B), which contain the DMP reagent (D).

Figure 2. Arrangement of the inlet streams for Case II. The three acid streams have equal volumetric flow rates, \( V \), and the base stream with the DMP has a flow rate \( 3V \).
Figure 3. Arrangement of the inlet streams for Case III. The four streams have equal flow rates. The acid streams (A) have equal volumetric flow rates and concentrations (C), and the base stream with DMP has a concentration of $3C$.

Figure 4. Geometry and grids of the main mixing chamber.
Figure 5. Conversion of DMP vs. Re in the MIVM for case I with equal flow rates and concentrations. ( ■: numerical simulation data. □: experimental measurements.)
Figure 6. Turbulent kinetic energy for case I with equal stream velocities and concentrations at: (a) Re=1371, (b) Re=2285 and (c) Re=4227.
Figure 7. Mass fraction of acid ($p_1$) for case I with equal stream velocities and concentrations at: (a) $Re=1371$, (b) $Re=2285$ and (c) $Re=4227$. 
Figure 8. Acid concentration at: (a) Re=1371, (b) Re=2285 and (c) Re=4227.
Figure 9. Conversion of DMP vs. Re in the MIVM for case II with unequal stream velocities. (●: numerical simulation data. ○: experimental measurement.)
Figure 10. Conversion of DMP vs. Re in the MIVM. (■: numerical simulation data for case I; ▲: numerical simulation data for case III; □: experimental measurement for case I; and △: experimental measurement for case III.)
Figure 11. Acid concentration at Re=2285 for symmetric (a) and asymmetric (b) arrangement of the inlet streams.
Figure 12. Acid concentration at \( \text{Re}=1371 \) for symmetric arrangement of the inlet streams (a) and asymmetric arrangement of the inlet streams (b).
Figure 13. Profiles at Y=0 plane of $\langle \xi^2 \rangle_{LS}$ for case I at $\bar{Z} = 0$, $\bar{Z} = 0.8$, and $\bar{Z} = -0.8$ for:

(a) Re=5600 and, (b) Re=7880, where $\bar{Z} = Z/H$ and $\bar{X} = X/R$. 
Figure 14. Profiles at Y=0 plane of SSS variance at $Z = 0$, $Z = 0.8$, and $Z = -0.8$ for (a):

Re=5600 and (b): Re=7880, where $Z = Z/H$ and $X = X/R$. 


Figure 15. Distribution of segregation zones defined by $\sigma=0.0122$ for $Re=1399$ for case I.

Figure 16. Distribution of Segregation Zones—$\sigma=0.0122$ for $Re=1399$: case I (a) and case III (b).
Figure 17. Conversion of DMP vs. Re in the MIVM. ( ■: numerical simulation data for reaction time 96.2 ms; ◊: numerical simulation data reaction time 48.1 ms; □: experimental measurement for reaction time 96.2 ms; and ●: experimental measurement for reaction time 48.1 ms.)
Figure 18. Numerical simulation results of the conversion of DMP vs. Re in the MIVM.

(☐: numerical simulation data for mixing with two inlet streams. Two streams are
opposite. One is acid stream and one is base stream with DMP. ■: numerical simulation
data of mixing with four inlet streams arranged as in case I.)
Table I. Simulation model and parameter setup for FLUENT 6.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Solver</td>
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<tr>
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<td>Steady</td>
</tr>
<tr>
<td>Viscous Model</td>
<td>k-epsilon (two equation) model</td>
</tr>
<tr>
<td>Near-wall treatment</td>
<td>Enhanced wall treatment</td>
</tr>
<tr>
<td>Discretization</td>
<td>Second order upwind</td>
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</tbody>
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